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Review

Hydroformylation of simple olefins catalyzed by metals and clusters supported on unfunctionalized inorganic carriers

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Abstract

The results, published in the open literature up to the end of 1995 on the hydroformylation of simple olefins in vapor and liquid phase catalyzed by metals or metal complexes adsorbed on inorganic oxides, clays, active carbons and zeolites, are reviewed.

Keywords: Hydroformylation; Heterogeneous catalysis; Clusters; Oxides; Zeolites; Pillared clays; Carbon; Supported catalysts

1. Introduction

Olefins hydroformylation was discovered in the late 1930s by Otto Roelen of Rurchemie, who found that alkenes can be converted to aldehydes by treatment with CO and H_2 in the presence of a cobalt catalyst at elevated temperatures and pressures. Today the oxo synthesis represents one of the largest industrial applications of soluble transition metal catalysts [1]. Ethylene and propylene are used primarily as the olefins. The technical importance of the reaction derives from the ease with which the primary oxo product, the aldehyde, can be converted into a multitude of industrially important secondary products [2]. Within the past 30 years the cobalt have been challenged by rhodium catalysts systems that are active at lower pressures and temperatures and, in the case of propene, give a better proportion of normal to *iso*-aldehyde in the final product. The oxo reaction in homogeneous phase has been extensively investigated and comprehensive reviews on the hydroformylation of unsubstituted [3–10] and substituted [11] olefins are available. A comprehensive review on the more recent industrial developments of the reaction has just appeared [12].

Much effort has been devoted to the conversion of homogeneous hydroformylation catalysts to heterogeneous catalysts because catalyst loss during its recovering can represent an expensive problem with rhodium based homogeneous catalysts. Conventional supported metal based catalysts have been studied, but much research has also been focused on the preparation of catalysts by immobilizing active transition-metal complexes or clusters on solid supports such as organic polymers, inorganic oxides or zeolites. The hope was that anchoring

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catalytically active transition metal complexes on solid supports will eventually give hybrid catalysts possessing the advantages of both homogeneous and heterogeneous catalyst systems.

Some general reviews on immobilized catalysts chemistry containing some examples of heterogenized hydroformylation catalysts are available in literature [7,13–15].

In this review the results obtained in the simple olefins hydroformylation in vapor and liquid phase catalyzed by metals or metal complexes adsorbed on inorganic oxides, clays, active carbons and zeolites, will be described.

The results obtained using supported carbonyl clusters as catalyst precursors will also be described. The surface chemistry of these compounds is strongly related to the chemistry of dispersed metal particles and the borderline between the two domains often appears very weak. Metal carbonyl clusters were in fact often used to produce small metal particles by decomposition and sometimes carbonyl clusters were supposed to be formed from metal particles in hydroformylation conditions.

Catalytic systems operating in CF (continuous flow) in SL-PC (supported liquid phase catalysis) conditions will not be described in the present review. The use of heterogenized hydroformylation catalysts in CF in SL-PC conditions was recently described in detail in an excellent book [16]. We will also not describe polymer or functionalized oxide anchored complexes used as hydroformylation catalysts.

A large number of patents on this subject are available, nevertheless this survey will cover only papers which appeared in the 'open literature' up to the end of 1995.

2. Supported metals

2.1. Metal exchanged zeolites and clays

2.1.1. Zeolites

Zeolites owing to their peculiar characteristics are largely used as catalysts and catalysts support. The highly thermally stable tridimensional structure, based on channels and cavities of constant size, confer in fact to these materials molecular sieving properties. The zeolitic cations can be reversibly substituted with almost every metal cation without destroying the tridimensional structure. Various metal exchanged zeolites have proved to be active catalysts of reactions of high industrial interest.

Zeolites of 13X, 4A and 5A type have been exchanged with cobalt cations by treatment with an aqueous cobalt nitrate solution and used as catalysts for the high pressure (20.2 ÷ 30.3 MPa) vapor phase propene hydroformylation in continuous flow [17]. The cobalt zeolites of A type were much more active than the 13X type. Selectivity to aldehydes was always over 99% with only traces of alcohols. Under steady-state conditions, the catalyst did not show remarkable cobalt loss. Regioselectivity appeared influenced by pressure but not by temperature. Catalytic activity under steady state conditions was tentatively attributed to unidentified cobalt carbonyls formed in the initial stage of the reaction by reductive carbonylation and stabilized inside the zeolite cavities.

A Na–Y zeolite was used to prepare a hydroformylation catalyst by equilibration with an aqueous solution of $[Rh(NH_3)_6]Cl_3$ [18]. The rhodium exchanged zeolite (1% Rh loading) was treated in autoclave at 403 K under a pressure of 81 MPa of $CO:H_2$ (1:1). The IR spectrum of the resulting material showed bands at 2095(vs), 2080(sh), 2060(w) and 1765(s) cm^{-1} distinctive of coordinated terminal and bridging carbonyls, attributed by the authors to the formation of carbonyl clusters entrapped within the zeolite cavities by the reduction of the exchanged metal. A clear identification of the entrapped carbonyl was not possible. The catalyst was used in the liquid phase hydroformylation of 1-hexene. The chemoselectivity for aldehydes formation was 95% ($R = 0.95$) [1]

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[1] R = Hydroformylation/olefin consumption.

and the selectivity for linear products S_L [2] was 50, analogously to that observed in the homogeneous phase using rhodium carbonyl clusters as catalysts [3]. An activity drop was observed after the first catalytic run and attributed to the loss of the catalyst adsorbed on the external zeolite surface. The results obtained in the 1,5-hexadiene hydroformylation were very interesting. In fact, using the rhodium–zeolite, dialdehydes were obtained with a 60% yield and monoaldehydes with a 40% yield, while with homogeneous cluster catalysts monoaldehydes were obtained in higher yield. The reasons leading to these results were not investigated further and no other papers were published on that subject by the authors.

If rhodium and cobalt are by far the most used hydroformylation catalysts, ruthenium is also known to catalyze, but with low chemoselectivity, the reaction in the homogeneous phase. Heterogeneous hydroformylation catalysts were prepared exchanging a Na–X zeolite with $[Ru(NH_3)_6]^{2+}$ [19]. A wine coloured Ru(III)-containing zeolite was formed, for which the species $[Ru(NH_3)_5OH]^{2+}$ was proposed. Two different batches of catalysts were prepared with 3.6% (sample A) and 4.7% (sample B) ruthenium content, respectively. Both catalysts were tested as ethylene hydroformylation catalysts in autoclave at 473 K and 10.1 MPa. The two catalysts behaved quite differently. Sample A actively catalyzed the reaction giving propan-1-ol and propan-1-al as main products. During the reaction some ruthenium was lost from the zeolite as monoruthenium carbonyl compound, identified by FT-IR spectroscopy and mass spectrometry. The recovered zeolite IR spectrum revealed the presence of an encased monocarbonyl and probably of a metal cluster. The catalyst was reused giving the same product distribution and a negligible metal lost. On the contrary the more concentrated sample B appeared to give alkanes and alcohols as major products. These results indicated that among many other factors the loading of metal complex played a vital role in such reactions. In the reducing environment, the reduced ruthenium species of the 'concentrated' (B) zeolite appeared to aggregate to form metal particles. At lower loading, metal carbonyls of various nuclearity were produced, but while the mononuclear species are lost from the zeolite, compounds of higher nuclearity may be trapped in the zeolite cage. The complex catalytic system was thought not promising and not further investigated.

The formation of zeolite encased carbonyl clusters, tentatively proposed by the authors of these papers [17–19], on the basis of only little spectroscopic evidence, was suggested to give an explanation of the catalysts' stability and selectivity. The use of cluster carbonyls as catalysts or catalyst precursors will be described in more detail in the third section.

A Na–13Y zeolite, exchanged with rhodium chloride (Rh% = 3.7) at pH < 6 and dried at 423 k, was used as catalyst for the ethylene and propene vapor phase hydroformylation in atmospheric flow reactor at 423 K. The catalyst's behaviour was described in a short note [20]. In the first 4 h the ethylene hydrogenation activity decreased while that of hydroformylation increased. The metal oxidation state of the fresh and used catalysts was estimated by XPS. The Rh $3d_{5/2}$ signal, found at 308.6 eV for the used catalyst, was attributed to Rh(I). Some reactivity data for propene and butene were also given and the following relative hydroformylation ease scale was suggested: ethylene > propylene > 1-butene. This olefin reactivity trend is quite general and will also be found with other catalytic systems.

The catalytic activity of a rhodium trichloride exchanged zeolite–Y in the vapor phase ethylene atmospheric hydroformylation was studied in detail by the Takahashi group [21–24].

The effects on the catalytic activity of the various pretreatments of the Rh–Y zeolite were studied [21]. Propionaldehyde and ethane were

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[2] The linear (normal) isomer selectivity SL is defined through all the text as linear/linear + branched · 100.

found to be the main products. It was found that the fresh catalyst irreversibly adsorbed a considerable amount of propionaldehyde. It was found that the fresh catalyst adsorbed irreversibly a considerable amount of propionaldehyde. This finding explained the induction period observed in the catalyst activity that in fact was remarkably shortened by preadsorbing the aldehyde. The pretreatment of the catalyst was found to remarkably affect the catalytic activity [21]. Pretreatment in the temperature range 338–453 K in He–H_2 flow enhanced the activity while the He–CO or He–CO–C_2H_4 pretreatment at 400 K reduced it. A slight decrease in the metal content was observed after the He–CO pretreatment; nevertheless, the detected activity decrease cannot be explained only by that. The observed larger decrease of the hydroformylation activity following the treatment with He–H_2 at 583 K compared with that of the hydrogenation activity, suggested that the larger rhodium metal particles formed during the pretreatment are active hydrogenation but not hydroformylation catalysts. A more detailed discussion on this topic can be found in the second part of this section, where the oxidation state and the steric requirements of the active sites of the hydroformylation and hydrogenation catalysts are analyzed [25–27].

The above described species pretreated at 583 K were found unreactive for hydroformylation but resulted to actively catalyze pentene formation from the adsorbed propionaldehyde [22]. Experimental results suggested that the reaction did not occur by ethylene and propylene co-dimerization.

Ethylene hydroformylation over Rh–Y zeolite was studied kinetically [23]. The rate of propionaldehyde formation was found approximately proportional to the partial pressure of ethylene, and inversely proportional to the pressure of carbon monoxide. Reaction rate was also found proportional to the square root of the partial pressure of hydrogen, and no appreciable isotope effect was observed when hydrogen was substituted with deuterium. On the basis of the results a reaction mechanism was proposed via the formation of propionyl intermediate by the reaction between an ethyl intermediate and adsorbed carbon monoxide. The propionyl intermediate-formation step was proposed to be the rate determining one (Scheme 1).

$$*(C_2H_4) + *(H) \longrightarrow *(C_2H_5) + *$$

$$*(C_2H_5) + *(CO) \longrightarrow *(C_2H_5CO) + *$$

$$*(C_2H_5CO) + *(H) \longrightarrow *(C_2H_5CHO) + *$$

$$*(C_2H_5CHO) \longrightarrow C_2H_5CHO + *$$

Scheme 1.

* and $^*()$ indicate the vacant site and the site occupied by the adsorbed molecule or atom in parentheses.

The atmospheric pressure hydroformylation of propylene and ethylene with Rh–Y zeolite was comparatively studied [24]. Pretreatment of the catalysts with He–H_2 (10%) considerably affected the steady-state rates, the apparent activation energies and product selectivity.

On the basis of the results obtained, the authors concluded that:

(1) hydroformylation of both ethylene and propylene can be, for steric reasons, catalyzed only by the active sites located either at the entrance of the pore or on the external surface of the zeolite.

(2) only the hydroformylation of ethylene but not of propylene can be catalyzed by the active sites formed in the pores even if they are at a very short distance from the entrance.

M.E. Davis and coworkers studied in detail rhodium exchanged zeolites as hydroformylation catalysts of simple olefins [28–36].

A direct comparison as vapor-phase propylene hydroformylation catalysts, of type X and Y zeolites exchanged with rhodium chloride by the Arai method [20], was reported [28].

Zeolites of the X and Y type are topologically the same but differ in chemical composition with the extra framework cations showing different distributions over the available sites. The higher selectivity to linear products (S_L = 66.6) compared with that of homogeneous binary rhodium carbonyls [3] was attributed to the zeolite structure. Although similar hydroformylation behaviour was observed for the RhNaX and RhNaY zeolites, different carbonylic species appeared to be present on the two zeolites. Infrared spectroscopy experiments showed the presence of the geminal rhodium dicarbonyl species $Rh(CO)_2^+$ on zeolite X while the cluster $Rh_6(CO)_{16}$ predominated on zeolite Y after hydroformylation (the nature of the various surface rhodium carbonyl will be discussed in more detail in Ref. [30] and in Section 2).

These studies were extended to propylene hydroformylation on variously prepared and preactivated Rh–X and Rh–Y catalysts [29,30]. The reactivity was studied in flow reactor at atmospheric pressure. All catalytically active preparations behaved similarly. A typical reactivity trend is shown in Fig. 1.

No hydroformylation activity was observed in any preparation where the rhodium was introduced as an ammine complex, while the exchange of aqueous $RhCl_3$ at pH 6 or above produced active catalysts. The concentration of rhodium within the zeolite did not significantly alter the reactivity. Regioselectivity, S_L was ≈ 66.6 in all cases. These values are approximately twice those observed in solution for binary carbonyls. Nevertheless, since a regioselectivity of 54.5 was found also for Rh/SiO_2 no shape selectivity was attributed to the zeolite structure. Chemoselectivity (R) was in the range 0.23 ÷ 0.15.

Hydroformylation activity for all the catalysts started when they were contacted with reactants at 423 K and steady state was achieved in approximately 16 h. Once activated the catalysts showed hydroformylation activity at temperatures as low as 353 K.

The authors believed that the activation process did not involve the reduction of rhodium but rather the formation of a rhodium carbonyl hydride. Indirect evidence of the hydride formation was presented in the following paper [30]. Selective poisoning experiments with phosphine on RhNaY catalyst were consistent with hydroformylation active sites located on the surface of the zeolite particles. The addition of the highly hindered hexyl diphenyl phosphine was found to dramatically alter the catalyst activity and selectivity. Consequently it was deduced

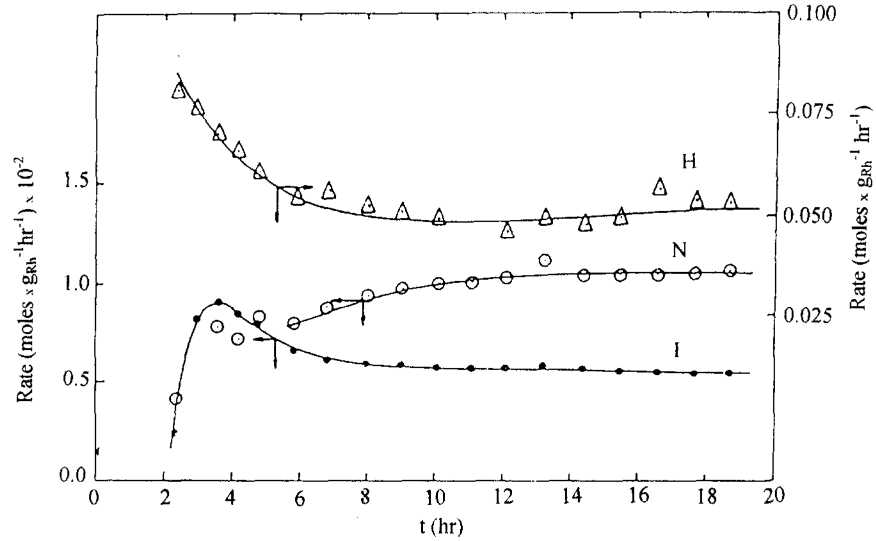

Fig. 1. Reaction rates versus process time for RhNaX. Reaction conditions: 423 K, 0.1 MPa. (△) Propane, (●) iso-butyraldehyde, (○) normal-butyraldehyde. (Reproduced from Refs. [28,29].)

that the active sites, at the steady state, were located on the surface of the zeolite crystals and not in the inaccessible internal cavities.

Analogously to what was previously found [22] a first-order dependence upon propylene, an inhibition by carbon monoxide, and an approximate half-order dependence upon hydrogen both for hydrogenation and hydroformylation were observed. These results in combination with in situ IR studies [30] led the authors to propose that propylene hydroformylation catalyzed by rhodium–zeolite proceeded with a mechanism similar to that proposed for the homogeneous reaction catalyzed by binary rhodium carbonyls [3].

Carbonyl formation and propylene hydroformylation on both RhNaX and RhNaY were studied by in situ FT–IR [30].

