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SiO_2-Supported Ru–Cu Catalysts: A TPR Study

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Temperature-programmed reduction measurements of SiO_2-supported Ru–Cu catalysts prepared from metal nitrates indicate the presence of only bimetallic particles in catalysts in which hydrogen chemisorption and catalytic activity measurements previously suggested a low degree of contact between the metals. It is proposed that the large effect of Cu addition observed in Ru–Cu catalysts prepared from $RuCl_3$ (Sinfelt, J. H., *J. Catal.* **29**, 308, 1973) takes place because a greater proportion of Cu is well spread on the surface of the bimetallic particles favored by the presence of chlorine adsorbed on Ru. Oxidation at high temperature causes the segregation of the metals into Ru-rich and Cu-rich bimetallic particles separated onto the support, as suggested by temperature-programmed reaction of C deposited on the catalysts.

INTRODUCTION

Historically the interest in bimetallic catalysts has focused on group VIII–group Ib combinations miscible in the bulk. Whereas the difference in the electronic structure between metals from these groups was the main reason for choosing this type of combination, the belief that metal–metal interaction was more likely to occur in a miscible system probably also suggested the study of this particular type of group VIII–group Ib combination. More recently, however, it has been observed that the existence of metal–metal interaction is not limited to miscible systems (*1*). This finding has opened up a very productive area of research.

Among immiscible systems, the most studied one has been Ru–Cu (*2*). The reason for this interest was the observation that the addition of Cu drastically suppressed the specific activity for hydrogenolysis of SiO_2-supported Ru. In an extensive work of characterization of supported and unsupported Ru–Cu by different techniques, Sinfelt and co-workers built up a picture of Ru–Cu interaction which essentially involved chemisorption of Cu on the surface of the Ru particles (*1, 3–6*).

In a very recent work by Yide and Bond a large degree of Ru–Cu interaction on SiO_2 was also observed (*7*). The authors suggested that only bimetallic particles were present after the initial reduction at 623 K for catalysts prepared similarly to those prepared by Sinfelt. Monometallic particles were obtained only after oxidation at 623 K and reduction at 433 K.

Although a large Ru–Cu interaction on SiO_2 has been generally reported, it has been found that the extent of the interaction depends on preparation variables like the texture of the SiO_2 and the Ru precursor used in the impregnation (*8*). A combination of a relatively low-area, nonporous SiO_2 and $RuCl_3$ gave rise to a large Ru–Cu interaction (similar to the one observed in (*1*)) whereas a high area, microporous SiO_2 and $RuNO(NO_3)_3$ combination lead to a relatively poor Ru–Cu interaction as observed in (*9*). This low degree of interaction was thought to be the result of a larger fraction on Ru deposited by an ion exchange mechanism giving rise to a segregation of the metals as the solution entered the support (*8*).

In order to further investigate the interac-

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tion between the metals in the catalysts used in (*9*) we have conducted a TPR study. The results obtained are reported in this paper.

EXPERIMENTAL

Details of the catalysts preparation and characterization are given elsewhere (*9*).

TPR runs were carried out in an apparatus similar to that described by Robertson *et. al.* (*10*) to which some modifications were introduced. The reducing mixture first circulated through an empty 6-mm-o.d. Pyrex tube positioned in the oven (the reference), then it passed through a Molecular Sieve 3A cold trap and, after passing through the reference branch of a thermal conductivity detector (TCD), it went to a 6-mm-o.d. Pyrex tube containing the sample (the reactor). After leaving the reactor the reducing mixture was passed through a Molecular Sieve 3A cold trap and the measuring branch of the TCD. The TCD was a flow-through type, microvolume, hot-wire Gow Mac cell. Standard methods of gas purification were used. The reference and the reactor were held in an oven that could be heated at a linear rate of 8 K min^{-1} from 273 to 703 K.

Prior to TPR measurements, the sample (about 40 mg) was treated *in situ* as follows: under flowing air the temperature was raised at 8 K min^{-1} to the desired value and maintained at that level for an additional hour after which it was cooled to 273 K in flowing N_2.

The TPR experiments were performed with a mixture of 5% H_2 in Ar. The flow rate of the reducing gas was 20 cm^3 min^{-1}.

