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Activity enhancement of bimetallic Rh-Ag/Al_2O_3 catalysts for selective catalytic reduction of NO by C_3H_6

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The catalytic performance of bimetallic rhodium–silver clusters for the selective catalytic reduction of NO by propylene has been examined over 1%(Rh-Ag)/Al_2O_3 catalysts of variable Ag content. It was found that substitution of small amounts of Rh by Ag results in a significant increase of the catalytic activity, which goes through a maximum for catalysts with metal compositions of *ca.* 95%Rh–5%Ag. This behaviour is tentatively attributed to the formation of rhodium-rich phase alloys, which may stabilize Rh in its reduced state at reaction conditions.

KEY WORDS: rhodium; catalyst; Rh-Ag; catalysts; bimetallic clusters; nitrogen monoxide; propylene; selective catalytic reduction; aluminium oxide.

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons (HC-SCR) over noble metal catalysts has been studied extensively in recent years due to the potential application of this process for the reduction of emissions of pollutants present in the exhaust of lean burn and diesel engines [1–3]. Noble metal catalysts are characterized by relatively high activity under strongly oxidizing conditions, which is not significantly affected by the presence of water and sulfur dioxide. The major problem associated with the performance of these catalysts is related to the relatively narrow temperature window of operation [1–3].

Several studies have shown that the catalytic performance of noble metal catalysts under conditions of NO_x reduction depends on the type and physicochemical characteristics of the active component and on the nature of the support [1–7]. Among the various noble metal catalysts examined, such as Pt, Pd, Ru, Rh and Ir, rhodium is characterized by high selectivity toward the formation of N_2 as opposed to N_2O, and relatively high light-off temperatures, compared with Pt catalysts [4]. The catalytic performance of rhodium is significantly affected by the nature of the carrier: Rh supported on Al_2O_3 exhibits significantly improved activity and selectivity for the HC-SCR of NO, compared with rhodium supported on materials such as ZrO_2, ZnO and TiO_2 [5]. The metal loading and dispersion of the noble metal have also been found to affect catalytic performance [6,7], thus providing evidence that the reduction of NO by hydrocarbons is a structure-sensitive reaction. For example, activity and selectivity of Pt/Al_2O_3 can be improved to a large extent by increasing the metal loading, which also results in the lowering of the light-off temperature [6].

Bimetallic catalysts have been extensively used in the past for structure-sensitive reactions, since it was found that the activities of metal catalysts for different reactions could be altered to markedly different degrees by the incorporation of a second metallic component into the catalyst structure [8,9]. This is particularly true for bimetallic catalysts consisting of Group IB–Group VIII metal components, which have been studied in detail because (a) many pairs form alloys over large composition ranges, and (b) their adjacent position in the periodic table results in a combination of filled and nearly filled *d* bands, respectively. However, studies of bimetallic clusters are not limited to combinations of elements that form bulk alloys, but also to pairs of metals which are practically immiscible in the bulk, such as Ru-Cu, Os-Cu, Ir-Au, Rh-Ag and Rh-Au ([9–11] and references therein).

In the present work, the SCR of NO by propylene in the presence of excess oxygen is examined over bimetallic Rh-Ag catalysts supported on Al_2O_3. Similar catalyst formulations have been employed in the past to study the effect of addition of Ag on the catalytic properties of Rh, with respect to several reactions, including hydrogenolysis of ethylene [11] and methylcyclopentane [12], hydrogenation of CO [13], and hydroformylation of ethylene [13].

2. Experimental

2.1. *Catalyst preparation and characterization*

Catalysts were prepared by impregnation of γ-Al_2O_3 (Alfa, surface area: 90 m^2/g) with aqueous solutions of

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Table 1
Physicochemical data of the 1%(Rh-Ag)/Al$_2$O$_3$ catalysts

Catalyst sample	Ag content in Rh-Ag (bulk)		Hydrogen uptake (cm^3/g)		H/Rh [a]	Exposed Rh surface area [a] (m^2/g Rh)	Apparent Rh crystallite size [a] (nm)
	wt%	at%	Total	Irrev.			
Rh-Ag(100-0)	0	0	0.347	0.260	0.24	106	45
Rh-Ag(97-3)	3	2.9	0.469	0.360	0.34	151	32
Rh-Ag(95-5)	5	4.8	0.396	0.300	0.29	129	37
Rh-Ag(93-7)	7	6.7	0.397	0.277	0.27	122	40
Rh-Ag(90-10)	10	9.6	0.337	0.251	0.26	114	42
Rh-Ag(85-15)	15	14.4	0.355	0.248	0.27	119	40
Rh-Ag(0-100)	100	100	–	–	–	–	–