A rhodium dicarbonyl, of the type $Rh(I)(CO)_{2-}$ bonded to the zeolite surface oxygens, appeared to form on RhNaX at 393 K in flowing CO with carbonyl bands at 2096(s), 2016(s) cm^{-1}. The species was observed also on a not previously dried zeolite sample. Also the two couples of bands, respectively at 2101(s), 2022(s), and 2116(s), 2048(s), found on NaY dried before exposition to carbon monoxide, were attributed to two analogous Rh(I) dicarbonyl species, $Rh(CO)_2(O_z)_2$ and $Rh(CO)_2(O_z)(H_2O)$ (where O_z was zeolite lattice oxygen). If the zeolite was not dried, $Rh_6(CO)_{16}$ was ultimately formed probably by reductive carbonylation of the Rh(I) species in the presence of water and carbon monoxide. In hydroformylation conditions two new bands were observed to develop on the previously carbonylated Rh-zeolites at 2040 cm^{-1}, and 1660 cm^{-1}, the respective being tentatively attributed to $Z{-}O{-}Rh(CO)_2(C_3H_6)$ and to the acyl $Z{-}O{-}Rh(COPr)L_2$ ($Z =$ zeolite, $L = CO$ or O_z). The assignment of the bands was made by analogy with the spectra of known structurally well defined soluble molecular carbonyls.

Similar spectroscopic data were obtained when the interaction of various rhodium catalysts supported on a variety of oxides with CO and H_2 were studied and will be described in detail in the second section.

Since the hydroformylation start-up, regioselectivity, and activation energies were nearly the same for catalysts RhNaX and RhNaY, the authors proposed that the catalytic active species were the same for the two catalyst. Although no Rh–H band was ever observed by IR spectroscopy, the authors suggested that the active species contained a carbonyl hydride group and that only a small percentage of the available rhodium was involved in the reaction. [3]

Both RhNaX and RhNaY zeolites were found to behave as bifunctional catalysts for the synthesis of C7 (2-methylhexan-3-one and heptan-4-one) ketones from C_3H_6, CO, and H_2 at atmospheric pressure and 393–423 K [31]. It was proven that the zeolite was responsible for converting butyraldehydes and propylene into ketones.

It is well known that rhodium phosphine complexes are more selective towards the production of linear compounds than binary rhodium carbonyls in the hydroformylation in homogeneous phase [3]. Therefore, rhodium phosphine complexes in situ synthesis on zeolite NaY was attempted by various methods and the catalysts resulted active for propene hydroformylation at 423 K and 0.1 MPa [32]. The catalysts were not stable, yet showed an enhancement in linear products yield together with an increased production of alcohols in comparison with rhodium–zeolites without phosphines.

The hydroformylation of 1-hexene, 2-hexene and cyclohexene at low temperatures and atmospheric or elevated pressure was comparatively studied using both soluble and zeolite-supported rhodium species [33,34].

All reactions were performed in toluene. The variously prepared immobilized catalysts were

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[3] As far as we know a band attributable to the Rh–H stretching was detected only recently on rhodium supported on alumina surface at high pressure (Ref. [37]).

found active only at elevated pressures. The presence of an excess of phosphine during homogeneous catalysis was shown to inhibit isomerization of 1-hexene, thus giving high normal/branched aldehyde ratios for all levels of conversion. The activity of the immobilized catalysts was affected by the type and amount of phosphine. Soluble and/or polymer supported mercaptans were found to poison both the homogeneous and heterogeneous catalysts, provided an excess of phosphine was not present. The data from the immobilized catalysts suggested that claims of intrazeolitic hydroformylation with rhodium-containing faujasites were to be taken with caution.

A novel procedure for the synthesis of rhodium containing zeolite A was described by Rossin and Davis [35]. Some rhodium exchanged zeolite A crystals were added to synthesis gels in order to produce a zeolite A with intracrystalline rhodium.

The catalytic activity both in the vapor and liquid phase for the 1-hexene hydroformylation of the Rh zeolite prepared by this method was compared with that of a rhodium zeolite prepared by ion exchange [36]. The catalysts showed similar activity in vapor phase at 423 K and 0.2 MPa total pressure and both showed rhodium lost after exposure to the reaction environment. The metal loss, detected by chemical analysis and XPS, after the pretreatment in flowing CO, was attributed by the authors to rhodium migration towards the zeolite surface and sublimation as volatile carbonyl.

The liquid phase activity (2.02 MPa and 323–393 K) was somewhat different. The cation-exchanged catalyst was found to elute most of the rhodium into the solution and consequently the observed catalysis was homogeneous. On the contrary the synthesized rhodium–zeolite did elute rhodium less significantly. In the presence of cyclohexylmercaptan, a poison for the rhodium in solution and on zeolite surface, the synthesized catalyst transformed 1-hexene exclusively to heptanal at 393 K. Thus no isomerization of 1-hexene and no hydroformylation to branched aldehydes occurred, suggesting that the reaction was selectivity catalyzed by only the intrazeolitic rhodium.

Attempts were made to synthesize intrazeolitic rhodium catalyst by reacting protonated or partially protonated zeolite Y and the tris allyl complex $Rh(C_3H_5)_3$ [38]. Metal carbonylic species such as $Rh(CO)_2^+$ and clusters $Rh_6(CO)_{16}$ were formed by CO treatment depending on the reaction conditions. Reactivity experiments in the presence of phosphines suggested that rhodium was lying both within the zeolite framework and on the zeolite surface. When the zeolite supported phosphine complexes were used as liquid phase hydroformylation catalysts, all of the observed activity appeared to come from the solution phase because the metal was leached from the support.

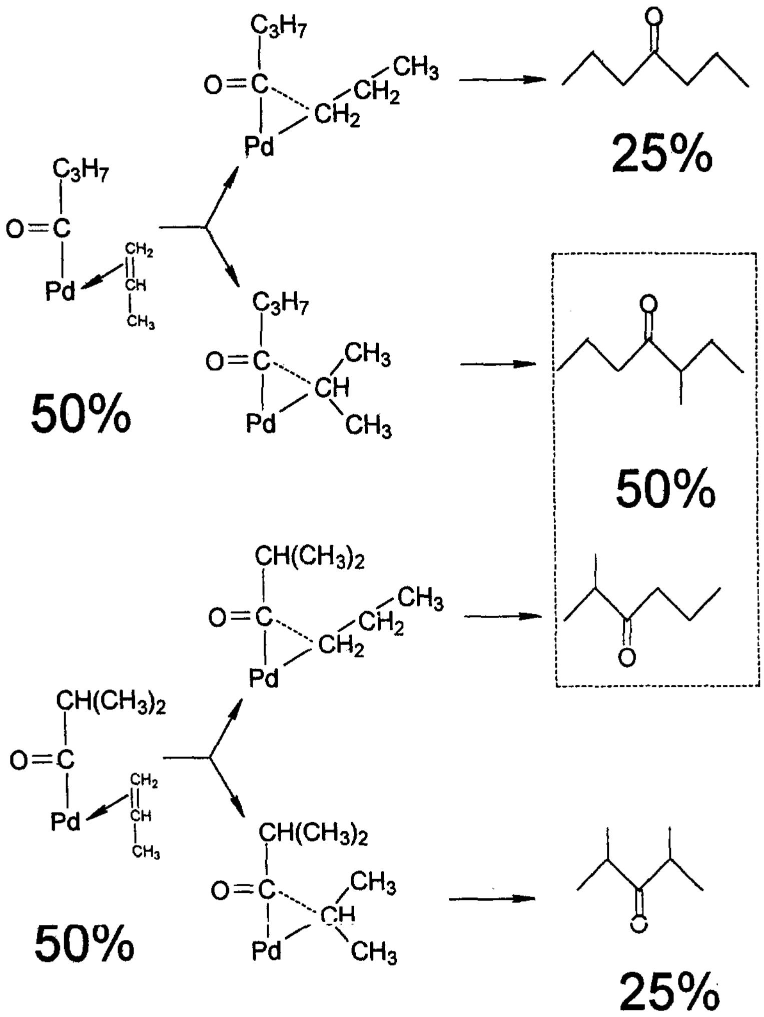
Iridium compounds were rarely used as hydroformylation catalysts, nevertheless a catalyst was prepared exchanging iridium trichloride $IrCl_3 \cdot 3H_2O$ on a NaZSM-5 zeolite [39]. The catalyst was tested for the liquid phase 1-hexene hydroformylation, (4.05 MPa, 423 K) in comparison with the soluble iridium catalyst $HIr(CO)(PPh_3)_3$. A metal carbonyl with bands at 2020 and 1880 cm^{-1} was detected by FT-IR spectroscopy on the zeolite after the reaction. The behaviour of the homogeneous catalyst and of the supported one in the presence of triphenylphosphine and formaldehyde were strikingly similar, with $S_L = 71.5$. The catalyst loss by leaching was found between 5 and 1%.

It has been reported that the selectivity of palladium complexes towards hydroformylation products was very poor [3]. The poor hydroformylation activity/selectivity of palladium could, at least in part, be attributed to its relative inability to form stable carbonyl clusters [40]. Catalyst heterogeneization did not improve the catalysts' performances and, for example, hydrogenation to saturated hydrocarbons predominated over hydroformylation with Pd/SiO_2 ($R = 0.05$). Nevertheless it was possible to prepare palladium trimethylphosphine carbonyl clusters encased in zeolite from a metal exchanged Y zeolite [41]. The catalyst was active and selective in the hydroformylation of propene at moderate pressure (1 MPa) and 445 K. During the hydroformylation, Pd clusters were observed to decompose with a consequent activity decrease. The authors proposed a reaction network basically consisting of two parallel paths, leading to propane and to C_4-aldehydes. The C_7-ketones were formed either from C_4-aldehyde and propene, or from adsorbed acyl and alkyl groups (Scheme 2).

The use of non-homodisperse catalysts in heterogeneous hydroformylation was briefly described by Huang et al. [42]. Non-homodisperse EGG-shell mono- and bimetallic catalysts were prepared by cation exchange of 13X zeolite with Ru and Co salts. The catalysts were used in the vapor phase α-octene atmospheric hydroformylation and the experiments showed that active metals located on the surface of zeolite particles were the main active sites and that the non-homodisperse catalysts were more active.

2.1.2. Clays

Smectite clays constitute a well-known naturally occurring class of inorganic catalysts. Re-



Scheme 2. Formation of C_7-ketones from C_4-acyl and C_3-alkyl species (the *n/iso* butyraldhyde ratio was assumed to be 1). (Reproduced from Ref. [41].)

cent progress in the intercalation chemistry of clays has aroused a renewed interest in these minerals as catalysts and catalyst supports.

The cationic hydroformylation catalyst precursor $Rh(COD)(PPh_3)^{2+}$, (COD = 1,5-cyclooctadiene), was readily intercalated into the swelling clay mineral hectorite by replacement of Na^+ ions of the interlamellar surfaces [43]. However, under hydroformylation conditions, the active rhodium complex was found to desorb from the clay interlayers in consequence of the formation of the neutral $RhH(CO)_x(PPh_3)_2$ ($x = 1, 2$) species.

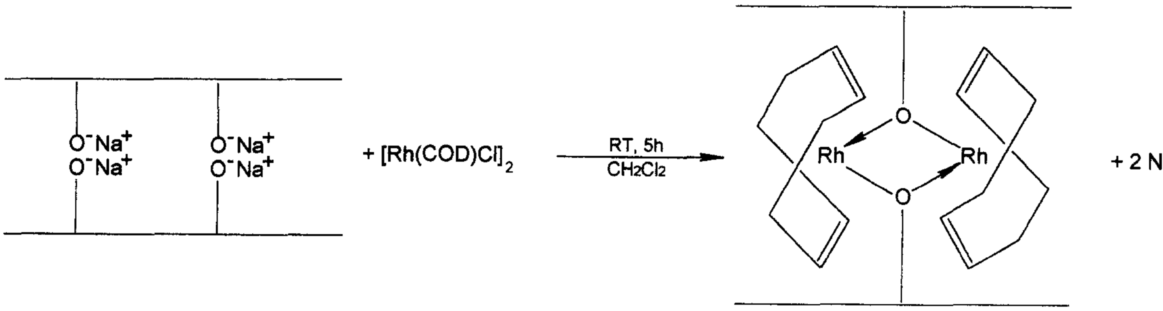
Rhodium complexes containing the positively charged phosphinophosphonium ligand $Ph_2P(CH_2)_2^+PPh_2(CH_2Ph)$, resulted to be much more suitable for catalyst intercalation. $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and $Rh(COD)^+$ all formed cationic complexes with this ligand which strongly bound to the clay interlayers and catalyzed the hydroformylation of 1-hexene at 373 K and 4.1 MPa of CO/H_2 with more than 95% yield, when acetone was the solvating medium. The polarity of the solvating medium was important in promoting hydroformylation in the interlayer regions of the intercalated clay catalysts. The selectivity to linear products were found somewhat higher for the intercalated catalysts ($S_L = 70.5 \div 75$) than for the homogeneous catalysts under analogous conditions ($S_L = 60 \div 68$).

The reaction of sodium montmorillonite with the dimer of chloro(1,5-cyclooctadiene rhodium(I) in dichloromethane to form a material in which rhodium is covalently attached to the silicate sheets of montmorillonite (Rh-clay) has been described recently [44].

The proposed intercalation reaction is schematically represented in Scheme 3.

The Rh-clay was shown to be an active catalyst for the regioselective hydroformylation of trialkylvinylsilanes, giving linear silyl aldehydes ($S_L = 96–100$) as the major products in good-to-excellent yields (90–98%). Since the interlayer expansion of Rh-clay was high (2.14 nm) and permanent, the choice of solvent and its polarity were not crucial unlike the above described system [43]. The authors suggested that regioselectivity, in the case of Rh-clay, could not be the result of spatial restriction, because the high value of interlayer spacing, but might be due to electronic factors.

Some years ago, it was found that permanent porosity could be induced in smectites by replacing the interlayer alkali metal ions with a variety of other robust cations including polyoxycations of various metals and the resulting materials were used as catalyst or catalyst support [45]. Some of these materials were used as hydroformylation catalysts [46,47]. The trimeric ruthenium amino cation $[Ru_3O_2(NH_3)_{14}]Cl_6$, 'ruthenium red' was readily and quantitatively exchanged in a sodium bentonite [46]. The multiply-charged ruthenium ions acted as cross-linking molecular rods and induced a clay layer separation of 0.5 nm. The modification of the clay spacing and the chemical modification of intercalated species, was monitored by UV



Scheme 3. Reproduced from Ref. [44].

spectroscopy, FT-IR spectroscopy and XRD. The interlayer cations of a sample pretreated in CO flow at 623 K, were transformed by thermal treatment in CO/H_2 between 423 and 543 K in a mixture of mononuclear carbonyls variously coordinated to the clay internal surface. The interlayer spacing of 1.32 nm suggested that some catalytic reactions could possibly occur in the constrained space within the clay layers. The catalytic activity of the clay for the vapor phase hydroformylation of ethylene and propene was tested in a flow reactor at atmospheric pressure. The reactivity decrease in hydroformylation on going from ethylene to propene was explained by the relative inaccessibility of propene molecules to the active catalyst located in the narrow interlayer clay site in analogy to what was found for the zeolites [28]. The best selectivity value to linear isomer was $S_L = 60$. Olefin dimerization caused by the clay acid sites and olefin hydrogenation appeared to limit the hydroformylation products yield.

In a successive study a commercial sodium bentonite (95% montmorillonite) pillared with aluminum polyoxocations was exchanged with a $RhCl_3$ solution [47]. The resultant pillared clay (Rh-PILC) had a surface area of 200 $m^2\ g^{-1}$, an interlayer spacing of 1.80 nm and a rhodium content of 0.46% w/w. The clay after thermal treatment at 623 K and activation in CO/H_2 flow at 493 K catalyzed the hydroformylation of ethylene and propene in vapor phase at atmo-

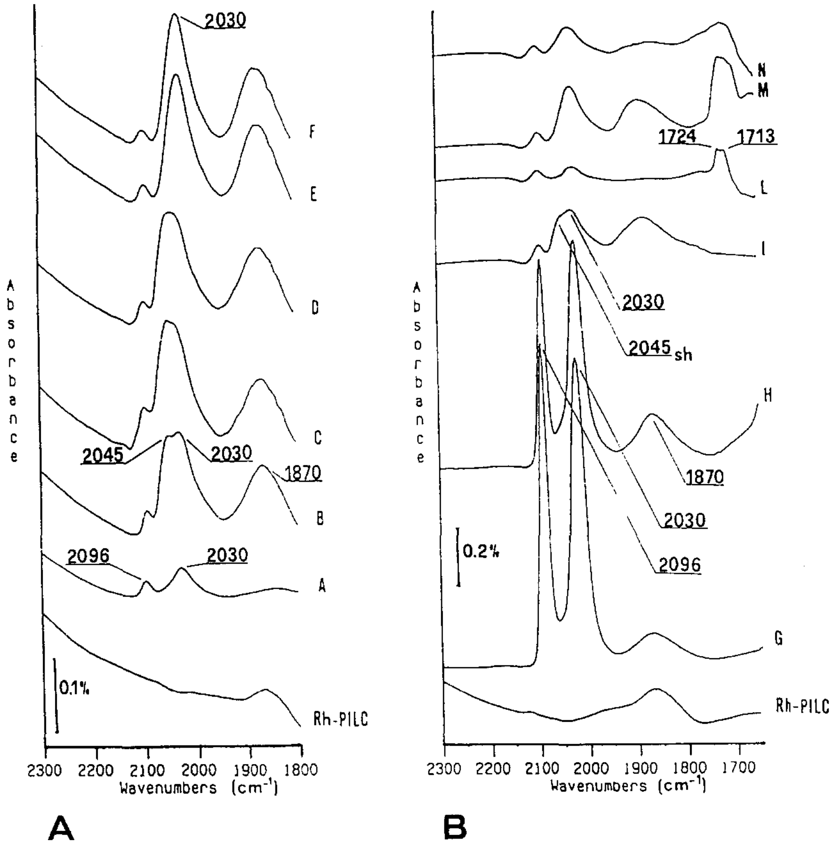


Fig. 2. (A) IR spectra of Rh-PILC in the ν(CO) region after exposure to: A, CO for 2 h at 393 K; B, CO/H_2 (1:3) for 2 h at 393 K; C, CO/H_2 (1:3) for 2 h a 453 K; D, CO/H_2 (1:3) for 24 h at 493 K; E, $CO/H_2/C_2H_4/N_2$ (1:3:1:15) for 1 h at 453 K; F, $CO/H_2/C_2H_4/N_2$ (1:3:1:15) for 24 h at 453 K. (Reproduced from Ref. [47].) (B) IR spectra of Rh-PILC in the ν(CO) region after exposure to: G, CO/H_2 (1:3) for 2 h at 423 K; H, CO/H_2 (1:3) for 2 h at 453 K; I, CO/H_2 (1:3) for 24 h at 453 K; L, C_2H_4/N_2 (1:10) for 2 h at 453 K; M, $CO/H_2/C_2H_4/N_2$ (1:3:1:15) for 2 h at 453 K; N, C_2H_4/N_2 (1:10) 30 min at 453 K. (Reproduced from Ref. [47].)

spheric pressure in the temperature range 373–473 K. The hydroformylation of propene proceeded with a good regioselectivity to normal products: $S_L = 78.5$ reasonably attributable to the constrained structure of the active sites located within the clay layers. The surface species formed in CO, CO/H_2 and under reaction conditions were studied by FT-IR spectroscopy (Fig. 2).

