

Liquid phase hydroformylation of ring substituted styrenes catalyzed by Rh–B and Rh–Zn–B systems supported on silica

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Abstract

Rhodium based catalysts supported on silica have been prepared by low temperature reduction of the preadsorbed salts with respectively NaBH_4 and $\text{Zn}(\text{BH}_4)_2$. The catalyst surfaces were characterized by ESCA, XRD and FT-IR spectroscopy. A remarkable boron and zinc surface enrichment resulted from ESCA data in both catalysts. From the FT-IR data it appeared that the bridging CO chemisorption is substantially suppressed, as was observed by others in similar systems, probably because boron and zinc oxide molecules cover most of the catalyst surface blocking the multicenter rhodium sites. Both catalysts are active in the liquid phase ring substituted styrenes hydroformylation. The reaction resulted was truly heterogeneous because no leaching of catalyst was observed. The chemoselectivity was always very high, close to 100%, and regioselectivity appeared to be controlled by the nature of the ring substituents.

Evidences were found that the heterogeneous reaction proceeds through elementary steps similar to those proposed for the homogeneous process.

Keywords: Hydroformylation; Substituted styrenes; Heterogeneous catalysts

1. Introduction

It is well known that the hydroformylation of alkenes is an important reaction for the production of aldehydes [1]. Many olefinic compounds containing various functional groups can be successfully hydroformylated [2], however, no commercial processes employing these substrates are operative to date, in spite of the synthetic interest and high commercial value of the products. Heterogeneous catalysts are often preferred in industrial processes to the more active and selec-

tive homogeneous ones because of their good recoverability. Rhodium-based systems are by far the most studied heterogeneous catalysts for the liquid phase hydroformylation of simple olefins [3–6]. Monometallic rhodium catalysts were reported to have low overall activity and poor chemoselectivity toward olefin hydroformylation, both in vapour and in liquid phase. An improved chemoselectivity in vapour phase was obtained doping the catalyst surface with S [7,8], Se [9] and Zn [10]. Recently we described highly chemoselective Rh–B and Rh–Al vapour phase hydroformylation catalysts prepared by the low temperature reduction of rhodium salts, adsorbed

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on silica and silica alumina, with respectively NaBH_4 and LiAlH_4 [11–13]. Oxidized boron and aluminum particles resulted to play an important role in preventing sintering of the metal and, partially covering part of the rhodium surface, prevent H_2 dissociation, substantially reducing the hydrogenation activity with a consequent chemoselectivity increase.

In this paper we describe the behaviour of Rh–B and of the related Rh–Zn–B system as catalysts for the liquid phase hydroformylation of styrene and of some ring substituted styrene derivatives.

2. Experimental

2.1. Materials

Rhodium chloride trihydrate (Acros) and zinc chloride 1 M in ether (Aldrich) were used as received. All the reagents and solvents were ACS grade, distilled before the use and made anhydrous if necessary. Silica was a Grace 432 silica catalyst support with surface area of $320 \text{ m}^2/\text{g}$, pore volume 1.2 ml/g and particle size $30\text{--}100 \mu\text{m}$.

2.2. Catalyst preparation

The catalyst Rh–B/silica was prepared as previously described [11].

2.2.1. Preparation of $\text{Zn}(\text{BH}_4)_2$

A zinc hydride $1 \times 10^{-2} \text{ M}$ ethereal solution was prepared as described in the literature [14]. A total of 10 ml of a ZnCl_2 1.0 M ethereal solution was added with a syringe to 0.76 g of NaBH_4 suspended in 50 ml of anhydrous ethyl ether. The suspension, cooled in ice, was stirred overnight under argon. The solution was separated by decanting and stored in refrigerator under argon in a stoppered bottle.

