Ethylene hydroformylation with the silica-supported $K_2[Rh_{12}(CO)_{30}]$ cluster: evidence for vapor-phase cluster catalysis

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The SiO_2-supported $[Rh_{12}(CO)_{30}]^{2-}$ cluster, as K^+ salt, is a stable and active catalyst for the heterogeneous hydroformylation of ethylene at atmospheric pressure.

Keywords: Hydroformylation; cluster; molecular catalysis

1. Introduction

Following the pioneering work of Palladino et al. [1], much work has been done in recent years to exploit carbonyl clusters of Rh as heterogeneous hydroformylation catalysts when supported on inorganic oxides [2–5]. Evidence for cluster catalysis was, however, rather poor. Takahashi and coworkers [6] showed that $Rh_6(CO)_{16}$ supported on zeolite or even $Rh^I(CO)_2$ species may only act as heterogeneous hydroformylation catalysts when reduced to metallic rhodium.

It is known that neutral metal carbonyl clusters suffer some major limitations due to their intrinsic low stability under catalytic conditions [7] and their potential volatility under CO atmosphere [8]. On the contrary, anionic carbonyl clusters, as alkaline salts, are non-volatile compounds with a much higher thermal stability. For this reason, the $[Rh_{12}(CO)_{30}]^{2-}$ cluster anion, easily obtained in high purity as K^+ salt [9], was studied as molecular heterogeneous hydroformylation catalyst. The presence of a metal cation on the Rh framework is likely to offer a further advantage for their use as heterogeneous catalysts in CO conversion. Indeed, the positive effect of Zn^{2+} [10-12] or Na^+ [13] addition to conventional oxide-supported Rh catalysts for vapor-phase hydroformylation of olefin has been clearly demonstrated.

In this communication, we will present evidence of cluster catalysis in the heterogeneous hydroformylation of ethylene with the silica-supported $K_2[Rh_{12}(CO)_{30}]$ cluster as the active catalyst.

2. Experimental

The crystalline $K_2[Rh_{12}(CO)_{30}]$ cluster was prepared according to the literature [13]. Silica (Davison 62, 80-100 mesh) was impregnated under inert atmosphere from a solution of the cluster in doubly-distilled water, to avoid the presence of residual organic solvents. The air-sensitive solid was overnight evacuated (10^{-3} mbar) at room temperature, and subsequently handled under inert atmosphere. Ethylene hydroformylation was performed under differential conditions in a fixed bed, glass flow-reactor at 180 ° C and atmospheric pressure ($CO:H_2:C_2H_4 = 1:1:1$). Product analysis was periodically carried out by on-line gas chromatography, using a 2-m, Porapak QS column.

Infrared spectra of the catalysts, as pressed wafers, were recorded *in-situ* in a special glass cell with a Digilab FTS-40 FTIR spectrophotometer.

3. Results and discussion

The IR spectrum region of $K_2[Rh_{12}(CO)_{30}]$ just after impregnation on SiO_2 (fig. 1A) shows bands in the νCO region at 2086w,sh, 2040vs and 1834s,br in close similarity to that of the pure cluster in THF solution [9]. This result clearly indicates that the cluster is deposited intact on the surface of silica. The broadening of the low-frequency band due to bridging CO molecules has in fact to be related to the occurrence of some weak interactions with the OH group of the surface, likely via hydrogen bonding.

The supported $[Rh_{12}(CO)_{30}]$ cluster is an active catalyst for vapor-phase hydroformylation of ethylene at atmospheric pressure (fig. 2).

A selectivity of about 40% to C_2H_5CHO is observed without any induction period, the parallel reaction being ethylene hydrogenation to ethane. Activity and selectivity for hydroformylation were nearly constant for about 100 h on stream. The absence of any induction period, together with the constant activity to hydroformylation seems to suggest that the cluster is stable under reaction conditions, as the catalytically active species.

Cluster reactivity under hydroformylation conditions has also been investigated in situ via FTIR spectroscopy. Even after 18 h on stream at reaction

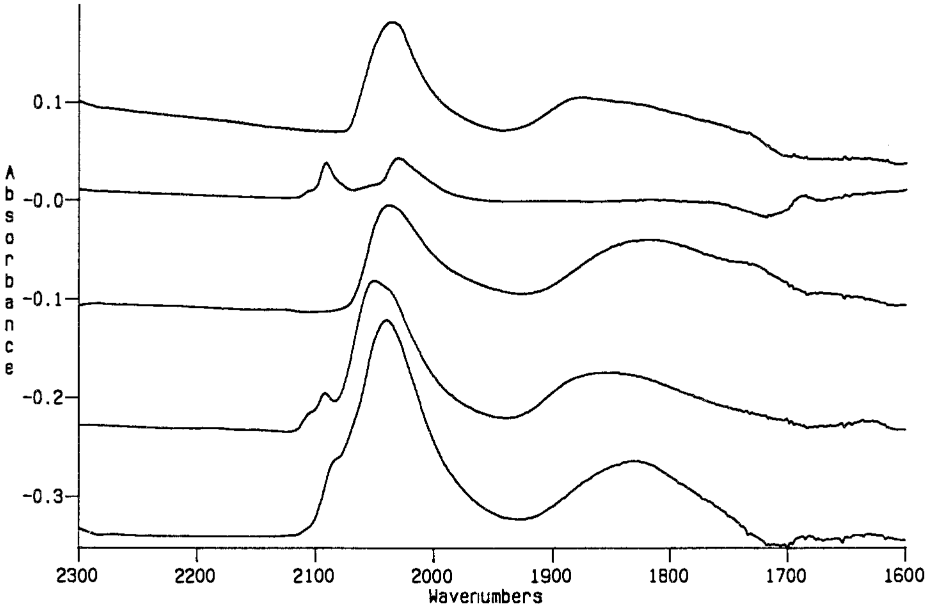

Fig. 1. Infrared spectra in the ν(CO) region: (A) $K_2[Rh_{12}(CO)_{30})$ on SiO_2 just after impregnation; (B) after 1 hr on stream at 180 ° C; (C) after further 17 hrs on stream at 180 ° C; (D) after exposure to air for 15 min at room temperature; (E) after 1 hr on stream at 180 ° C.

