

## **TPR INVESTIGATION OF BIMETALLIC Ru-Cu SAMPLES SUPPORTED ON SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> AND MgO**

*S. Galvagno\**, *C. Crisafulli\*\**, *R. Maggiore\*\**, *A. Giannetto\*\**  
and *J. Schwank*<sup>+</sup>

\*ISTITUTO CNR-TAE, VIA S. LUCIA 39 - PISTUNINA -  
MESSINA, ITALY

\*\*DIPARTIMENTO DI SCIENZE CHIMICHE - LABORATORIO DI PETROLCHIMICA,  
UNIVERSITÀ DI CATANIA, V. LE A. DORIA 6 -  
CATANIA, ITALY

<sup>+</sup>CHEMICAL ENGINEERING DEPARTMENT, UNIVERSITY OF MICHIGAN,  
ANN ARBOR, USA

(Received March 20, 1986)

Bimetallic Ru-Cu samples supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO were studied by the temperature-programmed reduction (TPR) technique. Experiments were carried out both on unreduced impregnated salts and after oxidation of already reduced samples.

The TPR profiles reveal a simultaneous reduction of ruthenium and copper precursors, even though the Ru and Cu in the monometallic catalysts exhibit reduction peaks which differ by up to 150 °C. It is suggested that the two metal salts interact during the stages of preparation and drying, and after reduction form bimetallic aggregates which are not stable and tend to separate.

The stability of the bimetallic particles was found to be strongly dependent on the support used, being higher on SiO<sub>2</sub> than on Al<sub>2</sub>O<sub>3</sub> and MgO.

It is suggested that the chemical nature of the support determines the different degree of interaction and/or agglomeration of the bimetallic particles.

Recent studies on Ru-Au supported on inorganic supports (MgO and SiO<sub>2</sub>), have shown that the chemico-physical properties and catalytic behaviour of this bimetallic system are strongly dependent on the oxide used to disperse the metals [1-7]. It has been reported that in the dispersed state Ru and Au, which are almost immiscible in the bulk, form bimetallic aggregates the composition of which depends on the support used. In the magnesia-supported samples a Ru surface enrichment was found, in contrast to the general tendency of the group Ib metal to cover the group VIII metal, while on silica the surface Ru/Au ratio was near to that of the bulk [1, 2]. It has been suggested that the surface composition is related to the way in which the metal particles form and grow.

In order to obtain more information on the influence of the support on the chemical properties of bimetallic systems, we have extended our investigations to a

similar system, Ru–Cu. For Ru–Cu/SiO<sub>2</sub>, it has been reported that the two metals interact in the form of bimetallic clusters, the surface of which is enriched in Cu atoms [8–10]. In contrast to the extensive work done on Ru–Cu supported on SiO<sub>2</sub>, the literature data on Ru–Cu disperse on other supports are rather scanty. It was therefore decided to investigate a series of Ru–Cu samples supported on Al<sub>2</sub>O<sub>3</sub>, MgO and SiO<sub>2</sub>.

In this paper we report the results of TPR experiments carried out to acquire information on: a) the chemical properties of the bimetallic system during the catalyst reduction, and b) its stability to thermal treatment.

A detailed study on the behaviour of the monometallic Ru and Cu samples supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO was reported recently [11].

## Experimental

Commercial hydrated ruthenium trichloride (Rudi Pont RuCl<sub>3</sub> · H<sub>2</sub>O, Reagent grade) and Cu(NO<sub>3</sub>)<sub>2</sub> (Baker Analyzed reagent) were used as precursor compounds.

The support materials were: MgO (Carlo Erba RPE–ACS) with a surface area of 15 m<sup>2</sup>/g; SiO<sub>2</sub> (Davison 951 N—650 m<sup>2</sup>/g); and Al<sub>2</sub>O<sub>3</sub> (Ketjen grade A—160 m<sup>2</sup>/g).

Catalysts were prepared by impregnating the support with a freshly prepared aqueous solution of the corresponding salt(s). The salt(s) concentration in the solution was such as to yield a total (Ru + Cu) metal content of about 2–4 wt% in the catalysts. The impregnated solids were dried for 4 h at 110°. The content of Ru and Cu, measured by atomic absorption spectroscopy, is reported in Table 1. The sample code used has the following meaning: the first two letters indicate the metals (*R* = ruthenium, *C* = copper), and the third letter the support used (*S* = silica, *A* = alumina, *M* = magnesium oxide), while the three digits indicate the atomic percentage of ruthenium in the metallic phase; e.g. RCSO34 indicates a bimetallic Ru–Cu sample supported on silica having a Ru content [Ru/(Ru + Cu)] equal to 34%.