2.2.2. Preparation of Rh–Zn–B supported on silica

A total of 0.15 g of rhodium chloride hydrate dissolved in the minimum amount of absolute ethanol was added to 4 g of silica, previously treated

at 120°C , suspended in ethanol. The suspension was slowly stirred in a Rotavapor at 50°C for an hour and then evaporated to dryness. The $\text{Zn}(\text{BH}_4)_2$ ethereal solution prepared as described above (60 ml) was added with a syringe to 100 ml of a slowly stirred silica suspension in ethyl ether. The suspension slowly blackened with a moderate gas evolution. The mixture was stirred in an ice bath for 2 h, filtered, washed with dry ether and dried under vacuum. The rhodium content determined by Atomic Adsorption was 2.0% w/w and the zinc was 6.7% w/w, Rh/Zn atomic ratio = 0.19.

2.2.3. Preparation of Rh(0)/silica

For comparison a catalyst was prepared by conventional silica impregnation with an aqueous solution of RhCl_3 and reduction with hydrogen at 450°C . The crystallite diameter was found 5.0 nm by XRD.

2.3. X-Ray photoelectron spectroscopy

XPS spectra were run on a Vacuum Generators ESCALAB spectrometer, equipped with an hemispherical analyzer operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 20 or 50 eV. Al $K\alpha$ 1,2 photons ($h\nu = 1486.6 \text{ eV}$) were used to excite photoemission. The binding energy (BE) scale was calibrated by taking the Au $4f_{7/2}$ peak at 84.0 eV. Correction of the energy shifts due to static charging of the samples was accomplished by referencing to the Si 2p peak from the support taken at 103.6 eV. The accuracy of the reported BEs is $\pm 0.2 \text{ eV}$ and the reproducibility of the results was within these values. The spectra were collected by a DEC PDP 11/83 data system and processed by means of VG 5000 data handling software. All samples were measured as powders pressed on a metal tip or spread on double-sided scotch tape.

2.4. FT-IR spectroscopy

The IR spectra were recorded on a Nicolet 750 interferometer at a resolution of 4 cm^{-1} .

The adsorption of CO, propylene and CO/H₂ (1:1) was studied in an evacuable IR Pyrex cell with CaF₂ windows. The catalysts were ground to a fine powder, pressed into self-supporting wafers at a pressure of ca. 6 MPa and mounted in the holder of the IR cell.

2.5. Catalytic measurements

All the catalytic tests were carried out in a 250 ml stainless-steel autoclave equipped with a manometer and a gas inlet/outlet. Typical reaction conditions were: 100 mg of catalyst, solvent = 10 ml, $T = 80^\circ\text{C}$, $P_{\text{tot}} = 100$ bar ($P_{\text{CO}}/P_{\text{H}_2} = 1$), reaction time = 24 h, Rh/olefin molar ratio = 1.5×10^{-3} .

3. Results

3.1. Catalysts characterization

3.1.1. XRD

The Rh–B/silica catalyst was described in previous papers [11,12]. The Rh–Zn–B/silica as prepared sample, analyzed by X-ray showed signals attributable to f.c.c. rhodium with crystallites diameter of ca. 3.5 nm.

3.1.2. ESCA

The ESCA data relative to Rh–B catalyst have been analyzed previously [11].

The nature of the Rh–Zn–B surface and its composition were studied by ESCA as reported in Table 1. The Rh/B and Rh/Zn atomic ratios were

calculated from Rh 3d_{5/2}/B 1s and Rh 3d_{5/2}/Zn 2p_{3/2} area ratios.

XPS analysis of the Rh 3d_{5/2} core level for the as prepared Rh–Zn–B showed the presence of a component falling at 308.0 ± 0.2 eV. The B 1s and the Zn 2p_{3/2} signals were found, respectively, at 193.2 ± 0.2 eV and 1022.7 ± 0.2 eV. No substantial modifications of the binding energies values of Rh, Zn and B were observed in the catalyst sample analyzed after a reaction run. The boron and zinc signals are clearly due to the elements in an oxidized state, probably B₂O₃ and ZnO. The rhodium signal can be certainly assigned to a reduced form of the metal. Nevertheless the Rh 3d_{5/2} binding energy value is slightly higher (308.0 eV) than the usual binding energy value (307.2 eV) attributed to metallic rhodium, as we found in a preceding case [13]. This is probably attributable to the extremely small crystallite dimensions but could also indicate that the electron density is closer to Rh(I) than to Rh(0) derivatives [8,15–18].