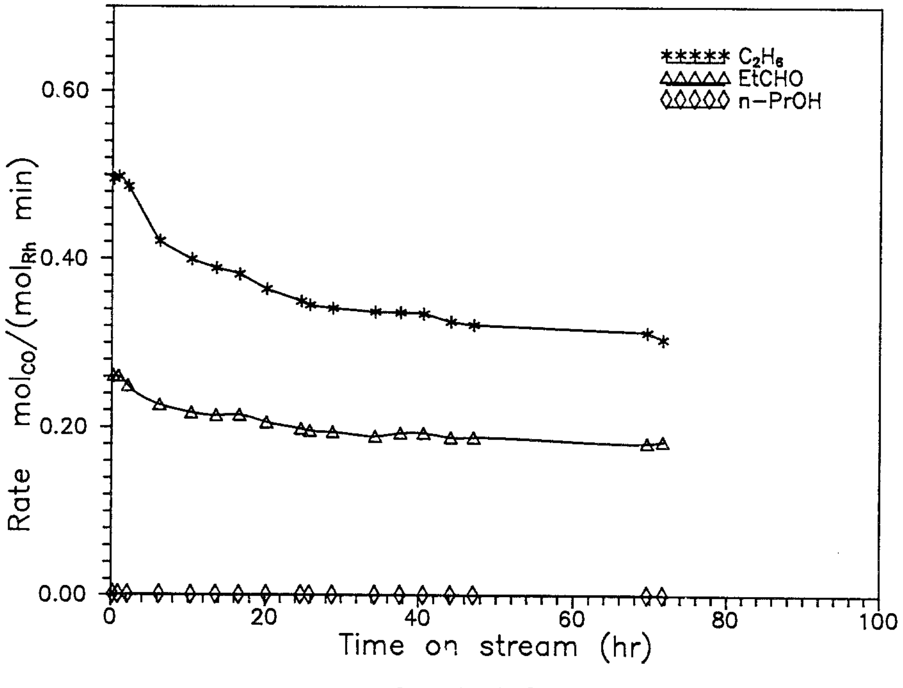

Fig. 2. Catalytic activity and selectivity of $K_2[Rh_{12}(CO)_{30}]/SiO_2$ in ethylene hydroformylation at 180 ° C and 1 atm.

temperature (fig. 1B,C), no significant changes in the ν region of the IR spectrum could be observed. The stability of the original Rh_{12} carbonyl anion under reaction conditions is thus confirmed.

A partial decomposition to traces of metallic rhodium or to surface-grafted Rh^I carbonyls can not be excluded on the only basis of the IR investigation. However, such a formation of metallic rhodium or Rh^I surface carbonyls, as the active species for ethylene hydroformylation, would have required a non-negligible induction time, together with a completely different catalytic behavior. Silica-supported metallic rhodium shows a negligible selectivity to propionaldehyde in ethylene hydroformylation [10], whereas Rh^I surface carbonyls are reported to be unable to catalyze olefin hydroformylation [6].

This behavior of surface Rh^I species is noteworthy, being in marked contrast with the very high activity of soluble Rh^I complexes for the homogeneous hydroformylation of olefins [14]. We therefore decided to confirm the findings of Takahashi et al. [6] via an independent experiment.

The hydroformylation reaction was stopped and the supported Rh_{12} cluster was briefly exposed to air at room temperature. The oxidative demolition of the cluster frame with formation of Rh(I) dicarbonyls was demonstrated by the appearance of the typical doublet at 2091, 2030 cm^{-1} (fig. 1D) in the IR spectrum [15]. After exposing the oxidized catalyst to reaction condition again, the catalytic activity was restored, with the IR spectrum (fig. 1E) indicating that the original cluster anion is regenerated. Processes of surface reaggregation to metal clusters are well-known [16]; however, aggregation to carbonyl anions just occurs on basic surfaces [17]. Consequently, the K^+ cation tends to stabilize the anionic Rh_{12} framework on the surface, likely via a local modification of the electronic properties of the silica surface, due to its strong Lewis-acid character. Preliminary results in our laboratory indicate that the same effect is shown by substituting K^+ with Na^+.

A similar explanation, based on the close contact between the Rh particle and the ionic promoter, was proposed by Sachtler [10] to explain the high selectivity to C_2H_5CHO of Zn^{2+}-promoted Rh catalysts.

The essential role of the ionic metal promoter is finally confirmed by the poor results reported by Ichikawa when using, as catalyst, the $[NBu_4]^+$ salt of the $[Rh_{13}(CO)_{23}H_{2\text{-}3}]^{3-}$ anion supported on ZnO [2].

In conclusion, this work is the first example, to our knowledge, of heterogeneous olefin hydroformylation catalyzed by a molecular carbonyl cluster supported on silica. The advantage of using a molecular Rh cluster as SiO_2-supported catalyst providing both the active metal center and the ionic precursor for the hydroformylation reaction of olefins is demonstrated by the very poor results obtained with conventional SiO_2-supported Rh catalysts [2].

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