[a] Obtained from the values of irreversibly adsorbed hydrogen.

the metal precursor salts. Weighed amounts of Rh(NO$_3$)$_3$ and/or AgNO$_3$ (Alfa Aesar), calculated to give the desired Rh-Ag composition to the final product, were dissolved in distilled water at 25 °C, followed by addition of known amounts of the carrier. After impregnation, the water was slowly evaporated by heating at 70 °C and the residue was dried at 110 °C for 24 h. The resultant solid was then ground, sieved and finally calcined in air at 500 °C for 2 h. The total metal loading (Rh + Ag) of all samples was 1% by weight. A set of seven catalysts has been prepared, with variable silver content of 0, 3, 5, 7, 10, 15 and 100 wt%, based on total metal content. For simplicity, the bimetallic rhodium–silver catalysts will be denoted using the percentage weight of the metals in parentheses. For example, Rh-Ag(95-5) refers to the sample with a Rh-Ag composition of 95%Rh–5%Ag, by weight.

Adsorption isotherms of hydrogen were determined with the volumetric technique employing a modified Fisons Instruments (Sorptomatic 1900) apparatus. Measurements were performed at 25 °C, in the pressure range 0–75 Torr. Prior to each measurement, the catalyst sample (*ca.* 1.0 g) was pretreated by (a) dynamic vacuum at 250 °C for 1 h; (b) reduction with 1 bar of H$_2$ at 250 °C for 1 h, (c) evacuation for 30 min at 250 °C and (d) cooling down to room temperature under vacuum. When the isotherm was completed, the weakly adsorbed hydrogen was removed from the catalyst by evacuating the adsorption cell at room temperature for 10 min to a pressure of approximately 10^{-6} Torr. A second isotherm was then run to determine the reversible hydrogen uptake.

The total and reversible hydrogen uptakes at monolayer coverage were obtained for each catalyst by extrapolating the adsorption isotherms to zero pressure. The irreversible hydrogen uptake was determined as the difference between total and reversible hydrogen uptake, at monolayer coverage. Dispersion of metallic Rh, expressed in terms of H/Rh ratio, was obtained from the values of irreversibly adsorbed hydrogen, assuming that Ag does not adsorb hydrogen and that each Rh metal atom chemisorbs one hydrogen atom. Results obtained are summarized in table 1.

2.2. *Catalytic performance tests*

The catalytic performance of the 1%(Rh-Ag)/Al$_2$O$_3$ catalysts for the SCR of NO by propylene was studied in a continuous flow reactor in the temperature range 150–550 °C, using an apparatus that has been described elsewhere [14]. In a typical experiment, an amount of 60 mg of the catalyst sample was placed in a quartz microreactor and the temperature was raised to 550 °C under flowing He (100 cm^3/min, STP). The catalyst was maintained at that temperature for 1 h and was then cooled to 150 °C under He flow. The feed was then switched to the reaction mixture and conversion of reactants and selectivities towards products were measured at steady-state using a gas chromatograph (Shimadzu) and a NO$_x$ analyser (Teledyne). After completion of the run the reactor was heated to the next reaction temperature. The feed composition consisted of 0.1% NO, 0.35% (or 0.1%) C$_3$H$_6$ and 5% O$_2$ (balance He). The total volumetric flow in the feed was kept constant at 200 cm^3/min ($W/F = 0.018\,\mathrm{g\,s\,cm^{-3}}$). All gases used were obtained from Meisser–Griesheim and were of ultra high purity.

3. Results and discussion

3.1. *Chemisorption of hydrogen*

As observed in table 1, replacement of small amounts of Rh with Ag results in an increase of the H/Rh ratio, which goes through a maximum for the Rh-Ag(97-3) catalyst. Further addition of Ag results in a progressive decrease of the H/Rh ratio, which is stabilized at a value close to that of the monometallic sample. Similar results were obtained from Yuvaraj *et al.* [15] over Rh-Ag/Al$_2$O$_3$ and from Chou *et al.* [16] over Rh-Cu/Al$_2$O$_3$ catalysts, who also observed an "abnormal" increase of hydrogen uptake observed upon addition of small amounts of Ag ($X_{\mathrm{Ag}} < 0.09$) or Cu ($X_{\mathrm{Cu}} < 0.10$) on Rh (but not on Rh-Au samples [15]). This increase has been attributed to the formation of rhodium-rich phase alloys [15,16]. Formation of such alloyed phases has been also observed by Guerrero-Ruiz *et al.* [17] in bimetallic Rh-Cu catalysts with low Cu content ($X_{Cu} = 0.05$). The higher capability of the above catalysts to chemisorb hydrogen, compared with monometallic Rh samples, was attributed to exchange of electronic cloud between the IB metal and Rh, during formation of the alloy crystallites [15]. This is in accordance with the results of Peebles *et al.* [18] who found that the transfer of net electron density between Ag and Rh takes place at very low Ag coverages on Rh(100) surface.