The bands at 2030 and 2045 cm^{-1} that appeared to belong to surface species most probably involved in the catalytic process were tentatively attributed to the νCO of a rhodium carbonyl hydride. The two bands at 1724 and 1713 cm^{-1} observed after ethylene adsorption (Fig. 2B, spectrum L) was attributed to propionaldehyde adsorbed on different sites of the clay surface. Selected examples of olefin hydroformylation on zeolites and clays supported catalysts are reported in Table 1.

2.2. *Metals and complexes supported on unfunctionalized oxides*

2.2.1. *Silica and alumina*

High surface area silica and alumina are largely used as catalyst support. Therefore several examples of hydroformylation catalysts supported on these oxides are available in literature.

Rhodium is by far the most common metal even if examples of other metals based catalysts are known.

Silica, alumina and all the other oxides commonly used in heterogeneous catalysis do not have the cation exchange properties characteristic of the zeolitic materials and therefore various techniques were developed to functionalize the oxide surface with suitable groups in order to anchor catalytic active complexes to the solid support. Nevertheless, some attempts have been made to catalyze olefin hydroformylation using the rhodium complexes known as active catalysts in homogeneous phase only adsorbed on inorganic oxides.

Hjortkjaer et al. [48,49] hydroformylated propylene using Wilkinson rhodium hydride catalyst on non-porous silica gel containing various excess of triphenylphosphine. A chemoselectivity increase with the phosphine loading and a decrease with the increasing carbon monoxide partial pressure was observed. Regioselectivity to *n*-products remained unchanged ($S_L \approx 90$) after about 400 h on stream, at 373 K and 1.11 MPa. These types of catalysts were further developed by these and other authors and the more important examples were described in P. Tundo's recent book [16].

The catalytic activity and selectivity of supported rhodium can be altered markedly by certain catalyst additives or promoters. The role

Table 1
Selected examples of olefin hydroformylation on zeolite supported catalysts

Olefin	Metal	Support	Reactor	Pressure (MPa)	Temperature (K)	S_L [a]	R [b]	Ref.
Propene	Co	13X	flow	20.26	438	65		[17]
Propene	Co	5A	flow	17.22	483	48		[17]
1-Hexene	Rh	Na–X	batch	8.10	373	50	0.95	[18]
Ethylene	Ru	Na–Y	batch	10.13	473		0.60	[19]
Ethylene	Rh	Na–Y	flow	0.10	423		0.16	[20]
Ethylene	Rh	Na–Y	flow	0.10	400		0.24	[21,24]
Propene	Rh	Na–Y	flow	0.10	423	53	0.03	[20]
Propene	Rh	Na–Y	flow	0.10	400	58	0.14	[24]
Propene	Rh	Na–X; Na–Y	flow	0.10	423	66	0.22	[28,29]
Propene	Rh	PILC [c]	flow	0.10	398	78.5	0.50	[47]

[a] S_L = linear/linear + branched $*$ 100.
[b] R = hydroformylation/olefin consumption ratio.
[c] PILC = aluminum pillared bentonite.

of the promoters was mainly studied in the two related reactions: CO hydrogenation and hydroformylation.

Two types of rhodium promoters were identified:

(a) Highly oxophylic elements such as Mn, Ti, or Zr and Nb oxides or suboxides that form an incomplete overlayer on the metal, enhancing CO dissociation through direct interaction with the oxygen atom of adsorbed CO;

(b) Fe, Zn, and Mg ions that promote oxygenate formation preventing CO dissociation and accelerating migratory insertion of adsorbed CO.

The effect of various promoters on silica supported rhodium hydroformylation catalytic activity was studied by Sachtler et al. [25–27].

A Rh–Zn catalyst on silica was prepared, with different Rh/Zn atomic ratios, by conventional coimpregnation of the corresponding chlorides followed by reduction with H_2 at 673 K, oxidation and H_2 reduction at the same temperature [25]. The reactivity was tested on ethylene hydroformylation in an atmospheric flow reactor in the range 423–473 K. Surface catalyst transformations were studied by FT-IR spectroscopy. The addition of Zn to Rh/silica led to an increase of the hydroformylation activity up to 50 times that of the unpromoted catalyst. Moreover, the selectivity towards hydroformylation R was improved by a factor of 15 for a Rh/Zn molar ratio between 0.05 and 0.3. The reaction profile is shown in Fig. 3

The nature of the surface carbon monoxide was studied by FT-IR spectroscopy on samples prepared adsorbing CO on a series of catalysts containing increasing quantities of Zn.

Two strong bands at 2065 and 1918 cm^{-1} for CO on Rh/SiO_2 were assigned, respectively, to linearly and bridged bonded carbonyls. With increasing Zn content the low frequency band attributed to bridged CO decreased significantly and the high frequency band broadened and splitted into a doublet.

The authors interpreted the data supposing that Zn ions blocked the multicenter ‘Freundlich’ sites of the Rh surface, forcing the adsorbing CO molecules into linear positions. In these conditions carbon monoxide dissociation could not occur. The Zn also appeared to increase the rate of CO insertion, suggested by the increase in selectivity for aldehyde formation.

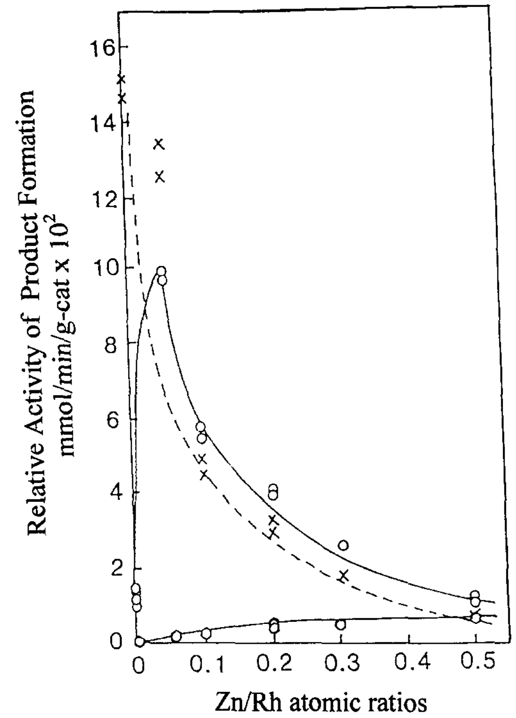


Fig. 3. Rates of product formation (mmol/min/g of catalyst) C_2H_5–CHO (circles), C_3H_7OH (hexagons), and C_2H_6 (Xs), by changing Zn contents (Zn/Rh atomic ratios) in SiO_2-supported Rh–Zn catalysts. Catalyst; 4.0 wt% Rh loading, 0.4–0.5 g. Reaction conditions: C_2H_4:CO:H_2 = 10:10:10 mL/min, 453 K, 0.1 MPa, SV = 1200 L/L/h. (Reproduced from Ref. [25].)

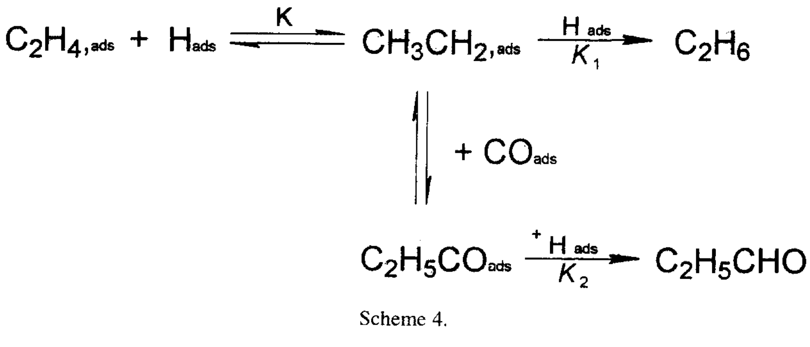
The catalytic site requirements for elementary steps in syngas conversion to oxygenates and ethylene hydroformylation were further studied using rhodium/silica promoted with Mn, Fe and Zn catalysts [26]. FT-IR spectroscopy, TPR and reactivity measurements suggested that highly oxyphilic Mn ions, when located at the rhodium surface, enhanced CO dissociation, possibly through direct interaction with the oxygen atom of tilted adsorbed CO. On the other hand iron and zinc ions appeared to block sites, thus inhibiting CO and H_2 dissociation. These steps in fact were thought to be characterized by large ensemble requirements. It was proposed that olefins hydroformylation, that is, in comparison with hydrogenation, selectively catalyzed by Zn and Fe promoted systems required only very small Rh ensembles. The importance of the dimensions of metal crystallites and of the exposed metal ensembles was pointed out before [21] and will also be stressed in other studies described in this section [27,50,51] and in the supported cluster section of this review [52,53].

The Zn promoted catalyst was used to study ethylene hydroformylation. The most striking results were the dramatic increase in hydroformylation yield observed for increasing amounts of added Zn ($Zn/Rh = 0.05–0.3$) to Rh/SiO_2, while the olefin hydrogenation was effectively suppressed. The preferential suppression of hydrogenation over hydroformylation due to Zn addition to Rh was thought to indicate that Zn ions not only blocked sites for dissociation but also impeded the H_2 dissociation, while the CO insertion remained active. A decreased rate of H_2 dissociation on the surface that was mainly covered with linearly adsorbed CO and Zn ions and their counterions implied a low steady-state concentration of H_{ads} and consequently a low chance for addition of two H atoms in rapid succession to an adsorbed ethylene molecule. The proposed mechanism is shown in Scheme 4.

In a successive paper Sachtler et al. studied how sulfur poisoning modified the catalytic properties of silica-supported rhodium [27]. The progressively increasing sulfur coverage of Rh surface strongly influenced the catalytic activity for ethylene hydroformylation and hydrogenation. It was found that adsorbed sulfur selectively inhibited the chemisorption of bridging CO. The rate of ethylene hydrogenation appeared strongly suppressed by adsorbed sulfur while the hydroformylation rate was little affected at low sulfur coverage. In terms of surface sites, counted by CO adsorption, the turnover frequency for hydroformylation to propionaldehyde actually increased. The authors proposed that sulfur was preferentially chemisorbed on the crystallites ‘hollow’ and flat sites blocking the centers where hydrogenation can favorably compete with hydroformylation, while protruding crystallite corner and edge atoms that are the most active in hydroformylation were not affected by sulfur coverage.

A good correlation between metal dispersion and catalyst activity and selectivity was found by Arakawa et al. studying vapor phase and pressurized ethylene hydroformylation on rhodium on silica [50]. The reaction was suggested to occur at the edge and corner rhodium sites.

The effect of the addition of sodium cations on the vapor phase propene hydroformylation over silica supported Rh, Pd, Pt, Ni was studied by Naito and Tanimoto [54]. The cation addition markedly lowered the activation energy of the hydroformylation process facilitating the CO insertion into propyl intermediates without affecting the regioselectivity. The mechanism of the hydroformylation of propene over silica-supported Rh and Pd catalysts was studied by isotope tracer technique with microwave spec-



Scheme 4.

troscopy, infrared spectroscopy and kinetic investigation [55]. The rate-determining steps of the hydroformylation were found to be different if the reaction was catalyzed by Rh or Pd. Hydrogenation of surface acyl species was proposed as the rate determining step in the case of Rh catalysts and CO insertion into surface propyl species in the case of Pd catalysts. The *n*-propyl species resulted more reactive for CO insertion than the *i*-propyl species.

It was found that the sodium cation addition on the hydroformylation increased the TOF (turnover frequency) and decreased the activation energies whether Pd or Rh were used as catalysts. Nevertheless, since the rate-determining steps proposed in the two cases were different, the sodium cation must have a different promoting action in the two cases.

In situ IR spectroscopy was extensively used by Chuang and coworkers, together with other techniques, to study ethylene and propylene hydroformylation on sulphur poisoned and not-poisoned group VIII metals on silica [56–63]. These studies gave more precise information on the nature of the surface species and on the presumed reaction mechanism confirming what was anticipated by the Sachtler studies [25–27]. Adsorbed acyl species were observed on Rh/SiO_2 catalysts by means of in situ IR spectroscopy during ethylene hydroformylation [56]. The finding of a band at 1678 cm^{-1} attributable to the metal acyl $C_2H_5(CO)$–Rh suggested that the insertion of CO into adsorbed ethyl species was taking place on Rh/SiO_2, in analogy to what was found by Davis [30]. Addition of H_2S to Rh/SiO_2 blocked the bridged-CO chemisorption sites, as found by others [27], but only slightly affected the vibrational frequency of linear-CO with no effect on the hydroformylation activity. Hydroformylation on sulfided Rh/SiO_2 appeared to resemble homogeneous hydroformylation to a greater extent than hydroformylation on Rh/SiO_2.

The effect of sulfur poisoning was also tested on Ni/SiO_2 [57]. Sulfidation of the catalyst with H_2S led to a blockage of bridge-CO sites, an upward shift in wavenumber of linearly adsorbed CO, an inhibition of ethylene hydrogenation, and an enhancement of the formation of propionaldehyde from ethylene hydroformylation. All these data suggested that isolated Ni-atom sites may be responsible for the reaction.

On the other hand it was found that adsorbed sulfur allowed the formation of propionaldehyde on Ru/SiO_2 but inhibited the desorption of this species, suggesting that desorption is the rate-limiting step on sulfided Ru/SiO_2 [58].

The reaction of adsorbed CO with C_2H_4/H_2 and ethylene hydroformylation over reduced (H_2, 1 h, 513 K), oxidized (air, 1 h, 513 K) and sulfided (H_2S, 1 h, 513 K) Rh/SiO_2 catalysts were investigated under reaction conditions by in situ-IR spectroscopy [59]. Both reactions involve a CO insertion step resulting in the formation of propionaldehyde. The linear CO adsorbed on the Rh^0 site of the reduced Rh/SiO_2 and the linear CO adsorbed on the Rh^+ site of the oxidized Rh/SiO_2 were consumed and propionaldehyde was produced as the adsorbed CO reacted with C_2H_4 and H_2. The results showed that both Rh^0 atoms and Rh^+ ion sites were active for the CO insertion reaction. In addition, a species with adsorption (2033 cm^{-1}) that can be assigned to a carbonyl hydride was present on the surface of the oxidized Rh/SiO_2 under hydroformylation conditions.

In situ infrared observations of steady-state ethylene hydroformylation showed that the oxidized Rh/SiO_2 containing considerable amounts of Rh^+ sites exhibited rate and selectivity for the formation of propionaldehyde higher than those of the reduced Rh/SiO_2. On the other hand the sulfided Rh/SiO_2 having mainly single Rh sites showed rate and selectivity for the formation of propionaldehyde higher than that of reduced Rh/SiO_2. The low selectivity of the reduced Rh/SiO_2 for ethylene hydroformylation was attributed to the high hydrogenation activity of the surface of Rh crystallites on this sample as previously proposed by others [27].

These findings were confirmed in a successive detailed in situ IR study on propylene hydroformylation on Rh/SiO_2 and sulfided Rh/SiO_2 [60].