Compositional analysis were done analyzing the effluent from the catalyst bed with a UTI Model 100 C mass spectrometer. A variable leak valve was used to introduce a constant leak of gas leaving the catalyst into the vacuum chamber housing the mass spectrometer probe. During an experiment the leak valve was adjusted to maintain a constant pressure of 2.5×10^{-6} Torr within the vacuum chamber. An ultimate pressure of 2×10^{-8} Torr could be achieved with the leak valve closed.

RESULTS

Figure 1 shows the results of TPR experiments after oxidation of the samples in air at 373 K for 1 h. The labeling of the catalysts gives the atomic percentage of Ru in the metal phase, i.e., the composition of 90-Ru-Cu is 90% Ru and 10% Cu.

Two peaks can be observed in all the TPR spectra with the exception of that corresponding to the group Ib metal which shows a single peak. With increasing Cu content, changes in the area and/or position of the peaks can be observed. Both low- and high-temperature peaks show a displacement towards higher temperatures. This displacement is small for the low-temperature peak, whereas it is significant for the high-temperature one. The area of the low-temperature peak increases with Cu content. The ill-defined shape of the high-temperature peak precludes any conclusion with respect to its area. A TPR after a second oxidation at 373 K showed the disappearance of the high-temperature peak. Only the first peak of each TPR remained, although at a lower temperature.

The low-temperature peak is assigned to the reduction of RuO_2 in the 100-Ru-Cu sample (*11*) and to a simultaneous reduction of Ru and Cu oxides in the bimetallics (this will be discussed later). The peak ob-

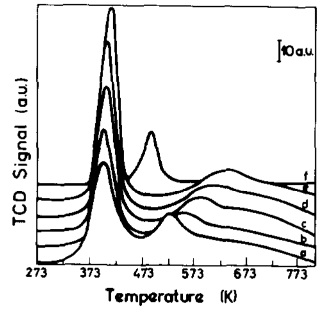

FIG. 1. TPR profiles of samples oxidized at 373 K. (a) 100-Ru-Cu, (b) 90-Ru-Cu, (c) 80-Ru-Cu, (d) 70-Ru-Cu, (e) 60-Ru-Cu, (f) 0-Ru-Cu.

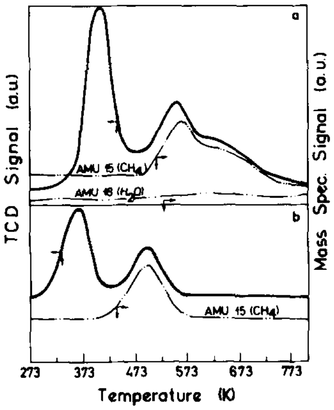

FIG. 2. TPR with simultaneous mass spectrometry analysis of a 200-mg 90-Ru-Cu sample. (a) After oxidation at 373 K, (b) after (a) plus a 2-h exposure to CO at 373 K.

served in the 0-Ru-Cu sample is due to the reduction of CuO (*12*).

The high-temperature peak was associated with the formation of CH_4 from C-containing species present on the surface of the Ru-containing catalysts, not removed by the treatment in air at 373 K. In order to verify this, we connected a mass spectrometer on line to analyze the effluent from the catalyst bed. A 200-mg 90-Ru-Cu sample was then treated in air at 373 K and a TPR with a simultaneous compositional analysis of the effluent was carried out. The results are shown in Fig. 2. Methane is formed at 570 K and, as expected, no H_2O is detected in the whole temperature range.

Having verified this, we now turn our attention to the notable shift of the CH_4 peak toward higher temperatures with the increase in Cu content, observed in Fig. 1. This effect is due to the decrease of the active surface by the inclusion of Cu atoms in it. A higher temperature is then required to carry out the reaction.

In order to see whether the increase in the difference between the temperature of the maxima with Cu content could provide us with a rough method to follow changes in surface composition, we performed the following: first, we checked whether a CO treatment could leave C on the surface to detect CH_4 formation in a subsequent TPR. Following the TPR measurement on the 200-mg 90-Ru-Cu sample the reduced catalyst was exposed to flowing CO at 373 K for 2 h after which it was flushed with N_2 at the same temperature and cooled to 273 K in N_2. Analysis of the effluent during the treatment showed the appearance of a CO_2 peak suggesting the ocurrence of CO disproportionation. The subsequent TPR showed two peaks as the TPR obtained after the oxidation treatment (see Fig. 2). In this case both peaks were located at lower temperatures. The simultaneous analysis of the composition of the gaseous stream indicated that the first peak was due to the reduction of oxidized Ru and the high-temperature peak is due to CH_4 formation. The exposure to CO leaves C on the metal surface via CO disproportionation. The Ru is partially oxidized by the oxygen product of the decomposition step.

