A molecular approach to heterogeneous catalysis. Ethylene hydroformylation catalysed by silica-supported $[Rh_{12}(CO)_{30}]^{2-}$ cluster anion: influence of the countercations Li^+, Na^+, K^+, Zn^{2+}

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Abstract

Cluster-derived rhodium catalysts, prepared from salts of the cluster anion $[Rh_{12}(CO)_{30}]^{2-}$ supported on silica, have been studied in ethylene hydroformylation. A catalyst pre-treatment was carried out in Ar at 393 K before the admission of the hydroformylation mixture. The selectivity for propanal formation depends on the alkaline countercation in the following order: $K \geq Li \geq Na$. The Zn-promoted catalyst is the most selective. The corresponding value for the unpromoted system, prepared from neutral $Rh_4(CO)_{12}$, was about 20% lower. In situ infrared studies suggest the oxidative disruption of the metal framework of the physisorbed Rh_{12} cluster to take place in isolated $Rh^I(CO)_2$ species. In catalytic conditions a reductive agglomeration of $Rh(I)$ into metallic particles occurred. Remarkable effects on activity and/or selectivity are induced on promoted systems only upon a catalyst pre-treatment in O_2 at 723 K. A simple exposure to the hydroformylation mixture at 393 K was enough to generate the active metallic phase.

Keywords: Promotion effect; Hydroformylation; Ethylene; Cluster-derived rhodium catalyst; Silica

1. Introduction

The CO insertion reaction is an excellent model for studying the relation between heterogeneous and homogeneous catalysis. Rhodium carbonyl clusters have been used as catalysts for the homogeneous hydroformylation reaction [1], the catalytically active species being mononuclear Rh carbonyls [2]. Following the pioneering work of Mantovani et al. [3], much work has been done to exploit Rh carbonyl clusters as heterogeneous hydroformylation catalysts when supported on inorganic oxides [4]. Cluster-derived catalysts

exhibited higher selectivity than those traditionally prepared from Rh salts [5]. A number of studies on Rh-zeolite catalysts suggested a hydroformylation pathway resembling that found in the homogeneous system [6]; oxidised $Rh^I(CO)_2$ surface species serve as precursors and/or active sites for the reaction [7–9]. On the contrary, Takahashi et al. [10] showed that $Rh_6(CO)_{16}$ supported on zeolite or even $Rh^I(CO)_2$ species may act as a heterogeneous catalyst only once reduced to metallic crystallites. On silica surface, Chuang et al. [11] observed that the adsorbed CO on various kinds of Rh surface sites can participate in CO insertion. Iwasawa et al. [12] reported the catalytic performance and dynamic behaviour of a silica-grafted Rh dimer indicating that a mini-

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mum of two bonded metallic centres are necessary for the hydroformylation and, on the basis of in situ spectroscopic characterisation, a metal-assisted CO insertion mechanism was proposed.

Another type of the promotion of CO insertion through the direct bonding of CO molecules with a Lewis acid added as co-catalyst has been proposed [13]. The addition of small amounts of zinc strongly increased the hydroformylation yield and the selectivity for propanal formation [14].

The proposal that a surface Lewis acid, Zn^{2+}, might promote the catalytic hydroformylation accounts for the well-known observations in organometallic chemistry that CO migratory insertion reaction is promoted by cations [15] and molecular Lewis acids [16]. The proposed metal–CO$\cdots$Lewis acid interaction necessarily requires an intimate contact between the metallic phase and the promoting ion. In order to explore this structural aspect, we choose the cluster anion $[Rh_{12}(CO)_{30}]^{2-}$ as potassium salt supported on silica as model system [17]. In this organometallic precursor the close contact between the metal framework and the promoter cation is inherently obtained at molecular level.

In this contribution, the same reaction was investigated at 393 K using silica-supported salts of $[Rh_{12}(CO)_{30}]^{2-}$. The aim of this study was to investigate the influence of the countercations Li^+, Na^+, K^+, Zn^{2+} on the catalytic properties.