CO adsorption on Rh/SiO_2 resulted (Fig. 4) in the formation of linear CO (2070 cm^{-1}) and bridged CO (1894 cm^{-1}) adsorbed on Rh^0 sites, and the gem-dicarbonyl on Rh^+ sites (2102 and 2036 cm^{-1}). The CO adsorption on S–Rh/SiO_2 resulted in a high wavenumber Rh(I)(CO) (2095 cm^{-1}) species in addition to linear CO adsorbed on Rh(0) (2073 cm^{-1}) and the gem-dicarbonyl adsorbed on Rh^+ (2036 and 2102 cm^{-1}). Sulfidation decreased the rate of CO adsorption and inhibited the formation of bridged CO on Rh/SiO_2 (only a very weak band was present at 1873 cm^{-1}). Sulfided Rh/SiO_2 was found to exhibit higher CO insertion selectivity, lower hydrogenation activity, and lower *n*-/*iso*-butyraldehyde selectivity than Rh/SiO_2 during steady-state propylene hydroformylation at 513 K and 0.1–1 MPa. In analogy with what was proposed by Konishi et al. [27] the authors proposed that protruding (corner) Rh atoms or ions were the catalytic active sites. It was suggested that enhancement of the *iso*-butyraldehyde formation induced by sulfidation could be due to the spacious environment of the protruding Rh^+ ion sites on the S–Rh/SiO_2 allowing -*n*-propyl groups isomerization before CO insertion.

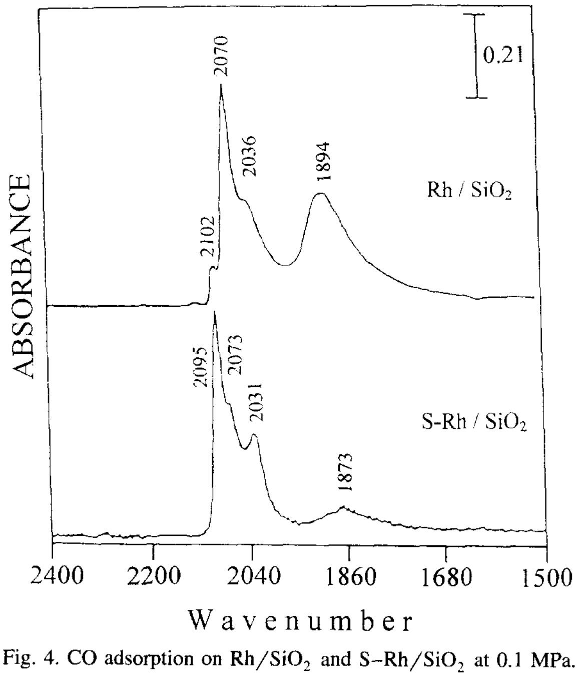


Fig. 4. CO adsorption on Rh/SiO_2 and S–Rh/SiO_2 at 0.1 MPa. (Reproduced from Ref. [60].)

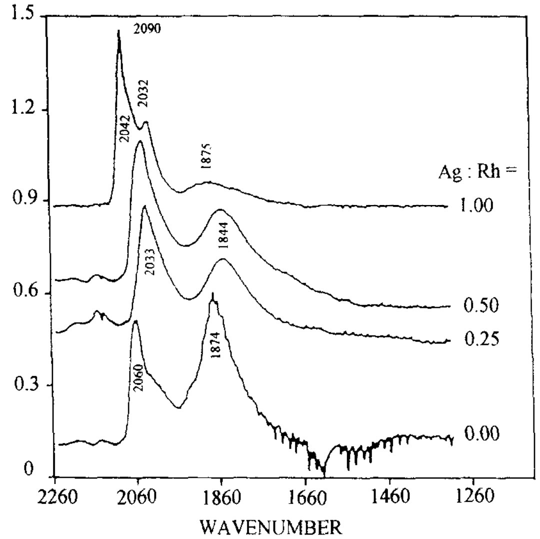


Fig. 5. Infrared spectra of adsorbed CO on Rh/SiO_2 and Ag–Rh/SiO_2 at 301 K. (Reproduced from Ref. [61].)

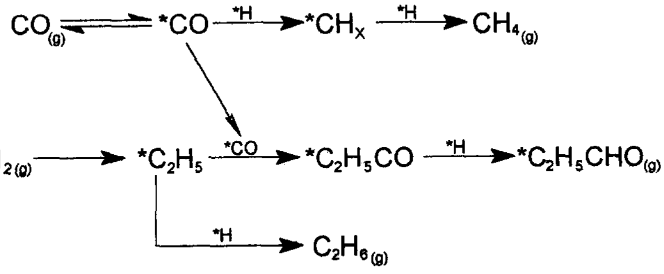
The effect of silver promotion on CO hydrogenation and ethylene hydroformylation over Rh/SiO_2 was studied [61]. X-ray diffraction (XRD) studies revealed that Ag and Rh formed separate crystallites on the support. CO and NO adsorption on Ag–Rh/SiO_2 at 301 K was followed by IR spectroscopy (Fig. 5).

The high linear CO/bridged CO sites ratio was explained supposing that the rhodium surface was decorated by Ag species that blocked the Rh ensembles required to bridge bind CO. The presence of gem-dicarbonyl bands, of bands attributable to linear CO on Rh^+ as well as high wavenumber NO^- bands, suggested that the Rh surface on the Ag–Rh/SiO_2 catalyst contained positive charges. XPS measurements confirmed the hypothesis. The increased activity and selectivity for C_3 and C_4 oxygenates was attributed to a high ratio of the linear CO to bridge CO sites and the possible presence of isolated Rh^+ sites under reaction conditions.

Incorporation of in situ infrared spectroscopy with steady-state isotopic transient kinetic analysis (SSITKA) may provide information on the surface coverages of IR observable species under reaction conditions and has the potential for distinguishing between reaction intermediates and surface adsorbed spectator species. The method was used to study methanation and ethylene hydroformylation over Rh/SiO_2 at 513 K and 0.1 MPa [62]. Analyzing the results the authors proposed that propionaldehyde was formed by insertion of linearly adsorbed CO into the adsorbed $^*C_2H_5$ species which was generated from hydrogenation of ethylene. A reaction scheme was proposed for methanation and hydroformylation (Scheme 5).

Interaction of C_2H_4/H_2 with $Rh^+(CO)_2/SiO_2$ and CO adsorbed on $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ and the activity of these catalysts for ethylene hydroformylation was studied by IR spectroscopy [63]. Chemisorption of CO on $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ at 298 K resulted in the formation of linear CO on Rh^+ (or Rh^{2+}) and Rh^{3+} sites as well as gem-dicarbonyls. Thermal stability of the adsorbed CO species was evaluated by temperature programmed decomposition (TPD). Thermal stability of surface carbonyls decreased in the following order: linear CO on Rh^+ of $RhCl_3/SiO_2 > Rh^+(CO)_2$ on $Rh(NO_3)_3/SiO_2 > Rh^+(CO)_2$ and linear CO on Rh^{3+} on $RhCl_3/SiO_2$. $RhCl_3/SiO_2$ showed, at 393 K and 1 MPa, higher hydroformylation selectivity than $Rh(NO_3)_3/SiO_2$. The $RhCl_3/SiO_2$ sample was found less susceptible to reduction by the reactant mixture than $Rh(NO_3)_3/SiO_2$ with a consequent higher hydroformylation selectivity. Under hydroformylation conditions (393 K, 1 MPa) the dominant CO species on $RhCl_3/SiO_2$ was the gem-dicarbonyl indicating that most of rhodium was present as Rh(I), while on $Rh(NO_3)_3/SiO_2$ both gem-carbonyls and CO linearly coordinated on Rh^0 were found. The participation of chlorine stabilized surface carbonyls species to the hydroformylation process was also proposed in other cases [31,63–65]. At 513 K both catalysts were reduced and selectivity to hydroformylation was significantly lowered. The low hydroformylation selectivity appeared related to the presence of Rh^0 which is known to be a highly active hydrogenation catalyst.

Selenium has an electronegativity similar to sulfur and its promoting effect on Rh/SiO_2 and Rh/ZrO_2 catalyzed ethene hydroformylation was studied by kinetics, FT-IR, XPS and EXAFS [66–68]. Se-modified Rh/ZrO_2 catalysts, prepared by the reactive deposition of $(CH_3)_2Se$ or coimpregnation method using SeO_2, were found to be active and selective for ethene hydroformylation [66,67]. XPS revealed that Se and Rh were, respectively, in the (2^-) and (0) oxidation states, and a direct Se–Rh bonding was suggested. The Se addition promoted the formation of propanol rather than propanal, the formation of which being increased more than 70 times compared to the unpromoted catalyst at an optimum Se/Rh ratio of 0.066. The intermediates propanoyl species were observed by IR at ca. 1770 cm^{-1} and converted reversibly to propionate species (bridge and bidentate) observed at 1425–1575 cm^{-1}. The ensemble of



Scheme 5.

Se^{2-}/Rh was suggested to promote both the CO adsorption and insertion into ethyl species. An electronic interaction of CO or propanoyl species with Se^{2-} was proposed. The observed isotopic effects suggested that the CO insertion step was not the rate-determining one, probably because the Se center assistance, and that the dissociative adsorption of H_2 was probably the slowest step of the reaction.

The study of the Se promoting effects on the ethene hydroformylation catalyst Rh/SiO_2 further confirmed these findings [68]. The H_2 adsorption decreased monotonously with the increasing selenium content and it was calculated that one Se atom was able to block 12 Rh sites. This caused a drastic suppression of ethane formation with a consequent increased selectivity to hydroformylation products (64.8%) for a Se/surface Rh ratio of 0.042. The reaction profile is shown in Fig. 6.

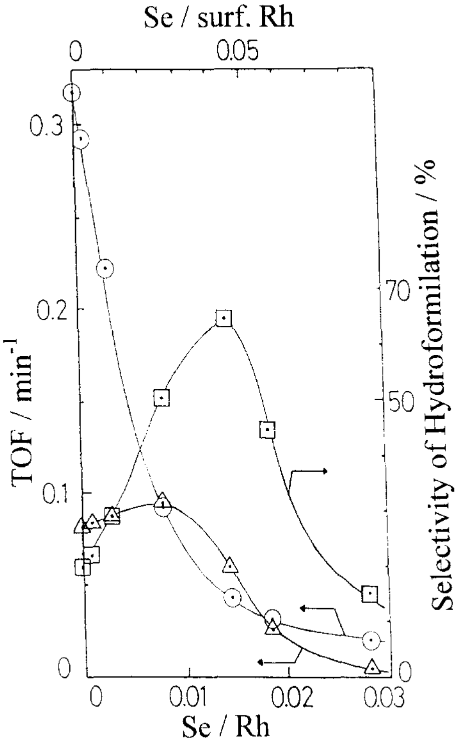


Fig. 6. Turnover frequencies (TOF) and selectivities of ethene hydroformylation on the Se-modified Rh/SiO_2 catalyst as a function of Se content; react. temp. 453 K; total pressure 40.0 kPa; C_2H_4:CO:H_2 = 1:1:1; ○, ethane; △, propanal; □, selectivity. (Reproduced from Ref. [68].)

It is well known that metallic salts reduction with boron and aluminum hydrides can produce nanocrystalline or amorphous metallic powders with unusual catalytic properties [69].

A Rh/B catalytic system with rhodium microcrystallites of $2 \div 4$ nm was prepared by reducing rhodium trichloride supported on silica and silica–alumina with $NaBH_4$ at low temperature [64,65]. Evidence of surface boron segregation, as a result of thermal treatments in Ar and/or CO/H_2 flow were obtained by XPS for the silica supported system. After treatment in Ar at 643 K in CO/H_2 the Rh/B system was found to catalyze the vapor-phase hydroformylation of ethylene and propylene at atmospheric pressure in a flow reactor. The ethylene hydroformylation resulted to proceed with a very good chemoselectivity towards hydroformylation products (at 398 K, $R \geq 0.7$). This was thought to indicate that boron particles partially covering rhodium ensembles prevented the H_2 dissociation on the surface, substantially reducing hydrogenation activity. The formation of the catalytic species was studied by FT-IR (Figs. 7 and 8) and XP spectroscopy.

The disappearance of the shoulder at 2040 cm^{-1}, attributed (see Ref. [47]) to a rhodium hydrido carbonyl or to carbon monoxide chemisorbed on relatively small rhodium ensembles [52], when the sample was treated with an ethylene flow, suggested that only this type of rhodium site was involved in the hydroformylation reaction. Propene hydroformylation at atmospheric pressure occurred with good regioselectivity towards normal isomers that remained constant with the increasing temperature, ($S_L = 88$). The surface composition of silica–alumina catalysts was apparently not affected by thermal treatments whether in argon or in CO/H_2 or in hydroformylation mixture flow. The authors tentatively attributed the high regioselectivity of the Rh/B system on silica and silica–alumina to the geometric arrangement of the active site that seemed to favor the linear alkyl formation over the branched one. The very low Rh/B atomic ratio of the surface

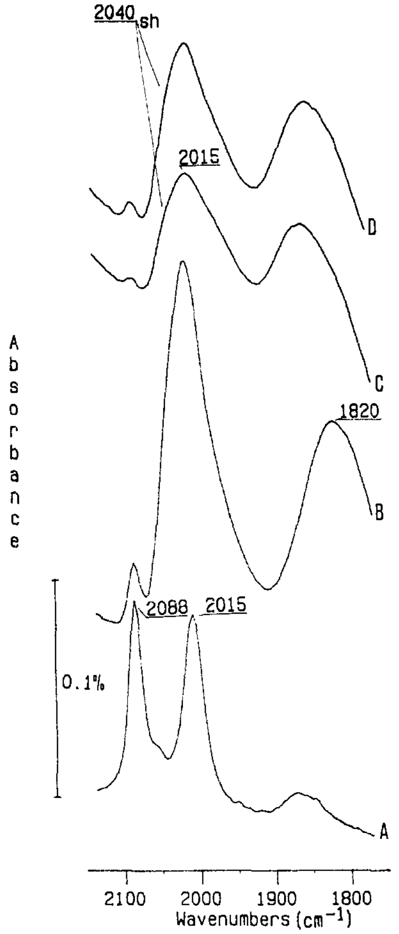


Fig. 7. IR spectra in the ν(CO) region of Rh–B successively treated in a flow of: (A) CO at 298 K; (B) CO/H_2 at 298 K; (C) CO/H_2 at 453 K; (D) hydroformylation mixture at 453 K. (Reproduced from Ref. [64].)

suggested that there were small isolated rhodium ensembles surrounded by oxidized boron or borates on which the coordination of the more hindered secondary alkyl was less favored than the linear isomer.

This preparation technique was extended to the Rh/Al system [70]. A Rh/Al system with rhodium nanocrystals was prepared by reducing rhodium trichloride supported on silica with lithium aluminum hydride at low temperatures in THF. After pretreatment in Ar and in CO/H_2 the system was found to be an active catalyst of vapor phase propene hydroformylation at atmospheric pressure. It was inferred from XPS measurements that Al was present as oxide and Rh as metal. The Rh BE (307.9 ± 0.2 eV) was slightly higher than the binding energy value (307.0 ± 0.2 eV) normally attributed to metallic rhodium. This could be probably attributed to the extremely small crystallite dimensions (1.8 ÷ 2.5 nm) (Fig. 9) but could also indicate that the electron density on the rhodium centers was close to that of a Rh(I) derivative.

Considerable changes occurred during thermal treatment within the catalyst layer analyzed by the XPS (2.0 nm) leading to an increase of Si/Rh and Al/Rh atomic ratios, attributable to the partial covering of rhodium particles by

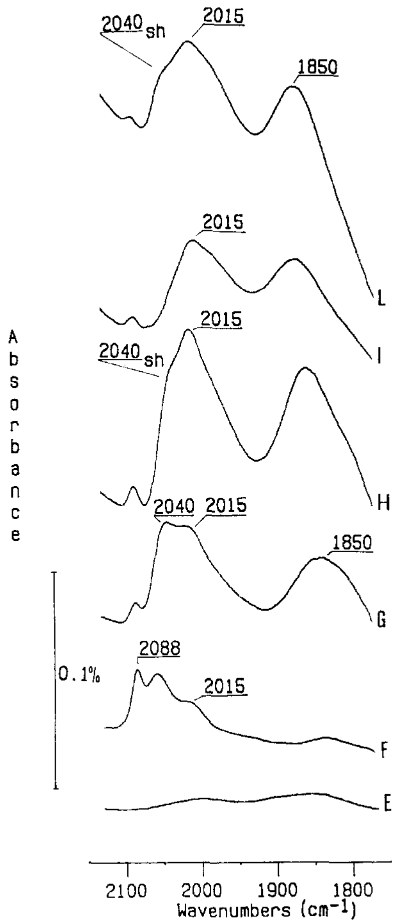


Fig. 8. IR spectra in the ν(CO) region of Rh–B successively treated in a flow of: (E) argon at 543 K; (F) CO at 298 K; (G) CO/H_2 at 453 K; (H) hydroformylation mixture at 453 K; (I) ethylene at 453 K; (L) CO/H_2 at 453 K. (Reproduced from Ref. [64].)