The TPR experiments were carried out in a typical gas-chromatographic apparatus, at a heating rate of 5 deg/min. The heating rate of the oven was controlled by a microcomputer, which was also used to store the signals from the thermal conductivity detector for the quantitative determination of the hydrogen consumed during the TPR. CuO and CuO/SiO<sub>2</sub> (after calcination at 700° for 1 h) were used as reference samples for quantitative analysis. The gas used in TPR was a mixture of 5 vol% H<sub>2</sub> in Ar, and the oxidizing gas was air. Before the reducing mixture (20 cc/min) was delivered to the TPR apparatus, the gas was purified by

passage through an oxygen adsorbent (Alltech Ass.) and a molecular sieve trap. The measurement procedure consisted of a first TPR on the fresh catalyst sample from 35 to 500° (TPR-), cooling to 300° in a H<sub>2</sub>/Ar mixture, oxidation of the sample in air (from 300 to 500° at 5 deg/min and for 30 min at 500°). After cooling to room temperature, a second TPR (TPR-2) was performed. TPR-3, TPR-4, etc. were measured by using a similar procedure.

## Results and discussion

Figure 1 shows the TPR-1 profiles (obtained in the range 35–500°) of the Ru–Cu/SiO<sub>2</sub> samples containing 8% and 34% Ru (RCS008 and RCS034, respectively). For comparison, the TPR-1 of the monometallic Ru/SiO<sub>2</sub> (RCS100) and Cu/SiO<sub>2</sub> (RCS000) taken from ref. [11] are also reported. TPR-1 (carried out on the unreduced samples) displays a different reduction profile depending on the amount of Ru present. For sample RCS034, a broad reduction peak is noted, with a maximum at a temperature slightly higher than that found in the TPR-1 spectrum

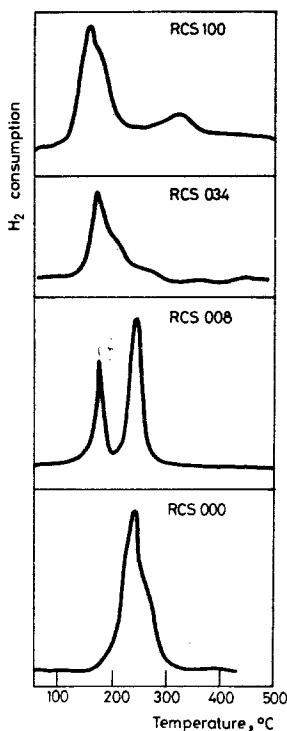


Fig. 1 TPR-1 profiles of Ru–Cu samples supported on SiO<sub>2</sub>,

of the monometallic RCS100. No maximum is observed at the temperature where  $\text{Cu/SiO}_2$  is reduced; only a weak shoulder is detected in this range. A quite different profile is obtained for the RCS008 sample. In particular, the presence of two sharp peaks is noted, the first of which has a maximum at a temperature close to that observed for RCS034, while the second maximum is close to that found for  $\text{Cu/SiO}_2$  (RCS000).

For RCS034 (containing 34 atom% of Ru, see Table 1), the quantitative analysis of  $\text{H}_2$  consumed shows that the observed peak cannot be attributed only to the reduction of Ru. In fact, if the peak is assigned to the reduction of the ruthenium salt, a H/Ru ratio of 6.8 is found. This ratio, well above the value of  $\text{H/Ru} = 4.6$  measured for the monometallic  $\text{Ru/SiO}_2$  sample [11], indicates that for RCS034 the copper salt is reduced together with the ruthenium salt. The amount of  $\text{H}_2$  consumed during the TPR-1 of RCS008 shows that in this case too the peak at lower temperature is not due only to the reduction of ruthenium. In fact, values of  $\text{H/Ru} = 12.4$  and  $\text{H/Cu} = 2.5$  are obtained if the first peak is assigned to the reduction of ruthenium and the second to that of copper. The higher H/Ru and the lower H/Cu ratios found for RCS008 with respect to the monometallic  $\text{Ru/SiO}_2$  ( $\text{H/Ru} = 4.6$ ) and  $\text{Cu/SiO}_2$  ( $\text{H/Cu} = 3.1$ ) samples [11] confirm that a fraction of the Cu is reduced at lower temperature, together with the ruthenium salt. For this sample, the reduction peak at higher temperature is likely to be related to isolated copper which has not interacted with Ru due to the very low concentration of the