2. Experimental

The $(M_x)^{2+}[Rh_{12}(CO)_{30}]^{2-}$ salts (M = Li, Na, K, Zn) and $Rh_4(CO)_{12}$ were prepared by reported methods [18]. Silica (Davison 62, 200 m^2/g) was grounded, washed with 1 M HNO_3, then with distilled water to neutrality and eventually dried overnight in vacuo (1.33 Pa, r.t.). The support was impregnated under Ar with an acetone or pentane ($Rh_4(CO)_{12}$) solution of the catalyst precursor. After removal of the solvent in vacuo, the solid was dried overnight (1.33 Pa, r.t.) and stored under Ar. The metal loading was about 1% by weight, as measured by AAS measurements.

The spectroscopic study has been performed on pressed wafers (18 mm, 50 mg), impregnated with a THF solution of $Na_2[Rh_{12}(CO)_{30}]$ in flowing Ar. The IR cell [19] allowed thermal treatment as well as operation in vacuo or under controlled atmosphere. Some IR experiments were also done in diffuse reflectance mode with a specially designed apparatus [20] for recording in situ spectra under real catalytic conditions.

The hydroformylation reaction was carried out in a fixed-bed, continuous-flow glass microreactor at 393 K and atmospheric pressure ($CO:H_2:C_2H_4$ = 1:1:1; total flow = 30 ml/min; catalyst = 0.3 g; space velocity = 2000 h^{-1}). Under these experimental conditions, the total ethylene conversion was kept below 2% by mole, in order to operate in the differential mode. The reactor was interfaced to a HP5890A gas-chromatograph and the product analysis was performed at sampling intervals of 1–4 h on a Porapack Q 25 m$\times$0.53 mm i.d. column, FID detector.

In the in situ catalyst pretreatments the flow of each gas was 10 ml/min.

3. Results

3.1. Spectroscopic characterisation

When the organometallic precursor $Na_2[Rh_{12}(CO)_{30}]$, as THF solution, was adsorbed on a pressed wafer of silica, the red–violet colour was maintained.

The IR spectrum in the v_{CO} region, obtained after only 3 min of treatment in vacuo is quite similar to that of the pure cluster for the linear CO adsorption, but the diagnostic strong band at 1778 cm^{-1} (Fig. 1A), typical of bridging CO, was lacking and new weak bands at 1856 and 1800 cm^{-1} appeared (Fig. 1B). A relevant decarbonylation occurred after a treatment in vacuo at r.t. for 20 h; the colour changed to brown, with the concomitant formation of shoulders at 2089 and 2031 cm^{-1} (Fig. 1C). This spectral transforma-
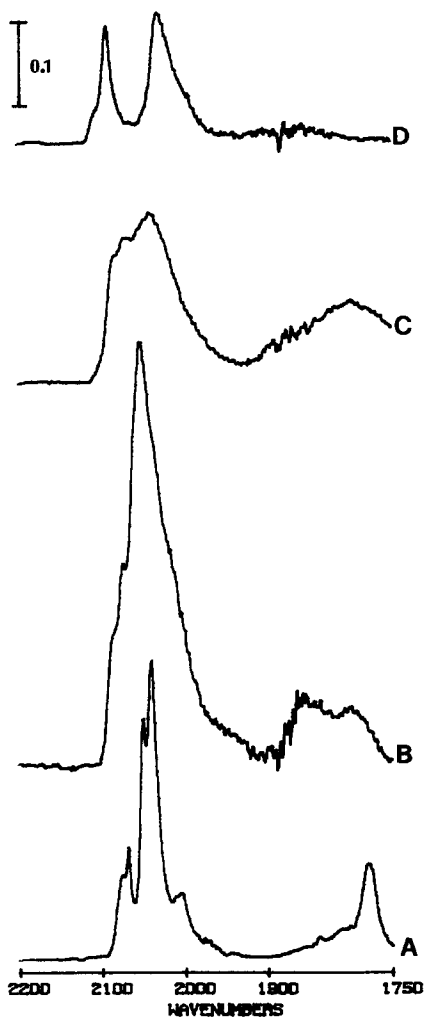
Fig. 1. Transmittance spectra of $Na_2[Rh_{12}(CO)_{30}]/SiO_2$: (A) in THF solution; (B) freshly impregnated on SiO_2; (C) as (B) after 20 h at 1.33 Pa and r.t.; (D) as (C) after 3 h under 40 kPa of Ar at 393 K.
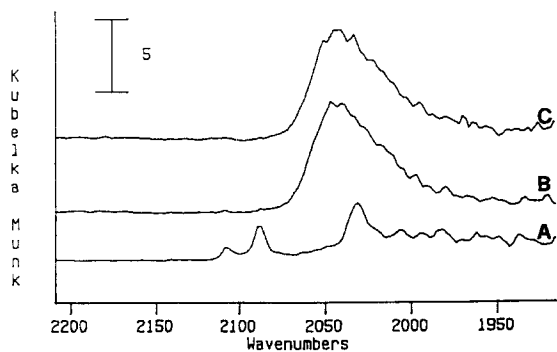