Second, we checked whether the difference between the reduction peak and the CH_4 formation peak was maintained after the CO treatment. Forty-milligram samples of 100-Ru-Cu and 60-Ru-Cu were exposed to CO at 373 K for 15 min following a first TPR interrupted immediately after the second peak was resolved. The TPR results after the CO treatment are shown in Fig. 3. As observed in the 200-mg 90-Ru-Cu sample, each TPR profile show two peaks located at lower temperatures. For the pur-

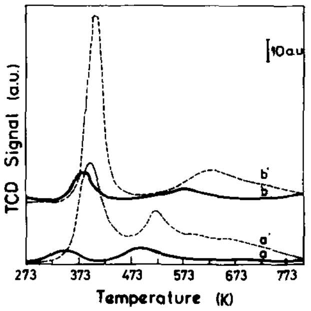

FIG. 3. TPR profiles after CO decomposition. (a) 100-Ru-Cu, (b) 60-Ru-Cu. For comparison TPR profiles after the first oxidation at 373 K on fresh samples are also included. (a') 100-Ru-Cu, (b') 60-Ru-Cu.

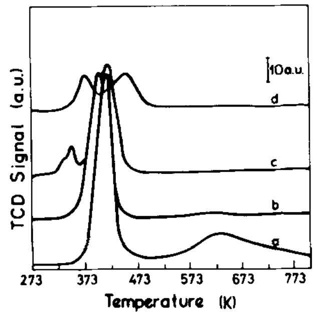

FIG. 4. TPR profiles of 60-Ru-Cu after successive oxidation treatments. Oxidized at (a) 373 K, (b) 373 K, (c) 623 K, (d) 773 K.

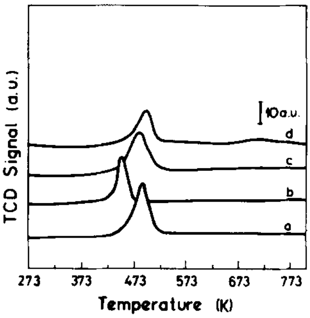

FIG. 6. TPR profiles of 0-Ru-Cu after successive oxidation treatments. Oxidized at (a) 373 K, (b) 373 K, (c) 623 K, (d) 773 K.

pose of comparison, the results obtained after the first oxidation treatment at 373 K on fresh samples are also included. It can be seen that the difference in temperatures between the maxima of the peaks are similar regardless of the treatment (approximately 130 K for the 100-Ru-Cu, approximately 200 K for 60-Ru-Cu).

The increase in the difference between the temperatures of the maxima with Cu content provides us, then, with a rough method to follow changes in the surface composition. This will be used in the study of the stability of a 60-Ru-Cu catalyst upon exposure to air at different temperatures. In this type of study, changes in particle size as well as changes in particle composition may occur.

The TPR spectra obtained in that study are shown in Fig. 4. Figures 5 and 6 show the TPR results for 100-Ru-Cu and 0-Ru-Cu catalysts subjected to the same oxidation treatments. The results of the application of the method to investigate possible changes in the surface composition of a 60-Ru-Cu sample after oxidation at 773 K are shown in Fig. 7.

DISCUSSION

Before discussing the behavior of the bimetallic catalysts when exposed to air at different temperatures we will focus our attention to the behavior of the monometallic ones. It can be observed in Fig. 6 that the TPR after the second oxidation at 373 K shows a shift of the CuO reduction peak to lower temperatures. As mentioned before, the same is observed for the Ru-containing samples (see Figs. 4 and 5 for 60-Ru-Cu and 100-Ru-Cu, respectively). These phenom-

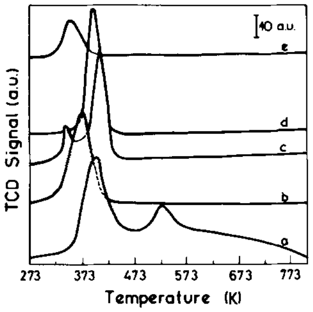

FIG. 5. TPR profiles of 100-Ru-Cu after successive oxidation treatments. Oxidized at (a) 373 K, (b) 373 K, (c) 623 K, (d) 773 K, (e) 623 K.