Fig. 9. XRD powder pattern of (A) Rh–Al as prepared (B) Rh–Al treated in air at 723 K, reduced in H_2 at 623 K and finally treated in CO/H_2 flow at 453 K for 24 h. (Reproduced from Ref. [70].)

aluminum oxide. The alumina appeared to prevent extensive sintering during the high temperature activation sequence. The active sites appeared different from the Rh/B system described previously [64,70], as could be deduced from FT-IR spectroscopy and reactivity experiments. When the Rh/Al based catalysts were subjected to the same experimental conditions, only the ν(CO) absorption at 2016 cm^{-1}, attributed to a carbonyl group bridge coordinated to the rhodium centers bonded to chlorine atoms (chlorine was detected by XPS), was observed and appeared to be involved in the catalytic process (Fig. 10). Moreover, apparent activation energies for hydroformylation where different viz. ca. 42 kJ/mol for Rh/B and ca. 26 kJ/mol for Rh/Al.

Rh–Co based catalysts supported on silica have been prepared by low temperature reduction of the preadsorbed Rh and Co salts with $NaBH_4$ in anaerobic conditions [71]. Three samples at different Rh/Co ratios (1/3, 1/1, 3/1) have been prepared and were compared with pure Rh/B and Co/B systems.

XPS analysis showed that in all the Rh–Co/B bimetallic systems, the surface was always enriched with cobalt. The rhodium was present only in the reduced form and cobalt was always found as Co^{2+}, most probably as oxide. Only signals attributable to nanocrystalline rhodium were found in the XRD spectrum.

IR studies of adsorbed CO confirmed the presence of Rh(0) (νCO at 2019 and 1880

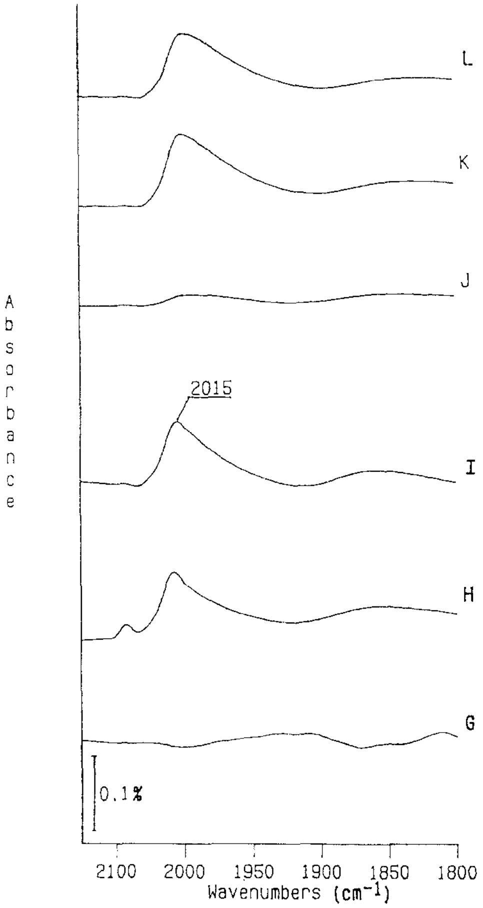


Fig. 10. IR spectra in the ν(CO) region of Rh/Al on silica, after exposure to: (G) air at 723 K for 24 h and H_2 at 623 K for 24 h; (H) CO at 298 K for 24 CO/H_2 at 453 K for 24 h; (J) C_3H_6 at 453 K for 15 min; (K) CO/H_2 at 453 K for 1 h; (L) $C_3H_6/CO/H_2$ (1:1:1) at 453 K for 1 h. (Reproduced from Ref. [70].)

cm^{-1}). No modifications were observed when the system was treated in CO/H_2 at 453 K.

TPR profiles of the 'as prepared' Rh–Co/B samples showed only the high temperature cobalt reduction bands. The TPR profile after oxidation in air at 673 K presented H_2 uptake in the rhodium reduction region shifted at 430 K attributable to bimetallic Rh–Co in intimate contact. An intimate contact of the two metals could be presumed also in the 'as prepared' samples with cobalt oxide decorating the rhodium crystallite surface.

The Rh–Co/B samples were tested in the vapor phase propene hydroformylation reaction. The system was active only above 0.5 MPa and presented a good chemoselectivity ($R = 2.7$) and very high regioselectivity towards the linear aldehydes ($S_L = 96$ at 403 K). The high selectivity was attributed (see Ref. [65]) to the constrained morphology of the active sites.

A very interesting contribution to the understanding of the rhodium catalyzed heterogeneous hydroformylation can be found in two papers by Asakura et al. [72,73] where the catalytic activity towards ethylene hydroformylation of a rhodium dimer attached to silica was described. The catalyst, studied by in situ EXAFS and FT-IR spectroscopy measurements, was more active and selective than conventional impregnation catalysts. It turned out from these data that a minimum of two bonded metal atoms are necessary for the hydroformylation, and that on such a catalyst the hydroformylation was largely favored compared to hydrogenation. The structural change of the Rh dimer sites in each reaction step for catalytic hydroformylation was followed by means of in situ FT-IR and EXAFS techniques. A metal assisted reaction mechanism involving metal–metal bond breaking by CO adsorption followed by CO insertion promoted by Rh–Rh rebonding was proposed.

Rhodium based heterogeneous hydroformylation catalysts are by far the most studied and other metals were seldom used. Some examples were already described [17,19,41,46,57] and some more will be presented in this part.

The hydroformylation of 1-pentene was studied over rhodium, cobalt and ruthenium supported on silica and alumina catalysts [74]. Reactions were also performed over metal on carriers modified in situ with triphenylphosphine and (+) or (−) DIOP. The activity of unmodified metals increased in the sequence: Co < Ru < Rh. The phosphines favored the formation of linear *n*-hexanal. In the presence of (−) DIOP asymmetric hydroformylation was achieved over Rh/alumina catalyst in the presence of a large excess of chiral ligand. A 'regioselectivity against enantioselectivity' effect was found over the modified rhodium catalyst. This effect was attributed to the participation of two types of active metal centers to the catalytic cycle.

Ru/SiO_2 catalysts, prepared by the reduction of supported $RuCl_3 \cdot H_2O$ were found active in gas-phase hydroformylation of propene and ethylene at atmospheric pressure [75]. Similarly prepared catalysts showed, at low pressure (ca. 0.3 MPa), high selectivity towards unbranched oxo-products ($S_L \approx 88$) but the rate of propylene hydrogenation was 10–15 times higher than that of hydroformylation ($R = 0.1 \div 0.06$) [76]. The low chemoselectivity towards the hydroformylation of the system, also observed in other cases [28], is not surprising taking into consideration the known high hydrogenation activity of ruthenium metal.

Some promising results were obtained using silica supported sulfided metals [77]. Nickel sulfide and sulfided group VIII metals including nickel, cobalt, iron, ruthenium, iridium and osmium were found to have hydroformylation activities at 423–573 K and 1.01 MPa. Using ethylene as reactant, ethane and propionaldehyde were the major products. Sulfided nickel appeared to be the most active catalyst. Nevertheless, these sulfided catalysts resulted more active and selective for the hydrogenation of alkenes than the current homogeneous hydroformylation catalysts. An improvement of the selectivity towards hydroformylation was thought by the authors necessary for a successful industrial development of the process.

$$CH_3{-}CH{=}CH_2 + CH_2{=}CH_2 + CO + H_2 \longrightarrow CH_3{-}CH_2{-}CH_2{-}CO{-}CH_2{-}CH_3$$

Scheme 6.

These studies were extended to some alumina supported bimetallic sulfided catalysts [78]. Sulfided alumina-supported Co, Ni, Co–Mo and Ni–Mo catalysts were found active for the hydroformylation of ethylene to propanal, in flow reactor at 513–563 K and 1 MPa. Among these catalysts, the nickel and cobalt catalysts presented the highest hydroformylation selectivity, while the presence of molybdenum enhanced the formation of undesirable side products (ethane) and sulfided compounds, lowering the hydroformylation selectivity. This behaviour was attributed to the formation of CoMoS and NiMoS mixed phases.

When these studies were extended to sulfided Rh, Ir and NiMo based catalyst supported on carbon, ketones (diethylketone, propylethylketone) formation was observed [79]. Diethylketone formed during hydroformylation appeared to be the result of the reaction of two molecules of ethylene with one molecule of CO and one of H_2, as suggested also by others [80,81]. To explain the presence of propylethylketone the authors supposed that propylene was formed by ethylene homologation on the coordinatively unsaturated molybdenum sites present in the sulfided NiMo catalyst. The formation of propylethylketone was easily explained considering a pathway similar to that proposed for ethylene (Scheme 6).

In the case of Rh and Ir catalysts, however, the authors supposed the existence of other sources of propylene because olefins homologation ability was never reported for the catalysts. Nevertheless, because traces of propanol were present among the reaction products, they proposed that propylene could also be formed by its dehydration (Scheme 7).

Kobayashi reported that Pd/SiO_2 was active for ethylene hydroformylation, where its catalytic activity was surprisingly found [40] to be comparable to that on Rh/SiO_2 [82]. Nevertheless, details concerning the catalytic behaviour of the system were not clarified.

A more detailed study on the catalytic activity and selectivity of Pd/SiO_2, as a function of catalyst dispersion, was published by Takahashi et al. [51]. In the ethylene hydroformylation over Pd/SiO_2 catalysts with 17 ÷ 85% Pd-dispersion, the turnover frequency for propionaldehyde formation increased with the Pd dispersion, suggesting the involvement of the atoms at the corners and at the edges of the Pd particles in the catalysis.

FT-IR spectroscopy measurements of adsorbed CO showed that the (linear-CO)/(bridged-CO) ratio increased with an increase in the Pd-dispersion, indicating an increase in the ratio of the protruding atoms against the total number of Pd atoms. EXAFS measurements on two representative samples confirmed these findings. The importance of metal dispersion to achieve a good chemoselectivity toward hydroformylation was evidenced also in various works on rhodium based systems [27,50,52,53].

Many studies of homogeneous olefin hydroformylation using the association of platinum complexes and tin salts as catalysts have been published, including asymmetric hydroformylation of olefins [12]. Heterogenization of several Pt/Sn complexes on silica, magnesia and alumina carriers was reported [83–85]. XP-spectroscopy was used to determine the surface composition and the nature of the anchored compounds. The observed BE values were found to correspond well to those expected for Pt^{2+},

$$CH_3{-}CH_2{-}CHO + H_2 \longrightarrow CH_3{-}CH_2{-}CH_2{-}OH \longrightarrow CH_3{-}CH{=}CH_2 + H_2O$$

Scheme 7.

Sn^{2+} and Cl^- species. In all cases a surface enrichment in tin species was noted.

The hydroformylation of styrene, allyl benzene [83], 1-pentene [84], and ethylene [85] was studied on this type of catalysts in batch conditions without solvents at 8.0 MPa. The hydroformylation activity was found to depend on the type of support and tin precursor used. Only the silica supported catalysts were active in the hydroformylation. Hydrogenation or isomerization reactions were not observed and a high selectivity to *n*-aldehydes was found [83]. Selectivity to *n*-hexanal of the silica-supported catalyst prepared from $SnCl_2 \cdot 2H_2O$ was as high as 94.4% at 39.2% conversion of 1-pentene [84].

Heterogeneous catalysts have been rarely employed for hydroformylate functionalized olefins [86,87]. Commercial rhodium on alumina (Rh–Al_2O_3 5%) was used as catalyst for the hydroformylation of ring substituted styrenes [86]. The reaction was performed in an autoclave, in the absence of solvent, at 8.0 MPa and 358 K. Product distribution resulted independent of substituents, since chemioselectivity as well as regioselectivity were always high.

Rhodium based catalysts supported on silica have been prepared by low temperature reduction of the preadsorbed salts with, respectively, $NaBH_4$ [65] and $Zn(BH_4)_2$ [87]. From the FT-IR data it appeared that the bridging CO chemisorption was substantially suppressed, as was observed by others in similar systems [26,27], probably because boron and zinc oxide molecules cover most of the catalyst surface blocking the multicenter rhodium sites. Both catalysts were active in the liquid phase hydroformylation of ring substituted styrenes. The reaction resulted truly heterogeneous because no leaching of catalyst was observed. The chemoselectivity ($R \approx 1$) was always very high, and the regioselectivity appeared controlled by the nature of the ring substituents. Examples of olefin hydroformylation on silica supported catalysts are reported in Table 2.

2.2.2. *Reducible oxides (titania, niobia)*

Reducible oxides were scarcely used as hydroformylation catalysts supports, nevertheless the few available results deserve some interest [88,89].

Table 2
Selected examples of gas flow ethylene and propene hydroformylation on unfunctionalized silica supported catalysts

Olefin	Metal (promoter)	Pressure (MPa)	Temperature (K)	S_L [a]	R [b]	Reference
Ethylene	Rh(Zn)	0.10	453		0.64	[25,26]
Ethylene	Rh(S)	0.10	453		0.26	[27]
Ethylene	Rh	1.96	453		0.39	[50]
Ethylene	Rh	1.01	393		0.64	[56]
Ethylene	Ni(S)	3.04	513		0.41	[57]
Ethylene	Rh(S)	1.03	513		0.36	[58]
Ethylene	Rh	1.03	513		0.27	[58]
Ethylene	Rh(Ag)	2.00	513		0.50	[61]
Ethylene	Rh(B)	0.10	418		0.74	[64]
Propene	Rh(Na^+)	0.10	388	74	0.23	[54,55]
Propene	Rh(B) [c]	0.10	393	88	0.70	[65]
Propene	Rh(B)	0.10	393	88	0.72	[65]
Propene	Rh(Al)	0.10	393	62	0.75	[70]
Propene	Rh(Co)	0.51	403	96	0.74	[71]
Propene	Ru	0.30	333	88	0.09	[76]

[a] S_L = linear/linear + branched * 100.

[b] R = hydroformylation/olefin consumption ratio.

[c] Supported on silica–alumina.

Coprecipitated Ni–TiO_2 catalyst, prepared by coprecipitation from aqueous solutions of metal nitrates, showed higher activities for ethylene hydroformylation at atmospheric pressure than conventional supported nickel catalysts. The preferential non-dissociative CO adsorption suggested by TPRE (temperature programmed reaction) measurements of adsorbed CO can explain the catalyst behaviour [88].

In a current model of SMSI (strong metal support interaction), a reduced oxide species (TiO_x NbO_x, etc.) formed by HTR (high temperature reduction) migrates onto metal particles and then blocks surface metal atoms, leading to the suppression of the capacity for H_2 and CO chemisorption and affecting preferentially those reactions which require a large ensemble of the surface active sites (decoration model) [90].

This model was invoked to explain the behaviour of HTR treated Pd/Nb_2O_5 hydroformylation catalyst [89]. The observed increase of hydroformylation rate after HTR, was in fact attributed to site isolation with consequent suppression of bridged CO chemisorption by physical blockage of Pd surface sites by NbO_x.

An analogous site isolation based model was used to explain the activity and selectivity of other promoted systems [25–27,64–71,78,79].

2.2.3. *Activated carbon*

Active carbon is a widely used support in heterogeneous catalysis and rhodium supported on this material has been found to be active for ethylene hydroformylation at atmospheric pressure [80,81]. Nevertheless, this system behaved very differently from the other rhodium supported catalysts and a considerable amount of pentan-3-one (diethylketone) was formed during the reaction, particularly at temperatures below 393 K. Particularly the Rh–C catalyst prepared from $RhCl_3$ resulted to be much more active for pentan-3-one formation than the catalysts prepared from $Rh(NO_3)_3$ or $Rh(CH_3COO)_3$. The effectiveness of chorine ions in stabilizing the catalysts active species was underlined also in other studies [31,63–65]. By using ^{13}C-labeled compounds, it was clarified that pentan-3-one was formed from two ethylene molecules and one molecule each of carbon monoxide and hydrogen over the active sites on the catalyst, and not from one molecule each of ethylene and propionaldehyde.

3. Metal carbonyl clusters or cluster derived metals on unfunctionalized inorganic oxides and zeolites

The idea of possible relations between molecular cluster and surface chemistry was suggested several years ago by Burwell and Peri [92] and developed in the following years [93]. Metal carbonyl clusters were studied as possible models for the important class of heterogeneous catalysts constituted by metal particles dispersed on a high surface area oxide support. Metal carbonyl clusters offer an alternative method of catalyst preparation since they can be imagined to contain preformed metal particles. Interaction with the support and ligand dissociation by thermal treatment can give origin to an anchored molecular catalyst or to a nanocrystalline metallic particle [94–96]. The distinction between catalysis by small metal particles and supported true molecular clusters is not always clearly defined in literature and the two types of catalysts will be treated together in this section.

The contribution of M. Ichikawa and coworkers to the study of supported carbonyl clusters and their use as catalysts in hydroformylation has been, from the end of the seventies up to date, continuous and remarkable. Bimetallic carbonylic clusters were used to prepare 'taylor made' bimetallic catalysts where the two metals were presumed to remain in intimate contact. The partners of rhodium in the metal couples were selected between the metals known as promoters of the hydroformylation and these papers can be considered complementary to those described in the preceding section [25–27].