Fig. 2. Sequential DRIFT spectra of $Na_2[Rh_{12}(CO)_{30}]/SiO_2$ at 393 K: (A) 3 h in N_2 flow; (B) 30 min in $CO/H_2/C_2H_4$ flow; (C) 2.5 h in $CO/H_2/C_2H_4$ flow.

tion resulted also by a simple treatment in Ar at 393 K for 3 h (Fig. 1D).

The same spectrum, characterised by a doublet at 2089 and 2031 cm^{-1} and a shoulder at 2106 cm^{-1}, was again obtained when the fresh catalyst was treated in the DRIFT cell in N_2 flow at 393 K (Fig. 2A).

Exposure to the hydroformylation mixture at 393 K for 30 min gave rise to the disappearance of the doublet and a new single broad band centred at 2040 cm^{-1} formed (Fig. 2B). This spectrum did not change with time on stream (Fig. 2C). The same spectrum was obtained when working in static conditions in transmittance mode (compare Fig. 3A and 2B).
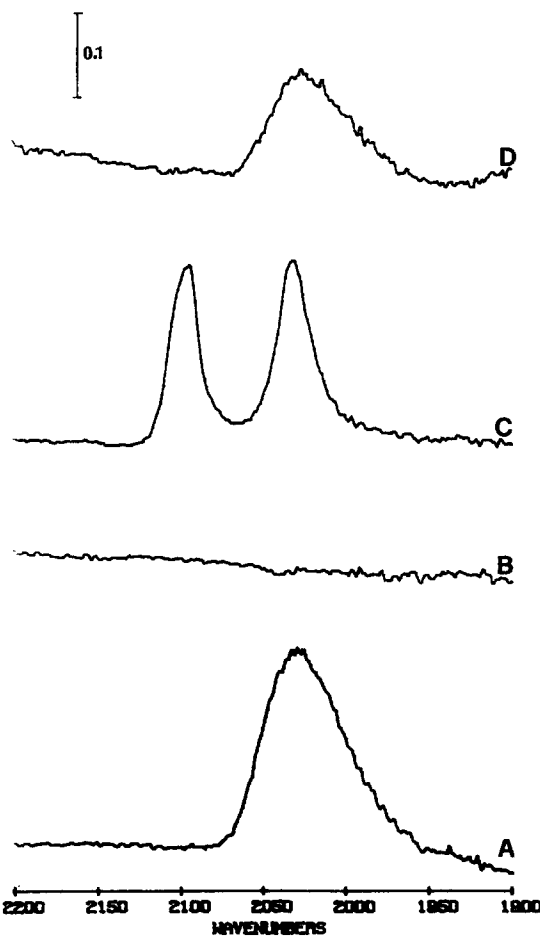

Fig. 3. Transmittance spectra at r.t. of $Na_2[Rh_{12}(CO)_{30}]/SiO_2$: (A) after 1 h under 40 kPa of $CO/H_2/C_2H_4$ at 393 K; (B) after 1 h under 40 kPa of O_2 at 723 K; (C) after 45 min under 40 kPa of $CO/H_2/C_2H_4$ at 393 K; (D) after 1 day under 40 kPa of $CO/H_2/C_2H_4$ at 393 K.

After calcination at 723 K a complete decarbonylation occurred (Fig. 3B). Re-exposure to the $CO/H_2/C_2H_4$ mixture for only 45 min led again to the doublet (Fig. 3C), which was then converted into a linearly bonded CO band (Fig. 3D).