The element atomic ratios (Table 1) indicate that the oxidized zinc and boron species are ten times more abundant than rhodium on the silica surface. Nothing is known of the mechanism of a transition metal reduction by Zn(BH₄)₂ but a superficial deposition of intimately mixed zinc and boron ions on the catalyst particles can be easily predicted from the catalyst preparation procedure. The permanence in atmosphere of CO and H₂ during the reaction did not appear to deeply influence the catalyst surface composition with the exception of a further relative boron enrichment.

3.2. FT-infrared spectroscopy

The surface chemistry of Rh is complex and strongly dependent on the metal oxidation states and on the crystallites dimensions [19]. The use of FT-infrared spectroscopy as a tool to study the adsorption of CO on Rh has been the subject of a large number of studies [8,20–34] and both the structure and the oxidation state of the metal can be reasonably deduced by its infrared spectra. The IR spectra of Rh–Zn/silica exposed to CO and

Table 1
XPS characterization (eV) of Rh/Zn catalysts on silica

Sample	Rh 3d _{5/2}	Zn 2p _{3/2}	B 1s	Rh/Zn	Rh/B	Zn/Si	B/Si
As prepared	308.0	1022.7	193.2	0.14	0.14	0.13	0.13
After reaction	307.5	1022.7	193.2	0.08	0.12	0.13	0.09
ZnO		1021.8					
Zn metal		1022.1					
Rh metal	307.2						
Rh ₂ O ₃	308.7						

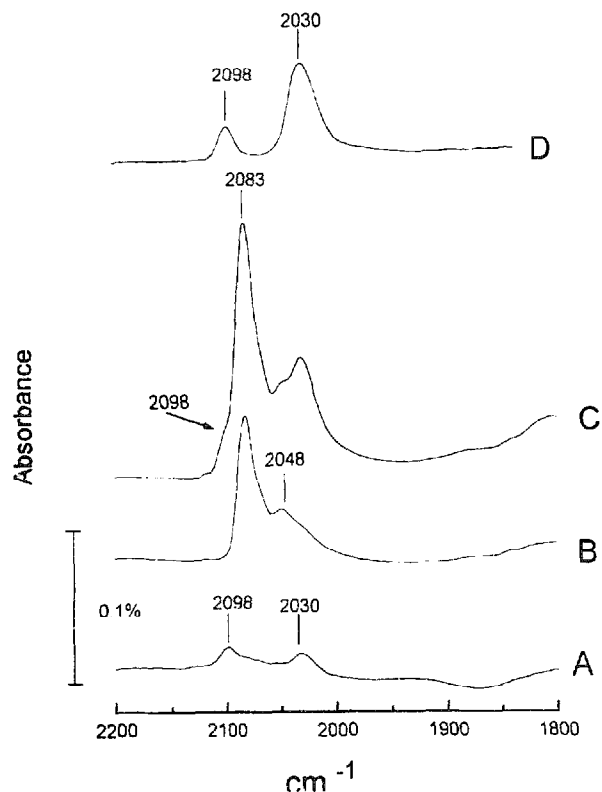


Fig. 1. IR spectra in the $\nu(\text{CO})$ region of the Rh-Zn-B/SiO₂ treated in a flow of: (A) 1 h CO at room temperature; (B) 24 h CO at room temperature; (C) 24 h CO/H₂ at room temperature; (D) 15 min propene at 150°C.

CO/H₂ flow in an evacuable cell at various temperatures are reported in Fig. 1. Treatment of Rh-Zn-B in CO atmosphere at room temperature for 1 h originated from two small bands of almost equal intensity at 2030 and 2098 cm⁻¹, which can be assigned to the asymmetric and symmetric stretching vibrational modes of two geminal carbonyl groups coordinated to an isolated Rh(I) center (Fig. 1A). After treatment of the sample in CO atmosphere for 24 h the most important feature of the spectrum is the presence of a strong band at 2083 cm⁻¹ and of a medium intensity one at 2048 cm⁻¹ (Fig. 1B). The two twin bands are still present as shoulders of the more intense ones. Further treatments of the sample in CO and CO/H₂ do not substantially modify the spectrum. The higher frequency band can be attributed to CO linearly bonded to dispersed rhodium [8,20–33]. The high value (2083 cm⁻¹) of the frequency prompted us to suppose that the oxidation state of the rhodium atoms bearing the coordinated CO is