3.2. Catalytic performance of bimetallic Rh-Ag catalysts

Results obtained on the performance of the monometallic Rh-Ag(100-0) catalyst for the SCR of NO by propylene, using a feed composition of 1000 ppm NO, 3500 ppm C_3H_6 and 5% O_2, are shown in figure 1(A). Catalytic performance is expressed in terms of steady-state conversions (X%) of NO and C_3H_6 and in terms of yields (Y%) of N_2, N_2O and NO_2, as functions of reaction temperature. It is observed that oxidation of propylene starts at 250–270 °C and increases sharply with increasing temperature. This is accompanied by conversion of NO to reduction products, N_2O and N_2, the formation of which goes through maxima at $T_{max} = 320\,°C$. Under these conditions, conversion of NO to reduction products (X_{NO}) reaches 56%. Increasing reaction temperature above T_{max}, where propylene is fully converted to CO_2, results in the gradual decrease of the yields of N_2O and N_2, while at temperatures above 350 °C oxidation of NO toward NO_2 starts taking place. The formation of NO_2 goes through a broad maximum at *ca.* 450 °C and then drops following thermodynamic equilibrium limitations (figure 1(A)).

The catalytic performance of the Rh-Ag(95-5) sample, obtained under the same conditions, is shown in figure 1(B). Comparison with the corresponding results obtained over the Rh-Ag(100-0) catalyst shows significant differences. In particular, oxidation of propylene starts at temperatures which are about 25 °C lower than those observed over the monometallic rhodium catalyst, and reaches completion at *ca.* 300 °C. The maximum conversion of NO to reduction products is significantly enhanced and reaches 78% at $T_{max} = 300\,°C$. At higher reaction temperatures, the yields of N_2 and N_2O are progressively suppressed and at temperatures above 350 °C oxidation of NO toward NO_2 prevails, in a manner which is qualitatively similar to that observed over the monometallic rhodium sample (compare with figure 1(A)).

Results presented in figures 1(A) and 1(B) clearly show that the catalytic activity of rhodium is significantly improved with the substitution of small amounts of rhodium with silver, and is accompanied by a substantial shift of the light-off temperature toward lower values. Interestingly, the yield of N_2 at the temperature of maximum NO conversion (T_{max}) increases by a factor