**Table 1** Chemical analysis of Ru-Cu supported samples

Sample, code	Support	Ru, w%	Cu, w%	Ru/(Ru + Cu) * 100
RCS100	$\text{SiO}_2$	2.10	—	100
RCS034	$\text{SiO}_2$	1.20	1.45	34
RCS008	$\text{SiO}_2$	0.30	2.10	8
RCS000	$\text{SiO}_2$	—	1.90	0
RCA100	$\text{Al}_2\text{O}_3$	2.20	—	100
RCA074	$\text{Al}_2\text{O}_3$	1.90	0.41	74
RCA041	$\text{Al}_2\text{O}_3$	1.19	1.08	41
RCA028	$\text{Al}_2\text{O}_3$	1.02	1.62	28
RCA009	$\text{Al}_2\text{O}_3$	0.36	2.27	9
RCA000	$\text{Al}_2\text{O}_3$	—	2.51	0
RCM100	MgO	4.50	—	100
RCM073	MgO	3.40	0.78	73
RCM048	MgO	2.70	1.85	48
RCM031	MgO	2.20	3.05	31
RCM013	MgO	0.93	3.80	13
RCM000	MgO	—	4.20	0

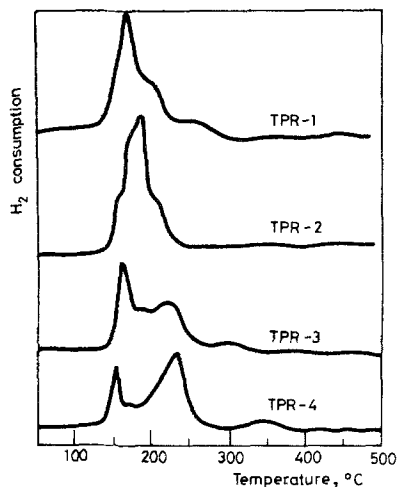


Fig. 2 Influence of TPR cycles on the reduction profiles of RCS034 sample

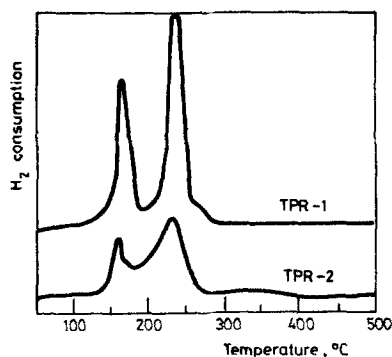
latter. This has been confirmed by a recent characterization of these Ru–Cu/SiO<sub>2</sub> samples, carried out by means of analytical electron spectroscopy. The EDS (Energy Dispersive X-ray spectroscopy) spectra in fact show that in RCS008 about 30% of the Cu exists as monometallic entities [12].

A comparison of our results with the previously published data of Bond et al. [13] on the TPR of Ru–Cu/SiO<sub>2</sub> reveals different reduction profiles. In the TPR spectra reported by Bond, the presence of a reduction peak due to isolated copper ions is in fact noted in samples with a Cu content lower than that present in our RCS034 sample. No apparent differences in the experimental procedure could explain these different results. It is possible that subtle variations in the preparative conditions and/or the lower surface area SiO<sub>2</sub> used by Bond lead to a different relative distribution of the two metal salts on the catalyst surface. It is confirmed, however, that the presence of ruthenium drastically reduces the temperature of reduction of Cu(NO<sub>3</sub>)<sub>2</sub> on SiO<sub>2</sub>. A decrease in the reduction temperature of CuO following the addition of Ru has been also reported by Gentry et al. [14].