higher than zero and closer to one as was suggested by Konishi [7] and Chuang [8] and in agreement with our ESCA findings. The stretching of a CO linearly bonded to a Rh(I) center is thought in fact to fall at 2090–2100 cm⁻¹ [25]. It is more difficult to attribute the other weaker band falling at 2048 cm⁻¹. A band in this position was attributed to linearly coordinated CO [25,26] or to carbonyl hydrides [32,33]. We prefer to think of this band as the stretching vibration of a carbon monoxide molecule linearly bonded to a formally zero oxidation state rhodium site. Another important feature common to all the spectra is the complete absence of any absorption attributable to bridge bonded CO. The phenomenon was already observed by other authors studying Rh/silica catalysts poisoned by sulphur [7] or promoted by Zn ions [10] and explained in term of site blocking. It was deduced from the experimental data that sulfur atoms or zinc ions together with the related counterions, cover in part the rhodium crystallites surface preferring positions where they are in contact with several surface metal atoms [10], the 'Freundlich sites', suppressing the bridging mode of adsorbed CO.

We can consequently deduce from the FT-IR and ESCA data that zinc and boron oxide are intimately in contact with the rhodium surface and partially cover the crystallite blocking the sites suitable to the bridge coordination of CO. The rhodium surface appears to contain positive rhodium ions on which the CO coordinates linearly (2083 cm⁻¹) and geminally (2098 and 2030 cm⁻¹) and some metallic rhodium sites. The linear 1:1 coordination appears to be the preferred. The presence of superficial rhodium ions and their coexistence with rhodium metal is not surprising and was detected by other authors in promoted Rh catalysts [8,34]. Exposition of the sample to a propene flow at 150°C (spectrum D) leads to the complete disappearance of the bands at 2083 and 2048 cm⁻¹. This finding suggest that the hydroformylation most probably occurs on these sites while geminal CO are spectator species [7–13]. Readmission of the CO/H₂ mixture regenerates the spectrum C feature.

Table 2
Hydroformylation of some ring substituted styrene in diglyme with Rh–Zn–B

Substituent	PPh ₃	S _R	S _{chem}	Yield(%)
<i>m</i> -NO ₂	–	92	88	81
<i>m</i> -NO ₂	Yes	94	92	84
–H	–	85	100	100
–H	Ycs	70	93	100
<i>p</i> -OCH ₃	–	58	100	90
<i>p</i> -OCH ₃	Yes	63	93	66

S_R = (α -isomer/total hydroformylation products ratio) \times 100.

S_{chem} = (hydroformylation/olefin consumption ratio) \times 100.

3.3. Catalytic activity

We report in Table 2 the data relevant to the hydroformylation of some ring substituted styrenes with electron donating and electron withdrawing groups catalyzed by Rh–Zn/silica. Solvent effects on styrene hydroformylation were studied on Rh–B and in part on Rh–Zn–B. The data are reported in Table 3. There are only few reports in the literature [35–38] on rhodium catalyzed hydroformylation of substituted styrenes and only two [35,36] refer to heterogeneous systems, but in one case [35] the catalytic activity was tested in the absence of solvent. In the other case leaching of the catalyst is presumed so the supported rhodium must be considered the precursor of the real homogeneous catalyst.

A key problem, in fact, related to the use of a supported catalyst in liquid phase is the detachment of the catalyst from the support and its possible dissolution in the reaction medium. The occurrence of the phenomenon not only can alter the reactivity data but can totally cancel the advantages of the supported catalysis. Therefore we carefully tested the presence of elemental rhodium or rhodium compounds in solution by atomic absorption and FT-IR. Moreover, the catalysts activity did not show any modification after several catalytic runs. From all these data we deduced that the catalyst was truly heterogeneous and remained attached to the support. On the contrary the Rh(0)\silica catalyst, prepared by conventional methods, showed extensive leaching of rho-

dium in solution even if the apparent reactivity was comparable with the other two catalysts.