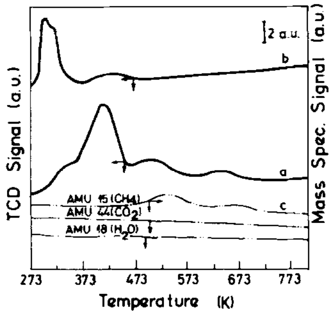

FIG. 7. TPR profiles after CO decomposition. (a) 60-Ru-Cu following TPR d in Fig. 4, (b) 100-Ru-Cu following TPR d in Fig. 5. Curve c is mass spectrometry analysis of CH$_4$ content vs temperature for a TPR like (a).

ena could indicate that the particles have sintered and that an oxide film formed by the second oxidation at 373 K prevents complete oxidation. A quantitative analysis show in all cases that, although small, there is a decrease in the area of the reduction peak after the second oxidation treatment. The location of the reduction peaks at lower temperatures compared to the result after the first oxidation treatment could be due to the following: (i) the unoxidized metal provides nucleation centers lowering then the reduction temperature and/or (ii) in the case of Ru-containing catalysts the unoxidized metal catalyzes the reduction of the oxidized part providing atomic hydrogen for an easy reduction at lower temperatures.

The Cu particles are again completely oxidized to CuO after oxidation at 623 K (see TPR c in Fig. 6). The decrease in the area of the peak corresponding to CuO reduction and the simultaneous appearance of a peak in the region 673–723 K after oxidation at 773 K can be the result of the stepwise reduction to metallic Cu of isolated Cu(II) ions as proposed in (*12*).

With regard to 100-Ru-Cu catalyst, the presence of two peaks in the TPR spectrum following oxidation at 623 K (see Fig. 5) suggests the existence of a bimodal distribution of particle sizes. The reduction of a relatively small number of large particles with a metallic core gives rise to the small peak at lower temperature. The larger peak is the result of the reduction of the completely oxidized smaller particles. The single peak observed after oxidation at 773 K suggests the return to a unimodal particle size distribution. This is consistent with the presence of a single peak in the TPR following the subsequent oxidation at 623 K. The increase in size of the TPR peak after oxidation at 773 K and its shift toward higher temperatures indicate that this treatment results in the complete oxidation of the Ru particles.

Having discussed the results corresponding to the monometallic catalysts we now turn our attention to those of the bimetallic catalyst. It can be observed in Fig. 4 that regardless of the treatment there is no peak in the range corresponding to the reduction of CuO. This observation, together with the presence of a single TPR peak after oxidation at 373 K and the similarity between the 100-Ru-Cu and 60-Ru-Cu TPR spectra after oxidation at 623 K, strongly suggest that the two oxides are reduced simultaneously.

The present of two peaks in the TPR of 60-Ru-Cu after oxidation at 623 and 773 K might indicate the existence of a bimodal distribution of particle sizes as already mentioned for 100-Ru-Cu after oxidation at 623 K. However, since the TPR of 100-Ru-Cu after oxidation at 773 K shows a single peak and since changes in particle composition as well as changes in particle size may occur in bimetallic catalysts exposed to air at high temperature, another phenomenon i.e., metal segregation may also explain the TPR of 60-Ru-Cu following the same treatment. In order to test this, we probed the surface of both catalysts after the TPR following the oxidation at 773 K. The method used involved the temperature programmed reaction of C deposited on the metal particles.

To be able to do a compositional analysis of the gaseous stream a 300-mg 60-Ru-Cu sample was subjected to the same sequence of oxidation–reduction treatments as the 40-mg 60-Ru-Cu sample. The TPR profiles were qualitatively identical in both cases. The mass-spectrometry analysis shown in Fig. 7 correspond then, to the 300-mg 60-Ru-Cu sample.