Various metal carbonyl clusters such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_2Co_2(CO)_{12}$,

$RhCo_3(CO)_{12}$ and $Co_4(CO)_{12}$ were deposited (0.1–0.5 wt% Rh loading) on ZnO from hexane or tetrahydrofuran solutions [97]. The monometallic rhodium based materials, derived from $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$, after pyrolysis in vacuo (433 K) or activation under oxo synthesis gas mixture (383–403 K), catalyzed the vapor phase ethylene and propylene hydroformylation. FT-IR spectra in the carbonyl region of the catalysts in hydroformylation conditions were found to resemble those of the anions $Rh_6(CO)_{15}^{2-}$ and $Rh_6(CO)_{14}^{4-}$ in solution. The author proposed, on the basis of these results, that the dispersed Rh crystallites on ZnO prepared by pyrolysis in vacuo might reconstruct to form carbonyl species catalytically active for olefin hydroformylation, similar to partly decarbonylated Rh clusters. Hydroformylation rates and regioselectivity appeared relatively structure sensitive to the precursor carbonyl clusters. The hydroformylation rate for the bimetallic catalysts was found to decrease with increasing Co content. Interestingly pyrolyzed $Co_4(CO)_{12}$ exhibited the highest selectivity to linear aldehydes ($S_L \geq 90$) and the lowest specific activity.

Later on these studies were extended to other neutral and anionic rhodium cluster precursors supported on ZnO and the highest activity values were found for the catalyst derived from $Rh_4(CO)_{12}$ [98]. Other basic oxides such as MgO, La_2O_3, TiO_2 and ZrO_2 were successfully used as alternative carriers in the preparation of the Rh cluster-derived catalysts active for olefin hydroformylation, [98] whereas poor catalysts were obtained when silica and alumina were used as supports. A confirmation of the different behaviour of the clusters on various oxides was found in the XPS data reported in the following paper [99]. It was in fact found by XPS measurements that the oxidation state of the more active rhodium catalyst obtained by cluster decomposition was between Rh(0) and Rh(I) [99]. The electronic state of the catalytically inactive Rh on Rh/SiO_2 was similar to that of rhodium metal. Evidence that rhodium sites in an oxidation state close to Rh(I) were necessary to selectively catalyze atmospheric olefin hydroformylation were found by several authors [25,56,59,62,87] and related to the proposed reaction occurrence with a homogeneous like mechanism.

Bimetallic catalysts, obtained from Rh–Co mixed metal carbonyl clusters precursors, were also tested. If the $Rh_4(CO)_{12}$ on ZnO derived catalyst appeared to be the most active, the catalysts derived from clusters having larger cobalt contents were 15 times less active, on metal weight basis, but more selective towards linear aldehydes, as found in the preceding paper [97]. On the other hand it was noted that if the activity was calculated on Rh basis the values found for bimetallic catalysts were comparable to that of those derived from $Rh_4(CO)_{12}$. The author speculatively proposed that Rh–Co clusters on ZnO might behave as 'highly dispersed alloys' with compositions similar to those of the corresponding precursors. The enhancement of the regioselectivity towards linear products found in Rh–Co based catalysts was attributed to electronic donation from cobalt to rhodium atoms.

Rh–Co and Rh–Fe bimetal catalysts were prepared from the metal carbonyl clusters $Rh_{4-x}Co_x(CO)_{12}$ ($x = 2, 3$) and $[Rh_4Fe(CO)_{15}][NMe]_2$ impregnated from suitable organic (THF or pentane) solutions on silica, ZnO and amorphous carbon [100]. The resulting materials (1–4% metal loading), after solvent vacuum evaporation, were subjected to heat treatment (293–473 K) followed by H_2 admission at different temperatures (473–673 K). Higher activities in the atmospheric gas phase hydroformylation of ethylene and propene (323–453 K) were achieved on carbon-supported Rh–Co and SiO_2-supported Rh–Fe bimetal clusters, compared with those of the Rh-, Co- and Fe-only catalysts as well as the conventionally prepared from the metal salts catalysts. Co atoms in the Rh–Co and Fe in the Rh–Fe bimetal catalysts resulted to promote the rates of hydroformylation catalyzed by Rh and to improve selectivities towards linear aldehydes. The catalysts were studied by in situ EXAFS (extended X-ray absorption fine structure), Mössbauer spectroscopy and HRTEM (high resolution transmission electron microscopy) and the formation of a directional bimetal bonding such as Rh–Co (or Rh–Fe), and a further bond with the oxygen of the support was proposed (Fig. 11).

On the other hand EXAFS data revealed that the conventional Rh–Co catalysts derived from metal salts had a heterogeneous metal composition with Co atoms covering the bulk Rh particle in the phase segregation. Higher activities of carbon supported Rh–Co bimetal clusters were explained by the low oxidation state of Co (hardly retained on metal oxide supports) of the Rh–Co ensemble on carbon Co in Rh–Co and Fe in Rh–Fe clusters on alumina or silica were found present in higher oxidation states even after a strong H_2 reduction (673 K), and they appeared coordinated with Rh atoms, having a direct Rh–Co–O and possibly Rh–Fe–O-bondings. Therefore, Co and Fe atoms appeared to prevent the Rh aggregation under the reaction conditions, to have a breaking action dividing the Rh ensemble as well as an electronic donor action stabilizing the acyl intermediates.

These studies were extended to the carbonyl clusters $[TMBA]_2[Fe_3(CO)_{11}]$, (TMBA = NMe_3CH_2Ph), $[TMBA] \cdot [FeRh_5(CO)_{16}]$, $[NMe_4]_2 \cdot [FeRh_4(CO)_{15}]$, $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$, and $[Fe_3Rh_2(CO)_{14}C]$ that were employed as molecular precursors for the preparation of Rh–Fe metallic catalysts. Impregnated catalysts were oxidized by air at room temperature overnight and reduced by flowing H_2 473–673 K and held at 673 K for 2 h. Hydroformylation reactions of ethylene and propylene in gas flowing reactor was carried out as diagnostic reaction [101]. The hydroformylation activity for both olefins was dramatically increased for catalysts derived from $FeRh_5$, $FeRh_4$, Fe_2Rh_4, and Fe_3Rh_2 carbonyl clusters compared with the Rh_4-derived or physically mixed Rh–Fe catalysts. The selectivity ($S_L \approx$ 75) for normal isomers was not affected by the Fe content in the precursor complexes. The results suggested, analogous to what was said in the preceding paper, that Rh–Fe bimetallic carbonyl clusters provided discrete ensembles of Rh–Fe atoms impregnated on SiO_2. Mössbauer spectroscopy data suggested that Fe in the Rh–Fe carbonyl cluster-derived catalysts existed as

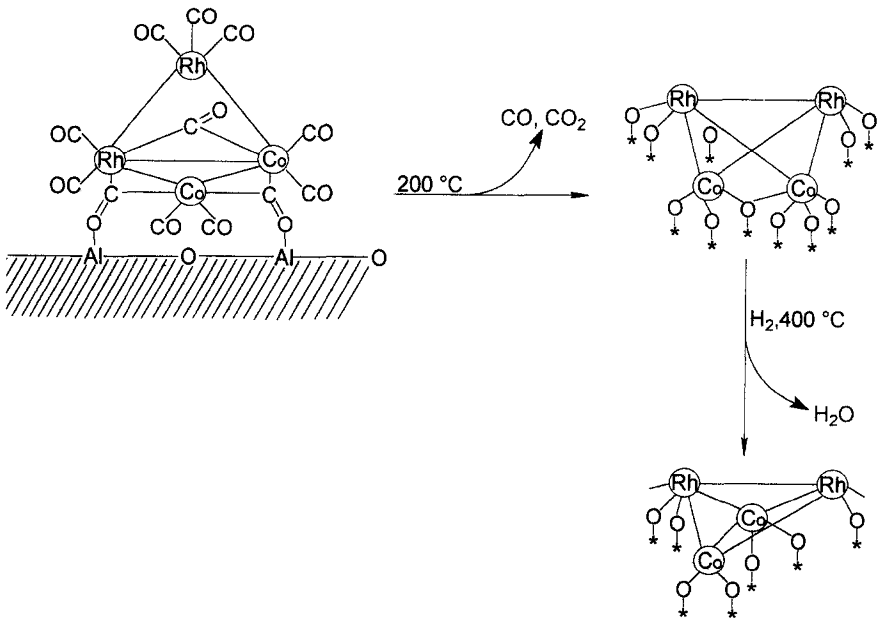


Fig. 11. Proposed model for the Rh–Co bimetal catalysts. (Reproduced from Ref. [100].)

a mixture of highly dispersed Fe^0 and Fe^{3+} and that Fe atoms were mostly in the state of Fe^{3+} ions even after H_2 reduction at 673 K.

FT-IR spectroscopy studies were performed on catalysts derived from Fe_2Rh_4 carbonyl clusters and subsequently exposed to CO. The band at 1806 cm^{-1} usually attributed to bridging CO was appreciably suppressed in comparison with the linear CO band (2058 cm^{-1}) on Fe_2Rh_4/SiO_2. The resulting bridge to linear CO was much lower than that found on Rh_4/SiO_2. The disappearance or the strong intensity reduction of the bridging CO band was reported in other studies on promoted rhodium catalysts [25–27] and attributed to site blocking caused by the promoter. Moreover, a low-frequency band appeared at 1628 cm^{-1}, attributed to CO having C-coordinated with Rh and O-coordinated with an adjacent electropositive ion Fe^{3+}. The authors proposed (Scheme 8) that bimetallic $Rh–Fe^{3+}$ ensembles were generated from Rh–Fe carbonyl clusters supported on SiO_2 and that they must have been very active for migratory CO insertion as could be deduced by their selectivity towards olefin hydroformylation.

Studies in this field were developed preparing catalysts using SiO_2-supported Rh_4Fe_2, Rh_5Fe, Ir_4Fe and Pd_6Fe_6 carbonyl clusters, reduced at 673 K in H_2 and NaY (or NaX) zeolite-entrapped RhFe and $Rh_{6-x}Ir_x$ ($x = 0–6$) carbonyl clusters, synthesized by means of a 'ship in the bottle synthesis' [102]. The bimetal cluster-derived catalysts were structurally characterized by EXAFS, Mössbauer and FT-IR spectroscopies in terms of their cluster frameworks and metal composition including their oxidation states in catalysis. Iron promotion in ethylene hydroformylation was again proposed to be associated with the heteronuclear activation of CO by the adjacent metals couples Rh–, Pd–, Ir–Fe(3+) located at the metal/oxide interface. The possible location of silica-supported Rh–Fe bimetallics is shown in Fig. 12.

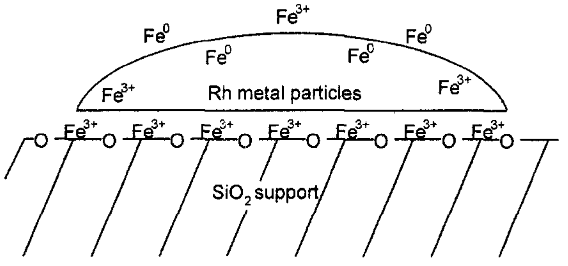
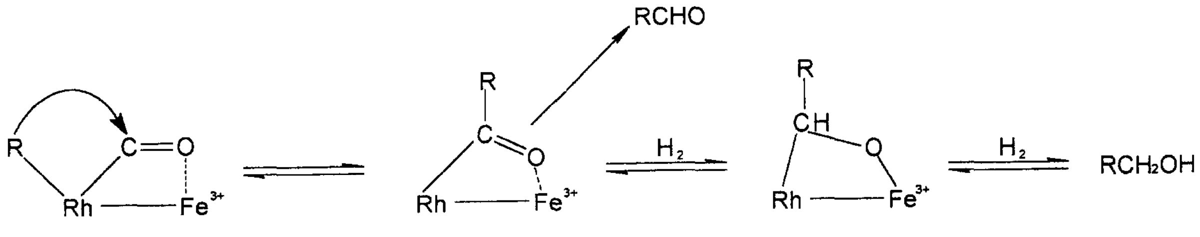


Fig. 12. A pictorial representation of the location of Fe (Fe^0, Fe^{3+}) in the reduced $Rh–Fe/SiO_2$ catalysts. (Reproduced from Ref. [102].)

Mono and bimetallic catalysts were prepared from $Rh_6(CO)_{16}$, a physical mixture of $Rh_6(CO)_{16}$ and $[HFe_3(CO)_{11}]^-$, and bimetallic RhFe carbonyl clusters which were presynthesized inside metal exchanged zeolite X supercages [103]. The catalysts structure was studied by EXAFS and FT-IR spectroscopy, and the presence of less than 1 nm particles was revealed. The catalysts derived from carbonyl clusters and clusters mixtures gave a mixture of aldehydes as the main oxygenated products in the hydroformylation of ethene and propene ($S_L = 56.8$). On the other hand bimetallic Rh–Fe/NaY catalysts exhibited higher yields and



Scheme 8.

selectivities towards linear alcohols ($S_L = 66$). The results were explained by the model previously described and the increased regioselectivity to linear products was attributed to the zeolitic structure. The claimed attribution of the increased regioselectivity to the zeolitic structure constraints must be taken with caution. An average $S_L = 66$ value was found in fact by Rode et al. [29] using Rh–NaX and Rh–NaY as propene hydroformylation catalyst. Nevertheless, the value was very close to that ($S_L = 64$) shown by Rh/SiO_2. This finding prompted the authors to say that the system regioselectivity was not attributable to the zeolitic structure and that the hydroformylation active sites were located on the zeolite external surface.

The hydroformylation of caged in zeolite Y rhodium carbonyls and clusters, formed by carbonylation of Rh–Y, was also studied by Takahashi et al. [104]. The modifications by thermal treatment in reaction atmosphere of the caged carbonyls were studied by FT-IR spectroscopy. The authors concluded in agreement with others [29] that, neither $Rh_6(CO)_{16}$, nor twin $Rh(I)(CO)_2$ species were themselves the active species for olefin hydroformylation. Furthermore, the catalytic activity of Rh–Y for ethylene hydroformylation was considerably enhanced by pretreatments of the fresh Rh–Y with hydrogen. The predominant rhodium species on the sample exposed to H_2 at 393 K was found by XPS to have a binding energy attributable to Rh(0). Consequently, metallic rhodium particles appeared to play an important role as precursors of the active catalysts.

Further multi-techniques studies on bimetallic FeRh, FePt, FePd, and FeIr CO hydrogenation and olefin hydroformylation catalysts supported on silica confirmed the benefits of the use of bimetallic anionic cluster precursors of the type used previously [101] for the preparation of tailored catalysts [105].

Fe_3Pt_3, Fe_6Pd_6, and $FeIr_4$, cluster catalysts gave methanol in high selectivity, while iron-rich Fe_4Pt and Fe_4Pd were not selective catalysts. The Rh–Fe cluster catalysts showed improved activity in hydroformylation of olefins [105,106]; propene hydroformylation gave substantially C_4-alcohols. The selective promotion of alcohol production in CO hydrogenation and olefin hydroformylation was proposed, as in the preceding papers, to originate from two-site interaction of $M–Fe^{3+}$ (M = Rh, Pt, Pd, Ir) sites with CO.

Molibdenum is another known rhodium promoter of the oxigenate selective carbon monoxide hydrogenation and can be presumed active in promoting the olefin hydroformylation [26]. Molybdenum-promoted Rh/SiO_2 catalysts were prepared from rhodium and molybdenum salts and from a Rh–Mo cluster precursor [107]. The catalysts were compared with unpromoted Rh/SiO_2 using ethylene hydroformylation as test reaction to verify the hypothesis that the CO insertion was specifically promoted by a Rh–Mo cluster supported on SiO_2. Hydroformylation tests at 523 K and 1 MPa demonstrated that probably the more intimate contact between the active metal and the promoter in the bimetallic particles of the cluster derived catalyst resulted in higher CO insertion probability.

A triruthenium ketenylidene cluster $[PPN]_2[Ru_3(CO)_9(CCO)]$ was deposited on MgO, SiO_2 and $SiO_2–Al_2O_3$ and the nature of surface species were studied by FT-IR spectroscopy and measuring the catalytic performances in ^{13}CO exchange reaction and hydroformylation of ethylene [108]. Hydroformylation of ethylene proceeded at atmospheric pressure with higher rates in propanal and 1-propanol on the catalyst derived by reduction from MgO supported Ru ketenylidene than on those supported on SiO_2 or $SiO_2–Al_2O_3$. The catalytic species for hydroformylation was not completely characterized, nevertheless the authors suggested that the basic groups OH^- and O^{2-} on MgO were likely to promote the catalytic CO insertion in the Ru clusters.

The group of Ugo of the University of Milan (Italy) pioneered and actively pursued during the last two decades the study of supported metal clusters synthesis, characterization and catalytic applications [94].

The heterogeneous atmospheric vapor phase ethylene hydroformylation was studied in flow conditions on the potassium salt of the cluster $[Rh_{12}(CO)_{30}]^{2-}$ supported on silica [109,110]. The use of a cluster with an alkali cation contiguous to the metallic framework was thought an elegant system to study promotion effects. The reaction did not show any induction period and proceeded at 453 K with constant activity for 100 h and $R = 0.4$. Cluster reactivity under hydroformylation conditions was investigated by in situ FT-IR spectroscopy on catalyst pressed disks. No significant changes in the CO region of the supported cluster IR spectrum were observed even after several hours in reaction conditions.