The reagents and products mass balance was carefully checked for every catalytic run. The only detected reaction products were aldehydes and ethylbenzenes and no traces of olefin polymerization were found even when the yield was less than 100%.

The catalytic behaviour of Rh–Zn–B and Rh–B in the styrene hydroformylation are similar. In both cases α -selectivity is very high and chemoselectivity is totally directed toward hydroformylation analogous to what was found in the homogeneous phase [37].

No or only slight activity modifications were observed changing the reaction solvent when benzene and diglyme were used. Tetrahydrofuran appears to modify the α -selectivity hindering by coordination to the metal center the formation of the branched metal–alkyl intermediate. On the other hand the catalytic system appeared totally inactive when DMF was used as solvent. We think that this is due to the strong coordinating power of the solvent, the molecules of which can compete with the other reagents for the catalyst active sites.

It clearly appears from the data in Table 2 that α -selectivity values are quite related to the nature of the ring substituent.

In particular it was observed that the presence on the ring of strong electron withdrawing groups such as –NO₂ lead to an increase of the α -selectivity in comparison with unsubstituted styrene while on the other hand electron donor groups like –OCH₃ and –Cl shift the selectivity toward the

Table 3
Hydroformylation of styrene in various solvents

Catalyst	Substrate	Solvent	S _R	S _{chem}	Yield(%)
Rh–B	Styrene	Diglyme	90	100	100
Rh–B	Styrene	THF	79	99	100
Rh–B	Styrene	DMF	n.r.	n.r.	0
Rh–Zn	Styrene	Diglyme	85	100	100
Rh–Zn	Styrene	Benzene	86	100	100

S_R = (α -isomer/total hydroformylation products ratio) \times 100.

S_{chem} = (hydroformylation/olefin consumption ratio) \times 100.

linear products. The results have a trend: $-\text{NO}_2 > -\text{H} > -\text{Cl} > -\text{OCH}_3$, which is similar to that found in homogeneous phase by other authors with $\text{HRh}(\text{PPh}_3)_4$ as catalyst [37]. Nevertheless the selectivity values found in the homogeneous phase are in general slightly higher and the variations less marked. No reduction of the nitro group was observed in the corresponding derivative. The lower conversion and chemoselectivity values found both in heterogeneous and in homogeneous phase [37] for the nitro derivative can probably be ascribed to the stronger metal–olefin coordination. An excess of triphenylphosphine was added to the reaction mixture in some experiments. Phosphine addition effects resulted in less important than those observed in homogeneous phase [37] but some slight reactivity modifications were observed.

These results confirm that the reaction activity and α -selectivity are mainly controlled by the polarity of the olefin vinyl group.

4. Discussion

The mechanism of the rhodium catalyzed olefins homogeneous hydroformylation was deeply investigated since the discovery of the reaction and it is quite well established since long time [1], but the paths of the heterogeneous reaction are far from being completely clarified. The carbon monoxide insertion in the metal alkyl bond is a crucial step of the homogeneous process but it appears to play an important role also in some carbon monoxide based heterogeneous reactions [8]. It was found that electropositive promoter ions that direct the conversion of the rhodium catalyzed Fischer–Tropsch synthesis toward oxygenates, are also active in increasing the catalyst selectivity toward heterogeneous olefin hydroformylation [7–10]. The promoter role was variously interpreted. Some authors proposed that they act as stabilizing positive charges on catalyst surface, preventing CO dissociation and accelerating migratory insertion of adsorbed CO [7–10], and the various interpretations are not mutually