3.2. Ethylene hydroformylation

Vapour-phase ethylene hydroformylation with our supported Rh clusters yielded ethane and propanal as the only products. Under the reaction conditions adopted, no or at most traces of 1-propanol were observed, because the low value of the contact time used prevents any further reaction of the aldehyde. The performance was nearly constant for over 3 days for all catalytic systems and no leaching of Rh as volatile carbonyl species was observed.

As reported in a preliminary study [21], the supported precursor was heated in situ for 3 h at 393 K in Ar flow before the catalytic run. By this treatment the time needed for the increase in total activity up to a steady-state was considerably shortened. In Fig. 4 the activity and selectivity data after 20 h on stream of the systems investigated are reported. The rates of hydrogenation and hydroformylation were of the same order of those

of an unpromoted reference material, prepared from the neutral cluster $Rh_4(CO)_{12}$. The systems derived from the metal salts of the $[Rh_{12}(CO)_{30}]^{2-}$ anion displayed, however, a selectivity for propanal greater than 50%, whereas the corresponding value for the unpromoted system was about 20% lower. In this experiment the Zn-salt was the most selective, followed by those of the alkali metals Na, Li and K, which differentiated only in activity. At the end of the catalytic run the colour of the supported catalysts derived from metal salts changed from brown to bright black.

We then decided to perform a conventional regeneration cycle oxidation/reduction.

The Li-salt system was chosen to identify the best reducing agent of Rh after the oxidation with O_2 at 723 K for 1 h. The treatment was performed in situ at 393 K for 1 h and was followed by Ar purge at 393 K before starting the catalytic run. The results are depicted in Fig. 5, and compared with that obtained upon the simple Ar pre-treatment. When the reduction occurred in H_2, a marked deactivation of the catalyst resulted; at very low values of total conversion, as those shown by this catalyst, the selectivity value is to be considered not fully reliable. On the contrary, when the calcined catalyst is immediately exposed
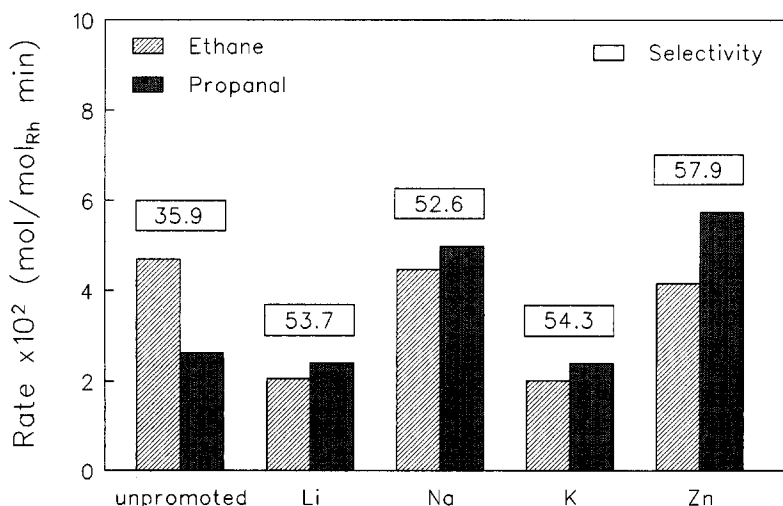

