PERFORMANCE OF SUPPORTED Ru-Cu BIMETALLIC CATALYSTS PREPARED FROM NITRATE PRECURSORS

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Bimetallic Ru-Cu catalysts supported on SiO_2, α-Al_2O_3, γ-Al_2O_3 have been prepared using precursors which do not contain chlorine and characterized by CO chemisorption and TPR. Catalytic activity has been tested in the propane hydrogenolysis. It has been observed that the degree of formation of bimetallic Ru-Cu aggregates depends on the support used. It is suggested that the degree of interaction between Ru and Cu is strongly influenced by the strength of the metal-support interaction.

1. Introduction

In recent yeards supported bimetallic catalysts have received growing attention because of the commercial success of these systems in controlling activity, selectivity and stability with an appropriate choice of the nature and composition of the components.

To obtain information on the nature of the interaction occurring in bimetallic aggregates, ruthenium-copper catalysts are of particular interest as model systems in that the two metals have been found to form bimetallic particles despite the fact that they are virtually immiscible in bulk [1,2].

Ru-Cu catalysts have been mainly investigated as unsupported or SiO_2-supported systems and quantitatively differing results are reported on the influence of Cu on H_2 chemisorption and on its effect on the catalytic properties of Ru [2-8]. These differences have been related to a different degree of formation of Ru-Cu bimetallic clusters which is influenced by the preparative conditions used. Damiani et al. [9] have recently reported that the relative amount of bimetallic Ru-Cu particles is enhanced by the use of $RuCl_3$ as precursor compound. They have suggested that the presence of chlorine favors the spreading of Cu on the Ru surface. In a recent investigation on the effect of the support on the catalytic activity of Ru-Cu we have reported that the rate of hydrogenolysis reactions is strongly dependent on the Ru/Cu ratio and on the support used [10]. However the use of $RuCl_3$ as precursor compound did not allow to exclude that the observed differences are related to a different amount of residual chlorine present on the catalyst as a result of different acid-base characteristics of the supports.

To clarify the role that residual chlorine can play on the formation of Ru-Cu bimetallic particles and to gain more information on the intrinsic role of the support, a study on Ru-Cu samples prepared using precursors which do not contain chlorine was undertaken. In this paper we report the results obtained on Ru-Cu supported on SiO_2, γ-Al_2O_3 and α-Al_2O_3 prepared using $Ru(NO)(NO_3)_3$ and $Cu(NO_3)_2$ as precursors.

2. Experimental

Ru-Cu samples were prepared by incipient wetness impregnation of the supports with aqueous solutions of $Ru(NO)(NO_3)_3$ and $Cu(NO_3)_2$ having an appropriate concentration of metals. The salt(s) concentration in the solution was adjusted to yield a total (Ru + Cu) metal content of 2 wt%. The supports used were: SiO_2 (Davison 951N, 650 $m^2\ g^{-1}$), γ-Al_2O_3 (Ketjen-grade A, 160 $m^2\ g^{-1}$) and α-Al_2O_3 (12 $m^2\ g^{-1}$) obtained by firing a sample of γ-Al_2O_3 at 1100 °C for 12 h. Formation of α-Al_2O_3 was verified by X-ray analysis. The 40–80 mesh fraction of all catalysts was always employed. Chemisorption of CO was measured in a conventional pulse system operating at room temperature. Negligible amounts of CO were found to chemisorb on the supports and on Cu. Catalytic activity was tested for propane hydrogenolysis. The reaction was carried out in a differential mode employing a tubular reactor at atmospheric pressure and using He as diluent. Before catalytic activity measurements, catalyst samples were reduced "in situ" at 400 °C in flowing H_2. Details on the experimental apparatus and on the procedure used to measure initial rates are reported elsewhere [10]. TPR (Temperature Programmed Reduction) experiments were carried out in a typical gas chromatographic apparatus at a heating rate of 5 deg/min using a mixture 5 vol % H_2 in Ar. Details on the TPR apparatus have been previously reported [11].