exclusive. Consequently we can reasonably think that the same promoters act similarly in the heterogeneous olefin hydroformylation and CO migratory insertion must be a crucial step of the hydroformylation in the heterogeneous phase too. Some promoters such as sulfur [7], selenium atoms [9] and zinc ions [10] almost totally suppress the catalytic activity of the metal toward olefin hydrogenation and increase hydroformylation selectivity, blocking sites used otherwise for the adsorption of CO and H_2 when added to a supported rhodium hydroformylation catalyst [7,9,10]. A homogeneous phase mononuclear rhodium complex needs at least three ligand free positions on the metal center to coordinate hydrogen, carbon monoxide and the olefin in order to actively catalyze olefin hydroformylation. It was hypothesized that this geometrical necessity is more easily fulfilled in a heterogeneous phase catalyst on metal crystal corner atoms that are accessible from various directions. Therefore it appears reasonable to regard the isolated corner atoms or ions [7,10], where most probably the hydroformylation occurs, as similar in this respect to the central atom of a mononuclear complex and to use some concepts of the homogeneous process formalism to describe the reaction in the heterogeneous phase. Hydroformylation is favoured with respect to hydrogenation on these particular sites as it happens with mononuclear complexes in the homogeneous phase. It was proved by FT-IR spectroscopy [8] that heterogeneous hydroformylation occurs prevalently on cationic $\text{Rh}(+1)$ sites and to a smaller extent on isolated $\text{Rh}(0)$ sites that linearly chemisorb CO, while rhodium sites, where CO is bridge chemisorbed, catalyze mostly olefin hydrogenation.

The present work adds various points to this picture. The performances of the two catalysts resulted very similar in many aspects though the FT-IR and ESCA data pointed out that the rhodium atoms on the Rh–Zn–B surface appear in a higher oxidation state compared to Rh–B. The vapour phase reactivity simulation experiment followed by FT-IR on the two catalysts clearly indicated that the reaction most probably occurs

in both cases on isolated rhodium sites, while gem dicarbonyl and bridging CO species are not involved in the reaction. It is noteworthy that in the case of Rh–Zn–B it was possible to confirm by ESCA and FT-IR data the presence on the surface of cationic rhodium sites hypothesised but not detected on similar catalytic systems [10].

The slight but detectable activity modification induced by the phosphine addition further suggest in our opinion a homogeneous-like reaction scheme.

It can be concluded that by low-temperature boron hydride reduction it is possible to prepare rhodium based nanocrystalline supported catalyst active in the styrenes hydroformylation with very high chemoselectivity and a regioselectivity comparable with the rhodium phosphine homogeneous system [37]. The system does not show any catalyst release and therefore can substitute the homogeneous ones to avoid catalyst recycling.