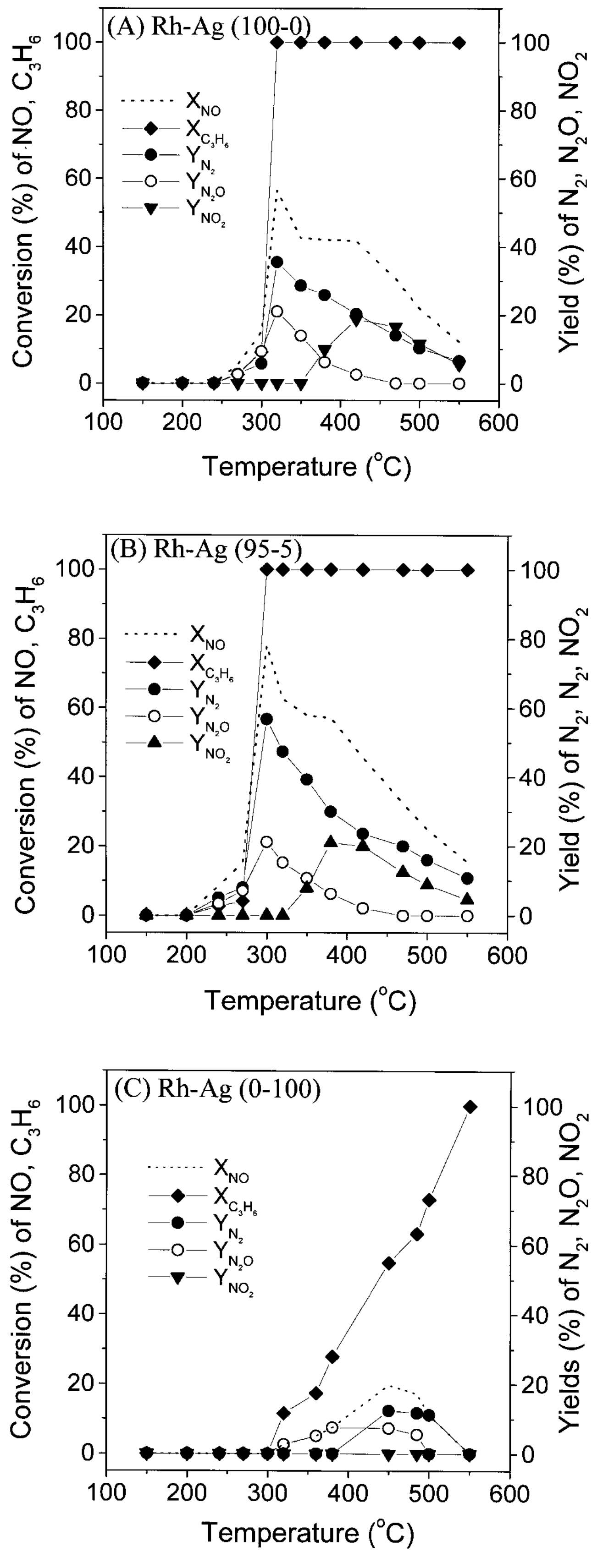

Figure 1. Conversions (%) of NO and C_3H_6 and yields (%) of N_2, N_2O and NO_2 as functions of reaction temperature over (A) Rh-Ag(100-0), (B) Rh-Ag(95-5) and Rh-Ag(0-100) catalysts. Feed composition: 1000 ppm NO, 3500 ppm C_3H_6, 5% O_2; $W/F = 0.018\,g\,s\,cm^{-3}$.

of 1.6 with the replacement of 5% of Rh by Ag, while that of N_2O remains almost unchanged. The beneficial effect of addition of Ag on the catalytic properties of Rh cannot be attributed to Ag itself, which is almost inactive for NO reduction in the temperature region of interest. This is clearly shown in figure 1(C), where the catalytic performance of monometallic Rh-Ag(0-100) catalyst is presented. It is observed that activation of propylene takes place above 300 °C and, in contrast to the Rh-Ag(100-0) and Rh-Ag(95-5) catalysts, its conversion increases slowly with increasing temperature and reaches completion at 550 °C. Conversion of NO to reduction products is relatively small and goes through a maximum of *ca.* 20% at $T_{max} = 450$ °C.

Similar catalytic performance tests have been performed over the whole range of the Rh-Ag catalysts. Results are summarized in figure 2(A), where the temperature at which the maximum conversion of NO to reduction products is observed (T_{max}), as well as the conversion of NO to reduction products (X_{NO}) and the selectivity toward nitrogen (S_N2) at T_{max} are plotted as a function of Ag content. It is observed that T_{max} decreases from *ca.* 320 °C to *ca.* 300 °C with increasing Ag content from 0 to 5 wt%, and remains at this level for catalysts containing up to 10 wt% Ag. Further increase of the Ag content to 15 wt% results in an increase of T_{max} to *ca.* 325 °C. The maximum conversion of NO to reduction products increases from 56% over monometallic Rh to 78% over Rh-Ag(95-5) and then decreases at higher Ag contents. Selectivity toward N_2 is also enhanced by the addition of Ag and increases from 63% over monometallic Rh to 71–75% over catalysts containing 3–10 wt% Ag. Further addition of Ag results in a decrease of S_N2 (figure 2(A)).

The catalytic performance of the 1%(Rh-Ag)/Al_2O_3 catalysts has been also examined using a feed composition consisting of 1000 ppm NO, 1000 ppm C_3H_6 and 5% O_2, *i.e.* with reduced reductant concentration by a factor of 3.5. Results are summarized in figure 2(B), where T_{max}, X_{NO} and S_N2 are plotted as functions of Ag content. The corresponding curves are qualitatively similar to those obtained using 3500 ppm of C_3H_6 in the feed (compare with figure 2(A)). In particular, T_{max} goes through a minimum over catalysts containing *ca.* 5 wt% Ag. The maximum conversion of NO is obtained again over the Rh-Ag(95-5) catalyst, assuming a value of *ca.* 30%, compared with 18% over the monometallic Rh-Ag(100-0) catalyst. Selectivity toward nitrogen is not significantly affected by the addition of Ag and takes values in the region of 53–57% (figure 2(B)).