Fig. 4. Catalytic activity and selectivity in ethylene hydroformylation at 393 K and 101.3 kPa of Rh/SiO$_2$ systems derived from different salts of [Rh$_{12}$(CO)$_{30}$]$^{2-}$ and from Rh$_4$(CO)$_{12}$ (unpromoted). Catalyst pretreatment in Ar at 393 K for 3 h; selectivity: %mol ratio propanal/propanal + ethane; data after 20 h on stream.
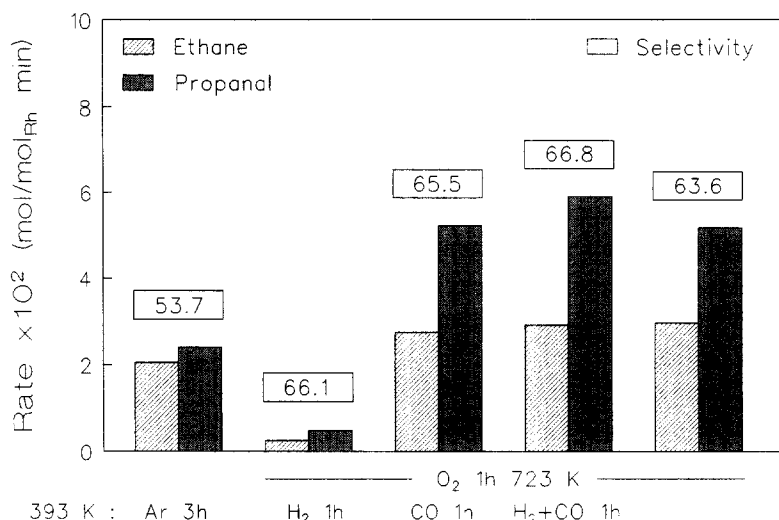
Fig. 5. Effect of the pretreatment on catalytic activity and selectivity of cluster-derived Rh–Li/SiO$_2$ system in ethylene hydroformylation at 393 K and 101.3 kPa. Selectivity: %mol ratio propanal/propanal + ethane; data after 20 h on stream.

to CO or to a H$_2$ + CO mixture, or directly to the hydroformylation mixture, a 50% increase in the rates of hydrogenation and hydroformylation was observed, accompanied by some 10% increase in selectivity. This latter regeneration cycle has been repeated many times with complete restoring of the total conversion and selectivity values.

The preoxidation treatment was then applied to all fresh catalysts. As can be seen from Fig. 6, remarkable effects on activity and/or selectivity were always obtained with the promoted catalysts.

The unpromoted system underwent a large decrease (about 50%) in the hydrogenation activity, with still the lowest selectivity. Among the other metal salt systems, the Na-salt nearly doubled its activity, but the rates of hydrogenation and hydroformylation became almost equal. The Zn-salt increased slightly its total activity without affecting its selectivity for propanal. The K-salt system exhibited on the contrary only an increase in selectivity of about 10%.
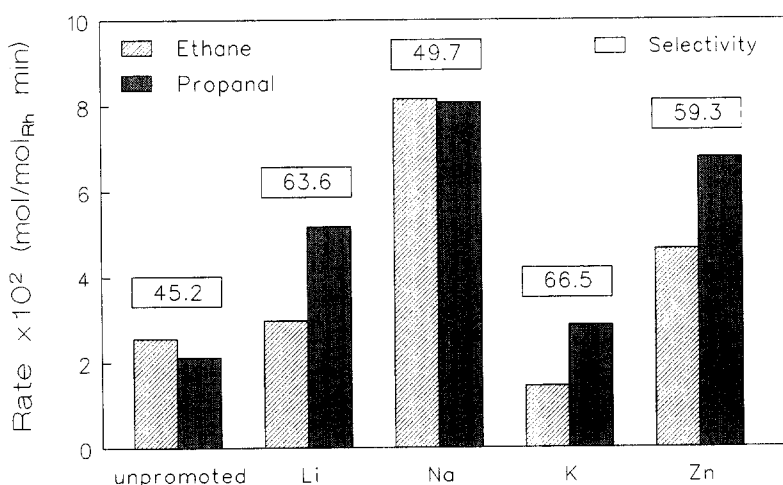

Fig. 6. Catalytic activity and selectivity in ethylene hydroformylation at 393 K and 101.3 kPa of Rh/SiO$_2$ systems derived from different salts of [Rh$_{12}$(CO)$_{30}$]$^{2-}$ and from Rh$_4$(CO)$_{12}$ (unpromoted). Catalyst pretreatment in O$_2$ at 723 K for 1 h; selectivity: %mol ratio propanal/propanal + ethane; data after 20 h on stream.

4. Discussion

The spectroscopic data indicate that the physisorbed Rh_{12} cluster salts slowly undergo an oxidative addition with the OH surface groups of silica. The disruption of the Rh cluster framework proceeds stepwise, probably through the intermediate formation of clusters of lower nuclearity. In the spectrum in Fig. 1B there are some features attributable to physisorbed $Rh_6(CO)_{16}$ [19].