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References

- [1] (a) P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Editors), *Organic Synthesis via Metal Carbonyls*, Vol. 2, Wiley-Interscience, New York, 1977, p. 43; (b) B. Cornils, in J. Falbe (Editor), *New Synthesis with Carbon Monoxide*, Springer-Verlag, Berlin, 1980, p. 1.
- [2] C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, *J. Mol. Catal.*, 40 (1987) 129.
- [3] F. Mantovani, N. Palladino and A. Zanobi, *J. Mol. Catal.*, 3, (1978) 285.
- [4] M.E. Davis, P.M. Butler, J.A. Rossin and B.E. Hanson, *J. Mol. Catal.*, 31 (1985) 385.
- [5] R.J. Davis, J.A. Rossin and M.E. Davis, *J. Catal.*, 98 (1986) 477.
- [6] M.E. Davis, J. Schnitzer, J.A. Rossin, D. Taylor and B.E. Hanson, *J. Mol. Catal.*, 39 (1987) 243.
- [7] Y. Konishi, M. Ichikawa and W.M.H. Sachtler, *J. Phys. Chem.*, 91 (1987) 6286.
- [8] (a) S.S.C. Chuang and Shyh-Ing Pien, *J. Mol. Catal.*, 55 (1989) 12; (b) S.S.C. Chuang and Shyh-Ing Pien, *J. Catal.*, 135 (1992) 618.
- [9] a) Y. Izumi, K. Asakura and Y. Iwasawa, *J. Chem. Soc. Chem. Commun.*, (1988) 1286; (b) Y. Izumi, K. Asakura and Y. Iwasawa, *J. Catal.*, 127 (1991) 631; (c) Y. Izumi, K. Asakura and Y. Iwasawa, *J. Catal.*, 132 (1991) 566.
- [10] (a) M. Ichikawa, A.J. Lang, D.F. Shriver and W.M.H. Sachtler, *J. Am. Chem. Soc.*, 107 (1985) 7216; (b) W.M.H. Sachtler and M. Ichikawa, *J. Phys. Chem.*, 90 (1986) 4752; (c) H.W. Jen, Y. Zheng, D.F. Shriver and W.H. Sachtler, *J. Catal.*, 116 (1989) 361.
- [11] M. Lenarda, R. Ganzerla, L. Storaro and R. Zaroni, *J. Mol. Catal.*, 78 (1993) 339.
- [12] M. Lenarda, R. Ganzerla, L. Storaro and R. Zaroni, *J. Mol. Catal.*, 79 (1993) 243.
- [13] M. Lenarda, R. Ganzerla, S. Enzo, L. Storaro and R. Zaroni, *J. Mol. Catal.*, 80 (1993) 105.
- [14] W.J. Gensler, F.A. Johnson and A.D. Sloan, *J. Org. Chem.*, 82 (1960) 6074.
- [15] Y. Okamoto, N. Ishida, T. Imanaka and S. Teranishi, *J. Catal.*, 58 (1979) 82.
- [16] S.L.T. Andersson and M.S. Scurrill, *J. Catal.*, 71 (1981) 233.
- [17] M. Kawai, M. Uda and M. Ichikawa, *J. Phys. Chem.*, 89 (1985) 1654.
- [18] H.J. Gysling, J.R. Monnier and G. Apai, *J. Catal.*, 103 (1987) 407.
- [19] S.H. Oh and J.E. Carpenter, *J. Catal.*, 80 (1983) 472.
- [20] A.C. Yang and C.W. Garland, *J. Phys. Chem.*, 61 (1957) 1504.
- [21] D.J. Yates, L.L. Murrell and E.B. Prestridge, *J. Catal.*, 57 (1979) 41.
- [22] J.T. Yates Jr., T.M. Duncan and R.W. Vaughan, *J. Chem. Phys.*, 71 (1979) 3908.
- [23] A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol and W.F. Graydon, *Inorg. Chem.*, 18 (1979) 3104.
- [24] R.R. Cavanagh and J.T. Yates, Jr., *J. Chem. Phys.*, 74 (1981) 41 50.
- [25] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin and A.R. Tarrer, *J. Chem. Phys.*, 74 (1981) 6487.
- [26] S.D. Worley, G.A. Mattson and R. Caudill, *J. Phys. Chem.*, 87 (1983) 1671.
- [27] J.T. Kiss and R.D. Gonzales, *J. Phys. Chem.*, 88 (1984) 898.
- [28] F. Solymosi, I. Tombácz and M. Kocsis, *J. Catal.*, 75 (1982) 78.
- [29] T. Iizuka, Y. Tanaka and K. Tanabe, *J. Catal.*, 76 (1982) 1.
- [30] F. Solymosi and M. Pásztor, *J. Phys. Chem.*, 89 (1985) 4789.
- [31] F. Solymosi and M. Pásztor, *J. Phys. Chem.*, 90 (1986) 5312.
- [32] J.L. Robbins, *J. Phys. Chem.*, 90 (1986) 3381.
- [33] F.G.A. van den Berg, J.H.E. Glezer and W.M.H. Sachtler, *J. Catal.*, 93 (1985) 340.
- [34] T. Beutel, H. Knoezinger, H. Trevino, Z. Conrad, Zhang, W.M.H. Sachtler, C. Dossi, R. Psaro and R. Ugo, *J. Chem. Soc. Faraday Trans.*, 90 (1994) 1335.
- [35] R. Lai and E. Ucciani, *J. Mol. Catal.*, 4 (1979) 401.
- [36] E. Ucciani and A. Bonfand, *J. Chem. Soc. Chem. Commun.*, (1981) 82.
- [37] T. Hayashi, M. Tanaka and I. Ogata, *J. Mol. Catal.*, 13 (1981) 323.
- [38] T. Fuchikami and I. Ojima, *J. Am. Chem. Soc.*, 104 (1982) 3527.