Preliminary XPS spectra have shown that addition of small amounts of Ag on Al_2O_3-supported Rh catalysts results in stabilization of rhodium in its reduced state under reaction conditions, which may be responsible for the observed improvement of catalytic performance. This may be correlated to an electronic-type effect of silver on rhodium. When alloying between two metals of different electronegativity takes place, charge transfer or shift of electron clouds occurs from the higher electronegativity metal atoms towards those of lower electronegativity. In the present system, electronic near-neighbour interactions result in charge transfer from Rh (electronegativity of 2.2) to Ag (electronegativity of 1.9). Thus, the catalytically active rhodium phase becomes more electropositive. In turn, this implies that the rhodium phase becomes more resistant to oxidation, in accordance with the XPS results mentioned above which show that, in the presence of small amounts of Ag, rhodium is in a more reduced state under reaction conditions.

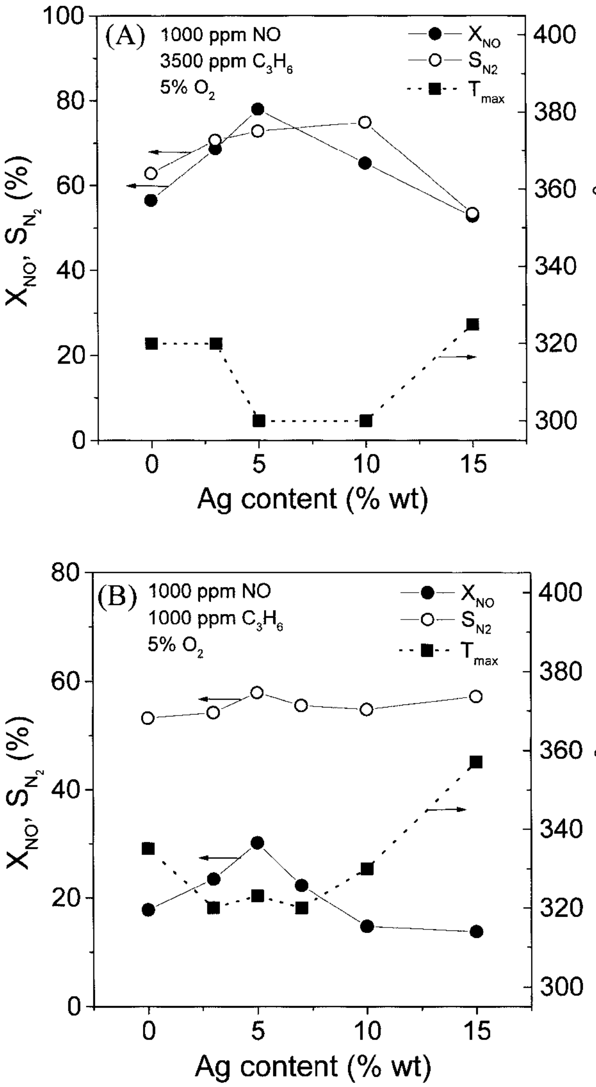

Figure 2. Effect of Ag content on the temperature of maximum NO conversion (T_{max}) and on conversion of NO (X_{NO}) and selectivity toward N_2 (S_N2) at T_{max}. Feed composition: (A) 1000 ppm NO, 3500 ppm C_3H_6, 5% O_2; (B) 1000 ppm NO, 1000 ppm C_3H_6, 5% O_2; $W/F = 0.018\ \mathrm{g\,s\,cm^{-3}}$.

It has been shown by many investigators [19–21] that under lean burn NO reduction conditions over noble metals, the catalytically active sites consist of reduced metal atoms. Thus, the enhanced activity of the Rh-Ag bimetallic clusters for NO reduction in the presence of oxygen can be attributed to higher concentration of reduced rhodium sites. At high silver contents, other factors come into play, such as significant surface enrichment with Ag and phase separation, which tend to reduce overall catalytic activity (figure 2).

Work is currently in progress to study in detail the effect of addition of Ag on the chemisorptive and catalytic performance of supported Rh catalysts, taking into consideration both electronic and geometric factors.

5. Conclusions

Substitution of small amounts of Rh with Ag results in an increase of H/Rh ratio, determined by hydrogen adsorption at room temperature, which, in agreement with the literature, is tentatively attributed to the formation of rhodium-rich phase alloys. The catalytic activity of Rh-Ag/Al_2O_3 catalysts for the SCR of NO by propylene in the presence of excess oxygen is significantly improved over samples with low Ag contents, compared with the monometallic Rh/Al_2O_3 sample. This behaviour is tentatively attributed to electronic type effects induced by Ag, which may stabilize Rh in its reduced state at reaction conditions.

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