After the thermal treatment in Ar, there are only isolated species $Rh^I(CO)_2$ on the surface (Fig. 1D), which is in agreement with the well-known chemistry of supported Rh carbonyl clusters [19,22].

From the DRIFT spectrum under real catalytic conditions only the presence of CO linearly bonded on small metallic Rh particles (Fig. 2B) is apparent; a surface restructuring by reductive carbonylation of the isolated $Rh^I(CO)_2$ sites has thus occurred. The proposed surface restructuring by treatment with $CO + H_2$ at 393 K is not unexpected. Silica-physisorbed $Rh_6(CO)_{16}$ cluster is regenerated from $Rh^I(CO)_2$ species by treatment with $CO + H_2O$ at r.t. and atmospheric pressure [23]. The reductive agglomeration to metallic state easily occurs also by treatment in H_2 at 323 K [19]. In the presence of CO this process occurs at and above 423 K, and is further favoured by the presence of H_2 [24]. The addition of different promoters to a supported Rh catalyst exerts a significant influence on its surface chemistry [25]. The presence of K_2O greatly favours the reductive agglomeration, while the opposite occurs with CeO_2 [25].

The comparison of the catalytic behaviour of the silica-supported systems prepared from the $[Rh_{12}CO)_{30}]^{2-}$ salts and from $Rh_4(CO)_{12}$ (Fig. 4) points to a positive influence of the metal cations on the rate of ethylene hydroformylation. The warning raised about un-intentional promotion by contaminants (Na^+, K^+, Fe^{3+}) in the silica [26] can be disregarded because in a blank run no hydroformylation catalytic activity resulted. The adopted washing procedure was hence effective.

The nearly constant selectivity in ethylene hydroformylation for all metal salts can be explained on the basis of a polarising effect of the promoting cation on the Rh particles, as proposed by different authors [27]. The nature of the metal cation is then proposed to influence the degree of dispersion of the active metal phase during the surface restructuring process following the reductive carbonylation of $Rh^I(CO)_2$ sites.

Conventional H_2 or CO chemisorption studies in promoted Rh catalysts are unlikely to give any information about the number of active Rh sites in catalytic ethylene hydroformylation, since the necessary O_2/H_2 pretreatments are demonstrated to significantly reduce the catalytic activity (Fig. 5).

More active and more selective materials are instead obtained when calcined catalysts are immediately subjected to catalytic conditions or CO-containing atmosphere. This observation points out for a peculiar role of CO in forming the active sites.

The oxygen treatment leads to the formation of highly dispersed Rh_2O_3, as previously confirmed by TPR experiments [28], in intimate contact with the metal oxide of the promoting cation.

The original frame structure of the starting cluster is totally destroyed by calcination, as it is also observed for the metallic particles (Fig. 3B). Upon admission of the hydroformylation mixture, the reductive carbonylation of Rh_2O_3 is demonstrated to occur stepwise through the intermediate formation of isolated $Rh^I(CO)_2$ species, leading to the reconstruction of CO covered metallic particles (Fig. 3C, D).

On the basis of catalytic data (Fig. 6), the global effect of the O_2 pre-treatment on supported Rh_{12} metal salts is two-fold: (i) redispersion of the metallic Rh phase leading to increased activity with little change in selectivity, as highly evidenced for Na^+; (ii) increased activity and selectivity for the insertion reaction to propanal are observed with Li^+ and K^+ as the promoting cation, which act as Lewis acid for CO molecules coordinated to the Rh metal particles [29].

The promoting effect of Zn^{2+} cannot be directly compared with that of alkaline ions, owing to their different M/Rh ratio (0.0833 instead of 0.167). It is reported that this ratio may have large effects on the catalytic activity and selectivity [13,14].

5. Conclusions

The use of Rh clusters as precursors of active supported metallic catalysts has an inherent advantage over the traditionally used Rh-salts, since higher metal dispersion is simply obtained by a low-temperature treatment under inert atmosphere. The effect of the promoting cation, which was present in the coordination sphere of the cluster precursor, is primarily to affect the selectivity. This intimate contact between the metal phase and the cationic promoter in the cluster salt precursor is likely to be the factor responsible for the enhanced performance upon oxidation and the subsequent reductive carbonylation under catalytic conditions.

Acknowledgements

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