3. Results and discussion

The results of CO chemisorption on the Ru-Cu samples are reported in table 1. On SiO and γ-Al_2O_3 the CO/Ru ratio is close to unity on all but one sample, namely the RCS020N sample (having a Ru content of about 20 at%) on which a value of about 0.5 was instead found. On α-Al_2O_3 CO/Ru ratios of about 0.3–0.4

Table 1
CO uptakes over Ru-Cu supported samples

Code	Support	Ru (wt%)	Cu (wt%)	Ru/(Ru + Cu) [a] (%)	CO/Ru
RCS100N	SiO_2	2.0	-	100	0.96
RCS080N	SiO_2	1.7	0.3	80	0.82
RCS040N	SiO_2	1.0	1.0	40	0.91
RCS020N	SiO_2	0.6	1.4	20	0.55
RCA100N	γ-Al_2O_3	2.0	-	100	0.89
RCA080N	γ-Al_2O_3	1.7	0.3	80	1
RCA040N	γ-Al_2O_3	1.0	1.0	40	1
RCA020N	γ-Al_2O_3	0.6	1.4	20	1
RCAA100N	α-Al_2O_3	2.0	–	100	0.34
RCAA080N	α-Al_2O_3	1.7	0.3	80	0.26
RCAA060N	α-Al_2O_3	1.4	0.6	60	0.31
RCAA040N	α-Al_2O_3	1.0	1.0	40	0.36
RCAA020N	α-Al_2O_3	0.6	1.4	20	0.44

[a] Atomic ratio

have been instead measured. It is likely that these lower values are related to the much lower surface area of the α-Al_2O_3 with respect to the other two supports. Table 1 also shows that the presence of Cu does not modify significantly the fraction of Ru atoms present on the surface. Hydrogenolysis activity of the Ru-Cu samples has been calculated, in terms of the initial rate of propane consumed, by the expression:

$V = FX/W$

where F is the feed rate of propane (mol s^{-1}), X is the fraction of consumed propane and W the weight (g) of Ru contained in the catalyst charge.

The influence of temperature on the reaction rate was studied at partial pressures of H_2 of 30 kPa and of propane of 9 kPa. The plot of log V against $1/T$ for all samples investigated always gave a straight line. The initial rates were always measured at increasing and decreasing temperatures and showed that the variations with temperature are reversible.

Table 2
Rates of propane hydrogenolysis (V), turnover frequencies (N) and activation energies (E_a) over Ru-Cu/SiO_2 catalysts

Code	V (mol s^{-1} (g Ru)$^{-1}$)	N (s^{-1})	E_a (kJ mol^{-1})
RCS100N	$9.80 \cdot 10^{-2}$	10.3	167
RCS080N	$1.85 \cdot 10^{-2}$	2.3	154
RCS039N	$3.20 \cdot 10^{-4}$	0.04	97
RCS020N	$6.38 \cdot 10^{-5}$	0.01	69

Table 3
Rates of propane hydrogenolysis (*V*), turnover frequencies (*N*) and activation energies (E_a) over Ru-Cu/γ-Al_2O_3 catalysts

Code	*V* (mol s^{-1} (g Ru)$^{-1}$)	*N* (s^{-1})	E_a (kJ mol^{-1})
RCA100N	$5.77 \cdot 10^{-2}$	6.55	167
RCA080N	$6.20 \cdot 10^{-3}$	0.63	179
RCA040N	$1.06 \cdot 10^{-3}$	0.11	150
RCA020N	$2.11 \cdot 10^{-3}$	0.21	163

From the slopes of the straight lines the activation energies were calculated, and reported in tables 2–4 together with the rates of reaction extrapolated at 200 ° C. In tables 2–4 the activities of Ru-Cu catalysts have been also expressed as turnover frequencies (*N*) on the basis of the results of CO chemisorption reported in table 1. Turnover frequencies of the monometallic Ru samples on the different supports show differences of only 2 or 3 times. Usually, effects of this magnitude are not considered important, and their interpretation could be very difficult [12].