The results of these tests, show the presence of four peaks, α, α', β, and β'. The two peaks at lower temperatures are interpreted as a result of the reduction of a Ru-rich phase (α) and a Cu-rich one (α'). Those at higher temperatures are attributed to CH_4 formation from C deposited on the Ru-rich (β) and on the Cu-rich (β') phases, respectively. These assignments are based on the compositional mass analysis showed in Fig. 7.

Since the difference between the temperature of the maximum of any peak attributed to the reduction of a metallic phase and the temperature of the maximum of any of the peaks assigned to CH_4 formation is different from the difference between the temperatures of the maxima of the remaining peaks, we conclude that the metallic phases have different compositions. The assignment of the α peak to the reduction of a Ru-rich phase and not to a pure Ru phase is based on the observation that it is close to the location of the peak corresponding to the reduction of pure Ru particles but at a higher temperature (see Fig. 7). Another suggestion that Cu atoms are present comes from the observation that the difference between the temperature of the maximum of the peak assigned to the reduction of the Ru-rich phase and the temperature of the maximum of any of the CH_4 peaks is greater than the difference observed in the 100-Ru-Cu catalyst.

The assignment of the α' peak to the reduction of a Cu-rich phase is consistent with the observation that it is the peak located closer to the region where Cu is reduced (see Fig. 6) but at a lower temperature. The Ru atoms present in this phase would catalyze the reduction of Cu. These Ru atoms would also allow CO decomposition on the Cu-rich phase but to a lesser extent than that on a Ru-rich one.

The assignments of the β and β' peaks to CH_4 formation on the Ru-rich and Cu-rich phases, respectively, are based on the facts that the larger the Cu content the smaller the amount of CH_4 formed (due to less C deposition) and the higher the temperature necessary to carry out the reaction. In conclusion, the temperature-programmed reaction experiment confirms the existence of two metallic phases of different composition after oxidation at 773 K and subsequent reduction.

The separation of Ru and Cu after oxidation of the bimetallic catalysts at 623 K has been previously proposed by Bond and Yide (*7*). Based on TPR and catalytic activity for butane hydrogenolysis measurements the authors concluded that the oxidation disrupts the clusters giving separate RuO_x and CuO_x phases which were simultaneously reduced due to spillover induced rapid reduction of CuO_x. Our results further suggest that in order to have a simultaneous reduction of both oxides, the two phases must be still in contact so the atomic hydrogen formed on reduced Ru directly spills over onto the adjacent CuO_x phase. If hydrogen migration over the support were significantly fast to reduce CuO_x indistinguishably from the RuO_x reduction we should always see a single reduction peak. The presence of two peaks after oxidation at 623 and 773 K indicates that oxidized particles of different sizes and/or different compositions exist separatedly on the support, and that hydrogen migration is not fast. The onset of the separation of the phases on the support occurs in our catalyst at a lower temperature than in Bond and Yide's catalysts.

One of the main conclusions which can be reached from the study, i.e., that Cu and Ru are completely in contact in these catalysts after the initial reduction, disagrees with the model previously proposed to explain the poor coverage of Ru by Cu evidenced by chemisorption and catalytic activity for hydrogenolysis measurements (*9*). Based on the similarity in catalytic activity before and after a H_2 treatment at 723 K for 24 h the authors discarded the possibility of having the two metals in contact and favored a model in which the two metals were envisioned as mainly present as isolated crystallites with only a small amount of Cu deposited on the surface of the Ru particles (*9*). The reasoning was that if the two metals had been in contact, a prolonged exposure to H_2 at high temperature would have caused an increase in the surface coverage of the Ru particles by Cu as observed in unsupported Ru–Cu catalysts (*3*). It is interesting to note that a similar experiment, i.e., H_2 treatment at 623 K for 16 h, did result in an exceptional decrease in catalytic activity for hydrogenolysis in catalysts believed to be composed by separate Ru and Cu particles (*7*).

As noted previously (*8*), the common feature in all the studies in which Cu had a profound effect on the catalytic activity for hydrogenolysis, is that $RuCl_3$ was used in the preparation of the catalysts. If the metals are in contact even when $RuNO(NO_3)_3$ is used in the preparation, as suggested in the present study, the difference in the effect of Cu must reside on the spreading of this metal on the Ru surface.

In our opinion, then, all of these results can be explained if one postulates that the presence of Cl on the Ru surface (known to be very difficult to remove (*13*)) favors the spreading of Cu atoms on top of it.

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