Diffuse reflectance FT-IR spectroscopy (DRIFTS) was used to study in more detail this supported catalyst in granular form thus overcoming many of the well known problems associated with the pressed disc approach [52]. The DRIFTS cell coupled with an on-line gaschromatograph allowed the observation of the catalyst under process conditions. The catalytic activity of the supported cluster anion was compared with that of analogous supported catalysts derived, respectively, from a mononuclear carbonyl $Rh(CO)_2acac$ (acac = acetylacetone), a neutral cluster $Rh_4(CO)_{12}$ and $RhCl_3$. The catalytic activity data indicated that neither Rh(I) isolated sites, prepared from the mononuclear carbonyl or the 4 nm metallic particles prepared from rhodium chloride were the active species for olefin hydroformylation. The unpromoted catalyst prepared from $Rh_4(CO)_{12}$ resulted scarcely chemoselective ($R = 0.2$). The total activity was higher at the beginning of the experiment but decreased by 40% after 50 h. DRIFTS experiments conducted on the supported anion evidenced that the $Rh(I)(CO)_2$ surface species (bands at 2086 and 2030 cm^{-1}) originated by oxidative disruption of the physisorbed cluster, reaggregated at 363 K in the presence of the hydroformylation mixture to very small metallic particles with carbonyls bands at 2056 and 1830 cm^{-1}. At 453 K, the temperature at which the catalytic test was carried out and aldehyde production was detected by on line GC, only a weak broad band around 2035 cm^{-1} was present, attributable to CO coordinated on very small metal particles (Fig. 13).

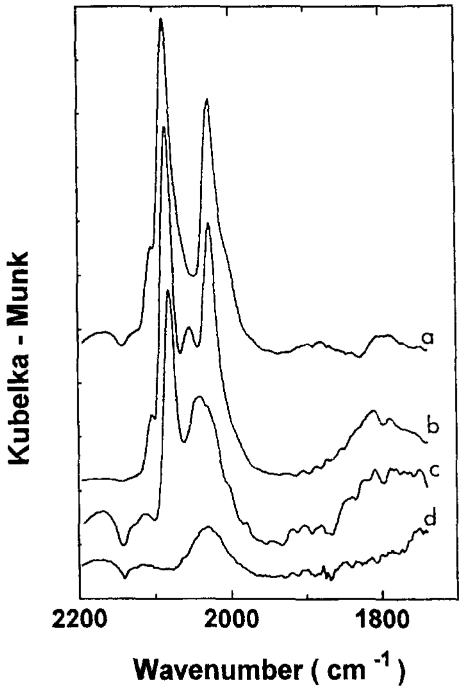


Fig. 13. Sequential DRIFT spectra of $Na_2[Rh_{12}(CO)_{30}]$ in reaction mixture flow: (a) at 303 K for 5 min; (b) at 363 K for 1 h; (c) at 383 K for 1 h; (d) at 453 K for 1 h. (Reproduced from Ref. [52].)

The DRIFTS results and the total absence of X-ray diffraction (XRD) signals (the technique has 2 nm sensitivity) prompted the authors to suggest an important role of very small metallic particles as active species for olefin hydroformylation. The alkali cations (Na, K) contiguous to rhodium atoms are supposed to prevent particle sintering. Successive oxidation–reduction experiments appeared to confirm this hypothesis.

It was concluded [111] from in situ DRIFTS characterization that:

(1) physisorbed cluster slowly transformed into the oxidized $Rh(CO)_2$ surface species.

(2) a surface restructuring during catalytic conditions (393 K and 1.0 MPa) of $Rh(CO)_2$ species into metallic particles occurred. Metallic particles of mean diameter lower than 2 nm were probably the catalytic active sites.

The promoting role of zinc [25,26] or sodium cations [55] on rhodium silica supported hydroformylation catalysts was studied in detail and the studies summarized in the preceding section.

To further prove the promoting role of the counter cations, cluster-derived rhodium catalysts prepared from Zn, K, Li, Na, salts of the cluster anion $[Rh_{12}(CO)_{30}]^{2-}$ supported on silica have been studied in ethylene hydroformylation. The effect of the promoting cation, which was present in the coordination sphere of the cluster precursor were found to affect primarily the selectivity as was found for the Rh/SiO_2 [25,26]. Chemoselectivity towards propanal formation followed the order: $Zn > K \geq Li \geq Na$ while the corresponding value for the unpromoted system, prepared from neutral $Rh_4(CO)_{12}$, was about 20% lower [112].

The atmospheric hydroformylation of ethylene and propylene at 443 K catalyzed by mono and bimetallic catalysts derived from $Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ supported on partially deoxydrilated silica (623 K) were investigated also by Huang et al. [113].

The bimetal cluster-derived catalysts showed activities and selectivities for the formation of oxygenated products similar to those found by Ichikawa on analogous bimetallic systems on ZnO [98,99]. On the basis of in situ IR studies on $RhCo_3(CO)_{12}$ supported on partially dehydroxylated SiO_2 speculatively suggested that the bimetal cluster framework may be, at least in part, preserved after decarbonylation under H_2 at 623 K and may be recarbonylated at room temperature. A strong physisorption of $RhCo_3(CO)_{12}$ on SiO_2 was proposed, due to a nucleophilic attack of surface oxygen on the Co atoms, which promoted a metal-support interaction stabilizing the bimetal cluster framework. Nevertheless, these statements, based only on FT-IR data, must be taken with caution because of the close similarity of the supported cluster carbonyl spectrum with that of carbon monoxide adsorbed on small rhodium crystallites. Furthermore, a nucleophilic interaction of the weakly acidic silica surface with the cobalt atoms is very hard to believe. A cluster skeleton retention after pyrolysis at 473 K and H_2 reduction at 673 K was proposed for similar Rh–Co clusters on dehydrated alumina on the basis of EXAFS data [91]. The suggested process (Fig. 9) involved the strong interaction of the coordinated carbonyls with the Al atoms of the surface, CO and CO_2 elimination with preservation of Rh–Co bonding and formation of bonds between metal atoms and the surface oxygens.

Atmospheric hydroformylation of ethylene was studied under differential conditions over $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ derived Rh/SiO_2 catalysts at different dispersion [53]. Chemoselectivity to hydroformylation was found to increase with the increasing metal dispersion in agreement with other studies [50–52]. The authors deduced from reactivity data that ethylene hydroformylation was structure sensitive and ethylene hydrogenation structure insensitive. In situ IR observations on pelletized catalyst samples showed that only the Rh sites that linearly chemisorb CO are catalytically active as previously proposed [59]. Supported $Rh_6(CO)_{16}$ was found catalytically inactive until the cluster structure was maintained and some activity was detected only after extensive decarbonylation.

The behaviour of large rhodium clusters in the hydroformylation of ethylene and propene was studied by Schmid and coworkers [114]. The clusters of the type $Rh_{55}L_{12}Cl_x$ [$L = P(tBu)_3$, $x = 20$, $L = PPh_3$, $x = 6$] was anchored on TiO_2 and Na–Y–zeolite. High resolution transmission electron microscopy (HRTEM), BET, and DSC investigations proved that the clusters, about 2 nm in diameter, were fixed on the entrances of the support mesopores. The supported clusters catalyzed the hydroformylation of ethylene and propene in different ways. When ethylene was hydroformylated in the absence of solvent the catalyst was inactivated after a few cycles. On the other hand no loss of activity was observed even after 27 experiments, if the olefin was hydroformylated in an aqueous medium. No problems of this kind appeared when propene was used [114]. The catalyst inactivation observed in the absence of solvent was attributed to active sites coverage by reaction products that are on the contrary removed when the reaction was done in water. The minor occurrence of the phenomenon in the case of propene was attributed to the lower reactivity of the olefin.

The 1-hexene hydroformylation in batch conditions in toluene at 373 K and 5.0 MPa was studied using as catalyst $Rh_2Co_2(CO)_{12}$ supported on alumina, silica, magnesium silicate and wide-pore zeolites [115]. The catalysts gave C_7-aldehydes in good yield. The alumina carrier appeared to bind the cluster more strongly, therefore the effects of different amines on the 1-hexene hydroformylation were studied with this catalyst. The catalyst gave a 85% yield of C7-aldehydes in the absence of cocatalysts. When NEt_3 was added to the hydroformylation solution, the C7-aldehydes were reduced to alcohols with a C7-alcohols maximum yield of 97%. The activity of the catalysts supported on the other oxides was similar (99% yield) but with a lower alcohols content.

It was later found that $Ru_3(CO)_{12}$ and 2,2′-bipyridine, supported on various silicas, silicates and glass was an active catalyst of 1-hexene and other olefins hydroformylation in toluene at 373 K [116]. The best yields in C7 alcohols (40–97%) were obtained on a silica with 400 m^2/g surface area. The alcohol yield increased with increasing reaction temperature, pressure and reaction time. $Ru_3(CO)_{12}$/2,2′-bipyridine/magnesium silicate resulted to catalyze 1-hexene hydroformylation both to C7 aldehydes (42%) and C7 alcohols (16%).

The stability of the catalyst was studied by determining ruthenium contents of the products and dissolution tests [117]. Ruthenium was found to dissolve from carriers in hydroformylation products. The active catalyst proved to be heterogeneous but partly in suspension in the reaction products.

Pulse impregnation, a method for preparing supported heterogeneous catalysts by successive impregnation cycles in liquid phase, was used in the preparation of $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst in a column-type reactor system [118]. A macroscopically uniform deposition was achieved and ruthenium content was observed to increase almost linearly with the number of preparation cycles. The effect of the preparation method on the catalyst activity was also tested in 1-hexene hydroformylation. Catalysts obtained by pulse impregnation resulted somewhat less active than conventionally impregnated catalysts, but reproducibility of the catalyst was clearly improved.

Iwasawa studied supported carbido and nitrido clusters to design new metal-based catalysts with well defined micro-frameworks ([96,119–121]).

The carbido cluster $[Ru_6C(CO)_{16}Me]^-$ with various cations was supported on SiO_2, Al_2O_3 and TiO_2 and characterized by means of EXAFS, TPD and FT-IR spectroscopy. The EXAFS analysis revealed that the Ru_6C cluster framework which has an interstitial carbon atom was stable at 473 K (SiO_2), 523 K (Al_2O_3) and 473 K (TiO_2) under CO or CO + H_2 [119].

The carbido cluster was regarded as a good precursor to study carbonyl insertion and ethene hydroformylation [120]. The catalytic activity towards ethene hydroformylation was tested on the supported silica carbido ruthenium cluster. The ruthenium carbido cluster supported on silica surface has been demonstrated to be stable under the reaction conditions, with neither destruction or aggregation of the cluster framework. The best selectivity ($R = 0.12$) to propanal and propanol was observed at 433 K. A 100% selectivity ($R = 1$) was achieved for catalytic ethene hydroformylation on the methyl cluster which had been produced after stoichiometric reaction of the methyl ligand with CO to give acetaldehyde or with $[Ru_6C(CO)_{16}Me]^-$

supported on silica pretreated at 823 K. It was proposed that the lower surface hydroxyl concentration should be one important factor and that perhaps a multimetal effect is involved.

4. Concluding remarks

A lucid outlook of the future developments of olefin hydroformylation industry can be found in the conclusive part of the just published review of Beller et al. [12].

Research activity, oriented to the improvement of the current industrial homogeneous hydroformylation processes appears to have been mostly addressed to the development of SL-PC systems operating in CF conditions or to the very promising water soluble catalysts based on rhodium complexes with sulfated phosphines [12,16].

In the concluding section of our survey we will try to give a summary of the scientific achievements obtained on the chemistry of the liquid and vapor phase olefin hydroformylation catalyzed by heterogeneous systems.

Papers on the subject are not numerous and mainly from academic sources, nevertheless it can be deduced from the available data that, at least in laboratory scale, heterogeneous hydroformylation of simple olefins (ethene, propene, butene) is feasible, even at atmospheric pressure, both in static and in flow conditions, using a variety of transition metal based catalysts.

The use of heterogeneous catalysts presents problems that are different according to whether the reaction is carried out in static or in flow conditions, in vapor or in liquid phase.

It was anticipated on the basis of the most probable mechanistic analogy of the heterogeneous process with the well established mechanism of the homogeneous hydroformylation that it would have been necessary to continuously remove the reaction products from the catalyst surface in order to observe hydroformylation activity in the heterogeneous phase [122].

The analogy of the homogeneous and of the heterogeneous reaction was confirmed by several authors on the basis of the experimental results [28–36,56–65,70,71] and a rapid decay of the catalyst activity was observed when the reaction was carried out in static conditions without solvent [107].

Catalyst loss by leaching in the solvent is considered a serious limitation to the feasibility of the process when the reaction is carried out in the liquid phase, nevertheless leaching was observed only in few cases and there are several examples of true heterogeneous processes in liquid phase.

On the other hand catalyst loss, caused by the formation of volatile molecular carbonyls, could have been a severe limitation during gas flow pretreatments or when the reaction was carried out in flow conditions, but evidence of the event was found only in some cases [36].

Several supported mono and bimetallic systems can give origin to active catalysts, nevertheless rhodium based systems appeared to be the most active, analogous to what is known for the homogeneous catalysts.

Olefin hydrogenation is known to compete with hydroformylation in the homogeneous reaction, when rhodium based catalysts are used, nevertheless the problem was overcome by appropriately adjusting the operating parameters [1,3].

Nevertheless, when supported metals (Pd, Ru, Rh) are used as catalysts olefin hydrogenation was found to largely dominate [20,21,24].

Several studies on supported metallic systems pointed out that the steric requirements of the two reactions were different and that there was a positive correlation of the chemoselectivity towards hydroformylation with the catalyst dispersion [21,27,50,51]. It was in fact demonstrated that the reaction competes favorably with the hydrogenation on the very small metallic ensembles present on the crystallites corners and edges. Therefore, the small metal clusters generated by the thermal decomposition of cluster carbonyls were considered promising candidates for selective hydroformylation catalysts [52,53].

Dopants as S [27,56–60], Se [66,67], boron and aluminum oxides [64,65,70] or promoters as Mn, Fe, Co, Zn [25,26,97,100–105,98,99,113], or alkali metals [54,55,112] resulted to be active in increasing the selectivity of rhodium based catalysts towards hydroformylation.

Dopants are supposed to work by totally or partially blocking the hollow or flat sites ('Freundlich sites') of the rhodium crystallites where dissociative CO and hydrogen chemisorption most favorably occur leaving only the protruded edges and corners of the crystallites available for the chemisorption of the reacting molecules.

Nevertheless, this partial surface coverage by dopants results in a increased chemoselectivity but at the expense of a dramatically reduced over-all catalyst activity.

Metals such as Mn, Fe, Co, Zn appeared to promote the reaction both by site segregation and by favoring migratory CO insertion by coordinating the oxygen atom of the chemisorbed CO molecule.

The role of the oxidation state of the rhodium active sites is controversial, but there is much spectroscopic evidence that Rh(I) species are probably present on the surface of active catalysts of the reaction. Most of the information on this topic comes from FT-IR and XPS data. Nevertheless, since FT-IR spectra are fit for various interpretations and binding energies values measured by XPS were found related to metal particles dimensions [123], data must be handled with care.

Regioselectivity to linear products is an important requirement of the reaction, when propene is hydroformylated, that can be adjusted in the homogeneous process by tuning the ancillary ligands of the catalyst [1–12]. Good regioselectivities to linear products were observed when the rhodium catalyzed reaction was carried out in flow conditions, but a clear correlation with the catalyst structure was hard to find.

It was thought it would have been possible to control the regioselectivity of the reaction using faujasite zeolites as catalyst support, nevertheless no improvement was observed because propene hydroformylation resulted to occur only on catalytic sites located on the external surface outside the zeolitic cavities [24,28–30]. The slight regioselectivity leaning towards the linear products observed in almost all the catalytic systems in flow conditions, independent from the nature of the support, can probably be attributed to the different adsorption–desorption energetics of the two aldehydes. High regioselectivity towards linear products values were observed when the reaction was catalyzed by pillared clay supported rhodium [47] and by boron or cobalt oxide doped catalysts [65,71]. The data encourage, in the first case, the attribution of the catalysts behaviour to the location of the active sites in the clay pores [47] or to the constrained environment of the active sites generated by the catalyst surface covering by the oxides [65,71].

Nevertheless, also in these cases the very low specific activity values do not enable the anticipation of a possible industrial use of these catalytic systems.

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References

[1] G.W. Parshall and S.D. Ittel, Homogeneous Catalysis, 2nd Ed. (Wiley, New York, 1992).

[2] I. Kirschenbaum and E.J. Inchalik, in: Kirk-Othmer, ed., Encyclopedia of Chemical Technology, 3rd Ed., Vol. 16 (Wiley, New York, 1981) p. 673.

[3] B. Cornils, in: J. Falbe, ed., New Synthesis with Carbon Monoxide (Springer, Berlin, 1980).

[4] I. Wender and P. Pino, ed., Organic Synthesis via Metal Carbonyls, Vol. 2 (Wiley, New York, 1977).