Addition of Cu leads to a significant decrease in the activity of the catalysts. The effect of the presence of Cu on the activity of Ru was found to depend strongly on the support used. On silica addition of 80 at% Cu (sample RCS020N) decreases the catalytic activity by about three orders of magnitude, whereas on Ru/γ-Al_2O_3 and on Ru/α-Al_2O_3 a similar amount of Cu decreases the activity of only 30 times.

It is also noted that on the two alumina supports bimetallic Ru-Cu samples show an activation energy similar to that of the monometallic Ru catalysts. On SiO_2 instead the activation energy decreases from 167 kJ/mol on the monometallic Ru sample (RCS100N) to 69 kJ/mol on the sample containing 80 at% of Cu (RCS020N).

In a recent paper on Ru-Cu supported on MgO, bimetallic catalysts (prepared by using the same salt precursors as those used in this work) behaved in a way

Table 4
Rates of propane hydrogenolysis (*V*), turnover frequencies (*N*) and activation energies (E_a) over Ru-Cu/α-Al_2O_3 catalysts

Code	*V* (mol s^{-1} (g Ru)$^{-1}$)	*N* (s^{-1})	E_a (kJ mol^{-1})
RCAA100N	$1.02 \cdot 10^{-2}$	3.03	121
RCAA080N	$1.92 \cdot 10^{-3}$	0.74	165
RCAA060N	$4.78 \cdot 10^{-4}$	0.15	135
RCAA040N	$6.88 \cdot 10^{-4}$	0.19	178
RCAA020N	$5.85 \cdot 10^{-4}$	0.13	158

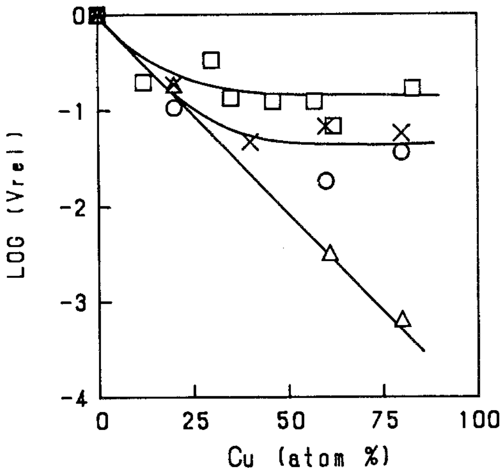

Fig. 1. Relative rates of propane hydrogenolysis (V_{rel}) over Ru-Cu catalysts as a function of Cu content. △, Ru-Cu/SiO_2; □, Ru-Cu/MgO; ×, Ru-Cu/α-Al_2O_3; ○, Ru-Cu/γ-Al_2O_3.

similar to that observed on the alumina supported samples; i.e. addition of Cu to Ru caused only a relatively small decrease of catalytic activity [13].

In order to better demonstrate the effect of Cu on the different supports we have reported in fig. 1 the relative rate of reaction as a function of the Cu content. For each support the relative rates have been calculated by dividing the values of V by the rate measured on the corresponding monometallic sample. The relative rates of Ru-Cu/MgO reported in fig. 1 have been calculated from ref. [13].

Since the first work of Sinfelt [14] on the Ru-Cu system, it has been suggested that the decrease in the catalytic activity observed by addition of inert Cu has to be attributed to an interaction between Ru and Cu which results in the formation of bimetallic Ru-Cu aggregates. This occurs in spite of the fact that the two metals are immiscible in the bulk state. A dilution of the active Ru surface atoms with inert Cu would mainly decrease catalytic reactions (such as hydrogenolysis) which occur on active sites made of a large number of adjacent surface atoms. It can be therefore suggested that the larger decrease of catalytic activity is correlated with a larger dilution of the Ru atoms or, in other words, with a larger formation of bimetallic Ru-Cu particles.

On the basis of these considerations, results of fig. 1 indicate that the degree of formation of bimetallic aggregates depends on the support used and that it can be ranked as $SiO_2 \gg Al_2O_3 > MgO$. A similar effect of the nature of the support on the formation of bimetallic Ru-Cu particles has been also reported on catalysts prepared from $RuCl_3$ [10]. This rules out a major role of the precursors on the observed phenomena.

Figure 2 shows the TPR spectra of the impregnated monometallic Ru and Cu precursors. Peak profiles show large differences depending on the support used. It

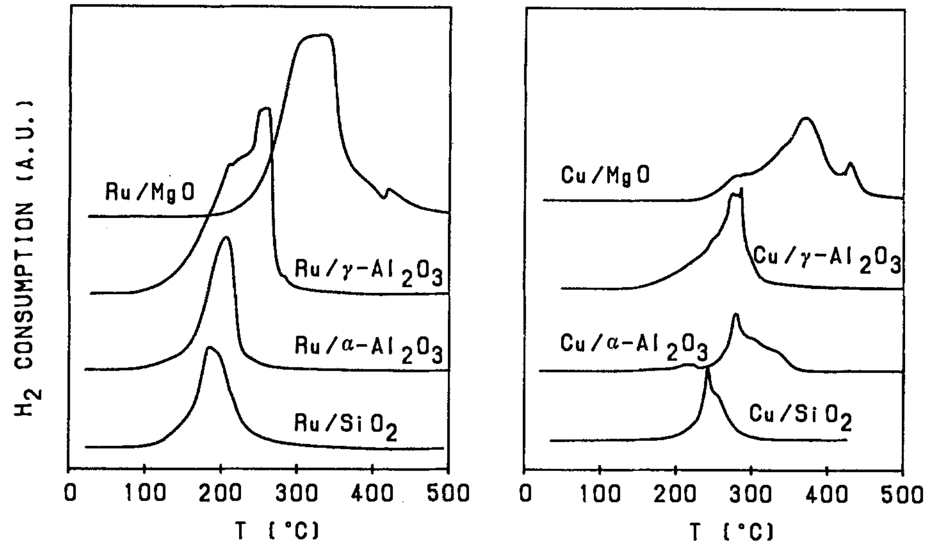

Fig. 2. TPR profiles of Ru and Cu supported samples. (Ru/MgO and Cu/MgO have been taken from ref. [13].)

is noted that moving from SiO_2 to Al_2O_3 to MgO the reduction temperature increases for both Ru and Cu precursors. This could be taken as an indication that regardless of the metal, the nature of the support plays an important role in determining the degree of interaction between metal and support, which in our case is in the order: MgO > Al_2O_3 > SiO_2. The same order of interaction has been previously reported for Ru samples prepared from $RuCl_3$ [15].

On the basis of the reported results a correlation seems to exist between the strength of the metal-support interaction and the degree of formation of bimetallic Ru-Cu particles. A higher interaction of the metals with the supports seems to lead to a lower degree of formation of bimetallic Ru-Cu aggregates. On SiO_2, on which TPR spectra show the lowest metal-support interaction (lowest reduction temperature), addition of Cu results in the largest decrease of catalytic activity. The opposite is observed on MgO on which the metal-support interaction is the strongest one.

4. Conclusions

Results reported in this paper confirm the influence of the support in determining the degree of interaction between Ru and Cu. The use of precursors which do not contain chlorine does not substantially modify the behaviour previously observed using $RuCl_3$ as precursor salt. It is suggested that the degree of interaction between Ru and Cu is strongly influenced by the strength of the metals-support interaction. The lower is the interaction with the support, the higher would be the formation of Ru-Cu bimetallic particles.

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