[5] L. Markò, J. Organomet. Chem. 261 (1984) 485.

[6] L. Pruett, Adv. Organomet. Chem. 17 (1979) 1.

[7] C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli and A. Gamba, Chim. Ind. (Milan) 62 (1980) 604, 757; 63 (1981) 29.

[8] I. Tkatchenko, in: G. Wilkinson, ed., Comprehensive Organometallic Chemistry, Vol. 8 (Pergamon Press, Oxford, 1982) p. 101.

[9] P. Pino, J. Organomet. Chem. 200 (1980) 223; G. Consiglio and P. Pino, Top. Cur. Chem. 105 (1980) 77.

[10] C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, J. Mol. Catal. 40 (1987) 129.

[11] F. Agbossou, J-F. Carpentier and A. Mortreux, Chem. Rev. 95 (1995) 2485.

[12] M. Beller, B. Cornils, C.D. Frohning and C.W. Kohlpaintner, J. Mol. Catal. 104 (1995) 17.

[13] F.R. Hartley and P.N. Vezey, Adv. Organomet. Chem. 15 (1977) 189.

[14] C.U. Pittman, in: G. Wilkinson, ed., Comprehensive Organometallic Chemistry, Vol. 8 (Pergamon Press, Oxford, 1982) p. 553.

[15] D.C. Bailey and S.H. Langer, Chem. Rev. 81 (1981) 110.

[16] P. Tundo, Continuous Flow Methods in Organic Synthesis (Ellis Horwood, Chichester-West Sussex, 1991).

[17] P. Centola, G. Terzaghi, R. Del Rosso and I. Pasquon, Chim. Ind. (Milan) 54 (1972) 775.

[18] E. Mantovani, N. Palladino and A. Zanobi, J. Mol. Catal. 3 (1978) 285.

[19] P.F. Jackson, B.F.G. Johnson, J. Lewis, R. Ganzerla, M. Lenarda and M. Graziani, J. Organomet. Chem. 190 (1980) C1–C4.

[20] H. Arai and H. Tominaga, J. Catal. 75 (82) 188.

[21] N. Takahashi, S. Hasegawa, N. Hanada and M. Kobayashi, Chem. Lett. (1983) 945.

[22] N. Takahashi, Y. Sato and M. Kobayashi, Chem. Lett. (1984) 1067.

[23] N. Takahashi, H. Matsuo and M. Kobayashi, J. Chem. Soc. Faraday Trans. 1 80 (1984) 629.

[24] N. Takahashi and M. Kobayashi, J. Catal. 85 (1984) 89.

[25] M. Ichikawa, A.J. Lang, D.F. Shriver and W.M.H. Sachtler, J. Am. Chem. Soc. 107 (1985) 7216.

[26] W.M.H. Sachtler and M. Ichikawa, J. Phys. Chem. 90 (1986) 4752.

[27] Y. Konishi, M. Ichikawa and W.H. Sachtler, J. Phys. Chem. 91 (1987) 6286.

[28] M.E. Davis, E. Rode, D. Taylor and B.E. Hanson, J. Catal. 86 (1984) 67.

[29] E.J. Rode, M.E. Davis and B.E. Hanson, J. Catal. 96 (1985) 563.

[30] E.J. Rode, M.E. Davis and B.E. Hanson, J. Catal. 96 (1985) 574.

[31] E.J. Rode, M.E. Davis and B.E. Hanson, J. Chem. Soc., Chem. Commun. (1985) 716.

[32] E.J. Rode, M.E. Davis and B.E. Hanson, J Chem. Soc., Chem. Commun. (1985) 1477.

[33] M.E. Davis, P.M. Butler, J.A. Rossin and B.E. Hanson, J. Mol. Catal. 31 (1985) 385.

[34] M.E. Davis, J. Schnitzer, J.A. Rossin, D. Taylor and B.E. Hanson, J. Mol. Catal. 39 (1987) 243.

[35] J.A. Rossin and M.E. Davis, J. Chem. Soc., Chem. Commun. (1986) 234.

[36] R.J. Davis, J.A. Rossin and M.E. Davis, J. Catal. 98 (1986) 477.

[37] J.P. Wey, W.C. Neely and S.D. Worley, J. Chem. Phys. 95 (1991) 8881.

[38] D.F. Taylor, B.E. Hanson and M.E. Davis, Inorg. Chim. Acta 128 (1987) 55.

[39] J.Z. Zhang, ZLi and C.Y. Wang, Stud. Surf. Sci. Catal. 75, 919, 10th ICC, Budapest (1992), L. Guczi. et al., ed. (Elsevier, 1993).

[40] J. Tsuji, Acc. Chem. Res. 2 (1969) 144.

[41] Z. Karpinski, Z. Zhang and W.M.H. Sachtler, J. Mol. Catal. 77 (1992) 181.

[42] W. Huang, L.H. Yin and C.Y. Wang, Stud. Surf. Sci. Catal. 75, 2359, 10th ICC, Budapest (1992), L. Guczi et al., ed. (Elsevier, 1993).

[43] F. Farzaneh and T.J. Pinnavaia, Inorg. Chem. 22 (1983) 2216.

[44] V.L.K. Valli and H. Alper, Chem. Mater. 7 (1995) 359.

[45] T.J. Pinnavaia, Science 220 (1983) 365; R.M. Barrer, Clays Clay Miner. 37 (1989) 85.

[46] M. Lenarda, R. Ganzerla, S. Enzo and L. Storaro, J. Mol. Catal. 67 (1991) 295.

[47] M. Lenarda, R. Ganzerla, L. Storaro, A. Trovarelli, R. Zanoni and J. Kaspar, J. Mol. Catal. 72 (1992) 75.

[48] J. Hjortkjaer, M.S. Scurrell and P. Simonsen, J. Mol. Catal. 6 (1979) 405.

[49] J. Hjortkjaer, M.S. Scurrell and P. Simonsen, J. Mol. Catal. 10 (1981) 127.

[50] H. Arakawa, N. Takahashi, T. Hanaoka, K. Takeuchi, T. Matsuzaki and Y. Sugi, Chem. Lett. (1988) 1917.

[51] N. Takahashi, T. Tobise, I. Mogi, M. Sasaki, A. Mijin, T. Fujimoto and M. Ichikawa, Bull. Chem. Soc. Jpn. 65 (1992) 2565.

[52] L. Sordelli, R. Psaro, C. Dossi and A. Fusi, in: Catalysis and Surface Characterization, ed. T.J. Dines, C.H. Rochester and J. Thompson (The Royal Society of Chemistry, Cambridge, 1992) p. 127.

[53] L. Huang, Y. Xu, W. Guo, A. Liu, D. Li and X. Guo, Catal. Lett. 32 (1995) 61.

[54] S. Naito and M. Tanimoto, J. Chem. Soc. Chem. Commun. (1989) 1403.

[55] S. Naito and M. Tanimoto, J. Catal. 130 (1991) 106.

[56] S.S.C. Chuang and S.I. Pien, J. Mol. Catal. 55 (1989) 12.

[57] S.S.C. Chuang and S.I. Pien, Catal. Lett. 6 (1990) 389.

[58] M.W. Balakos, S.I. Pien and S.S.C. Chuang, Stud. Surf. Sci. Catal. 68 (1991) 549.

[59] S.S.C. Chuang and S.I. Pien, J. Catal. 135 (1992) 618.

[60] G. Srinivas and S.S.C. Chuang, J. Catal. 144 (1993) 131.

[61] S.S.C. Chuang and S.I. Pien, J. Catal. 138 (1992) 536.

[62] M.W. Balakos, S.S.C. Chuang and G. Srinivas, J. Catal. 140 (1993) 281.

[63] S.S.C. Chuang, G. Srinivas and A. Mukherjee, J. Catal. 139 (1993) 490.

[64] M. Lenarda, R. Ganzerla, L. Storaro and R. Zanoni, J. Mol. Catal. 78 (1993) 339.

[65] M. Lenarda, R. Ganzerla, L. Storaro and R. Zanoni, J. Mol. Catal. 79 (1993) 243.

[66] Y. Izumi, K. Asakura and Y. Iwasawa. J. Chem. Soc. Chem. Commun. (1988) 1327.
[67] Y. Izumi, K. Asakura and Y. Iwasawa, J. Catal. 127 (1991) 631.
[68] Y. Izumi, K. Asakura and Y. Iwasawa, J. Catal. 132 (1991) 566.
[69] R.C. Wade, D.G. Holah, A.N. Hughes and B.C. Hui, Catal. Rev. Sci. Eng. 14 (1976) 211; R.C. Wade, Some Industrial Processes using Borohydride-Reduced Catalysts in Catalysis of Organic Reactions, W.R. Moser, ed. (Marcel Dekker, NY, 1981) p. 165; J. Mol. Catal. 18 (1983) 273; B. Ganem and J.O. Osby, Chem. Rev. 86 (1986) 763.
[70] M. Lenarda, R. Ganzerla, S. Enzo, L. Storaro and R. Zanoni, J. Mol. Catal. 80 (1993) 105.
[71] M. Lenarda, R. Ganzerla, L. Storaro, S. Enzo and R. Zanoni, Proc. of the IXth Natl. Congr. of Catalysis, Pisa, Italy (1994) p. 90; M. Lenarda, L. Storaro, R. Ganzerla, R. Zanoni and G. Righini, J. Mol. Catal., submitted for publication.
[72] K. Asakura, K. Kitamura-Bando, K. Isobe, H. Arakawa and Y. Iwasawa, J. Am. Chem. Soc. 112 (1990) 3242.
[73] K. Asakura, K. Kitamura-Bando, Y. Iwasawa, H. Arakawa and K. Isobe, J. Am. Chem. Soc. 112 (1990) 9096.
[74] J. Kijenski, M. Glinski, K. Bielawski, Stud. Surf. Sci. Catal. 41 (1988) 379.
[75] D.S. Jordan and A.T. Bell, J. Phys. Chem. 90 (1986) 338; J. Catal. 107 (1987) 338.
[76] S.B. Halligudi, M.M. Taqui Khan, B.L. Moroz, A.L. Chuvilin, I.P. Prosvirin and V.A. Likholobov, React. Kinet. Catal. Lett. 44 (1991) 139.
[77] S.S.C. Chuang, Appl. Catal. 66 (1990) L1.
[78] Z. Vit, J.L. Portefaix and M. Breysse, Appl. Catal. A 116 (1994) 259.
[79] Z. Vit, J.L. Portefaix, M. Zdrazil and M. Breysse, Catal. Lett. 32 (1995) 55.
[80] N. Takahashi, H. Arakawa, A. Kano and Y. Fukagawa, Chem. Lett. (1990) 205.
[81] N. Takahashi, T. Takeyama, T. Yanagibashi and Y. Tanaka, J. Catal. 136 (1992) 531.
[82] M. Kobayashi, Chem. Lett. (1984) 1215.
[83] N. Homs, N. Clos, G. Muller, J. Sales, P. Ramirez de la Piscina and J.L.G. Fierro, J. Mol. Catal. 74 (1992) 401.
[84] P. Ramirez de la Piscina, J.L.G. Fierro, G. Muller, J. Sales and N. Homs, Catal. Lett. 14 (1992) 45.
[85] P. Ramirez de la Piscina, J.L.G. Fierro, G. Muller, J. Sales and N. Homs, Stud. Surf. Sci. Catal. 75 (1993) 2363.
[86] R. Läi and E. Ucciani, J. Mol. Catal. 4 (1978) 401.
[87] M. Lenarda, R. Ganzerla, S. Paganelli, L. Storaro and R. Zanoni, J. Mol. Catal. 105 (1996) 117.
[88] T. Hayasaka, Y. Obayashi, S. Uchiyama and N. Kawata, Chem. Lett. (1986) 1405.
[89] A. Maeda, F. Yamakawa, K. Kunimori and T. Uchijima, Catal. Lett. 4 (1990) 107.
[90] D.E. Resasco and G.L. Haller, J. Catal. 82 (1983) 279.
[91] M. Ichikawa, in Yu. Yermakov and V. Likhobolov (Editors), Homogeneous Heterogeneous Catalysis, VNU Science Press, Utrecht, 1986, P. 1127.
[92] R.L. Burwell and J.B. Peri, Ann. Rev. Phys. Chem. 15 (1964) 131.
[93] E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, Chem. Rev. 79 (1979) 91; J. Evans, Chem. Soc. Rev. 10 (1981) 159; G. Ertl, in: Metal Clusters in Catalysis, ed. B.C. Gates, L. Guczi and H. Knözinger, Stud. Surf. Sci. Catal. 29 (1986) 577.
[94] R. Psaro and R. Ugo, in: Metal Clusters in Catalysis, ed. B.C. Gates, L. Guczi and H. Knözinger, Stud. Surf. Sci. Catal. 29 (1986) 427.
[95] L. Guzci, in: Metal Clusters in Catalysis, ed. B.C. Gates, L. Guczi and H. Knözinger, Stud. Surf. Sci. Catal. 29 (1986) 547; S.C. Davis and K.J. Klabunde, Chem. Rev. 82 (1982) 153; M. Ichikawa, Chem. Tech. (1982) 674; H.H. Lamb, Catal. Today 18 (1993) 3.
[96] Y. Iwasawa, Catal. Today 18 (1993) 21.
[97] M. Ichikawa, J. Catal. 56 (1979) 127.
[98] M. Ichikawa, J. Catal. 59 (1979) 67.
[99] M. Kawai, M. Uda and M. Ichikawa, J. Phys. Chem. 89 (1985) 1654.
[100] M. Ichikawa, in: Homogeneous Heterogeneous Catalysis, ed. Yu. Yermakov and V. Likhobolov (VNU Science Press, Utrecht, 1986) p. 1127.
[101] A. Fukuoka, M. Ichikawa, J.A. Hriljac and D.F. Shriver, Inorg. Chem. 26 (1987) 3643.
[102] M. Ichikawa, Polyhedron 7 (1988) 2351.
[103] A. Fukuoka, L.-F. Rao, N. Kosugi, H. Kuroda and M. Ichikawa, Appl. Catal. 50 (1989) 295.
[104] N. Takahashi, A. Mijin, H. Suematsu, S. Shinohara and H. Matsuoka, J. Catal. 117 (1989) 348.
[105] A. Fukuoka, T. Kimura, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominaga and M. Ichikawa. J. Catal. 126 (1990) 434.
[106] M. Ichikawa, L.-F. Rao, T. Kimura and A. Fukuoka, J. Mol. Catal. 62 (1990) 15.
[107] A. Trunschke, H. Ewald, H. Miessner, A. Fukuoka, M. Ichikawa and H.C. Boettcher, Mater. Chem. Phys. 29 (1991) 503.
[108] F-Shou, Xiao, A. Fukuoka, W. Henderson, D.F. Shriver and M. Ichikawa, Catal. Lett. 6 (1990) 361.
[109] C. Dossi, A. Fusi, L. Garlaschelli, D. Roberto, R. Ugo and R. Psaro, Catal. Lett. 11 (1991) 335.
[110] C. Dossi, A. Fusi, L. Garlaschelli, R. Psaro and R. Ugo, Stud. Surf. Sci. Catal. 75 (1993) 2345.
[111] R. Psaro, A. Fusi, C. Dossi and L. Sordelli, in: Advances in Catalyst Design Vol. 2, ed. M. Graziani and C.N.R. Rao (World Sc. Publ., Singapore, 1993) p. 303.
[112] A. Fusi, R. Psaro, C. Dossi, L. Garlaschelli and F. Cozzi, J. Mol. Catal. A, Chemical (1996), in press.
[113] L. Huang, Y. Xu, G. Piao, A. Liu and W. Zhang, Catal. Lett. 23 (1994) 87.
[114] G. Schmid, R. Kuepper, H. Hess, J.O. Malm and J.O. Bovin, Chem. Ber. 124 (1991) 1889.
[115] L. Alvila, T.A. Pakkanen, T.T. Pakkanen and O. Krause, J. Mol. Catal. 75 (1992) 333.
[116] L. Alvila, T.A. Pakkanen and O. Krause, J. Mol. Catal. 84 (1993) 145.
[117] L. Alvila, J. Pursiainen, J. Kiviaho, T.A. Pakkanen and O. Krause, J. Mol. Catal. 91 (1994) 335.
[118] M. Aukka and T.A. Pakkanen, J. Catal. 148 (1994) 315.
[119] Y. Izumi, Tai-Hui Liu, K. Asakura, T. Chihara, H. Ya-

mazaki and Y. Iwasawa. J. Chem. Soc. Dalton Trans. (1992) 2287.

[120] Y. Izumi, T. Chihara, H. Yamazaki and Y. Iwasawa, J. Chem. Soc. Dalton Trans. (1993) 3667.

[121] Y. Izumi and Y. Iwasawa, Chem. Tech., 24 (1994) 20.

[122] G. Henrici-Olivé and S. Olivé, The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide (Springer-Verlag, Berlin, 1984) p. 104, 197.

[123] W.F. Egelhoff, Jr., Surf. Sci. Rep. 6 (1987) 253; M.G. Mason, Phys. Rev. B 27 (1983) 748; S.B. Di Cenzo and G.K. Wertheim, Comments Solid State Phys. 11 (1985) 203.