Figure 2 shows the reduction profiles of RCS034 subjected to successive reduction cycles (TPR–2, TPR–3, TPR–4). It is noted that, as a consequence of the TPR cycles, there is a tendency for Ru and Cu to give separate reduction peaks in positions close to those observed for the reduction of RuOx/SiO<sub>2</sub> and CuOx/SiO<sub>2</sub> [11]. This can be taken as evidence of a progressive formation of separate Ru and Cu crystallites. The formation of separate Ru and Cu entities after the TPR cycles was also observed for the RCS008 sample through quantitative analysis of the hydrogen consumed. Table 2 shows the H/Ru and H/Cu ratios measured for Ru/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>, and those for the RCS008 sample calculated from Fig. 3 by assigning the

**Table 2** Hydrogen atoms consumed per ruthenium (H/Ru) and copper (H/Cu) atom in the TPR experiments for supported SiO<sub>2</sub> samples

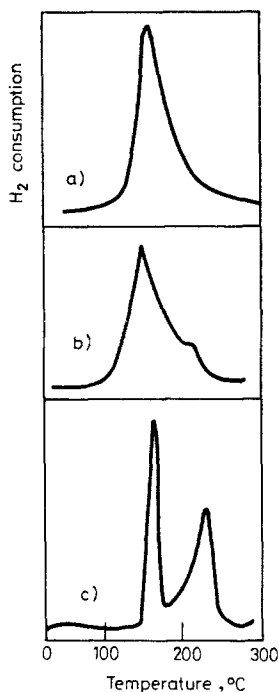
	H/Ru		H/Cu	
	TPR-1	TPR-2	TPR-1	TPR-2
RCS100	4.64	3.72	—	—
RCS008	12.41	5.21	2.45	1.73
RCS000	—	—	3.14	1.81

**Fig. 3** Influence of TPR cycles on the reduction profiles of RCS008 sample

first peak to the reduction of Ru and the second to the reduction of Cu. It may be seen that during TPR-2 the H/Ru and H/Cu ratios tend to approach the values found for the monometallics, confirming the formation of separate particles.

Separate reduction peaks are more readily observed if the bimetallic sample is left for a longer time (90 min) under H<sub>2</sub> at 500° before reoxidation. It is suggested that during the first TPR the reduction of the precursors leads to bimetallic aggregates, in agreement with previous observations based on catalytic activity measurements and chemico-physical characterizations carried out on similar samples [8–10, 13]. These aggregates, however, are not stable, due to the immiscibility of the metals, and have a tendency to form separate Ru and Cu particles.

For RCS034, a single TPR peak (more or less broad) was obtained when the sample was reduced, following the TPR procedure, up to 280° (at which temperature both ruthenium and copper are reduced) and then oxidized for 30 min at 280° before the temperature was raised up to 500° in air (Fig. 4B). Subsequent TPR cycles carried out using the above procedure did not lead to separate reduction peaks, it seems that ruthenium and copper tend to form separate particles only when they are kept at high temperature in the metallic state. If they are transformed to the corresponding oxides at low temperature, this tendency is slowed down. This latter hypothesis has been verified by the TPR results reported in Fig. 4C, where the



**Fig. 4** Influence of pretreatments on TPR profiles of RCS034 sample. a) TPR-1 of unreduced sample. b) After reduction up to 280 °C and oxidation in air from 280 to 500 °C. c) After reduction up to 280 °C and heating under nitrogen from 280 °C to 500°C before oxidation in air at 500 °C

TPR profile of the RCS034 sample is shown after it has been reduced up to 280°, flashed with nitrogen, heated under nitrogen up to 500°, and kept at this temperature for 90 min before reoxidation in air. After this treatment, Ru and Cu are reduced separately and give a TPR profile similar to that obtained when the bimetallic sample is heated at 500° under hydrogen for the same time. This confirms that the “demixing” of Ru and Cu occurs only if the elements are kept at high temperature in the metallic state. A similar phenomenon does not occur if Ru and Cu are first transformed to oxides. It should also be noted that, once separate particles were formed, it was not possible to reobtain a single reduction peak.

Figure 5 shows the TPR profiles of the Ru-Cu/Al<sub>2</sub>O<sub>3</sub> samples and those of the monometallic Ru/Al<sub>2</sub>O<sub>3</sub> (RCA100) and Cu/Al<sub>2</sub>O<sub>3</sub> (RCA000) samples taken from Ref. [11]. Sample RCA074 shows a TPR-1 with a broad reduction peak in the range 100–250° and a weaker signal at about 450°. This latter peak has also been observed for the monometallic Ru/Al<sub>2</sub>O<sub>3</sub> sample and attributed to Ru species interacting more strongly with the support [11]. The first peak is found at a temperature about 50° higher than that observed for the monometallic Ru/Al<sub>2</sub>O<sub>3</sub> sample. No peaks are found in the range where Cu/Al<sub>2</sub>O<sub>3</sub> is reduced.

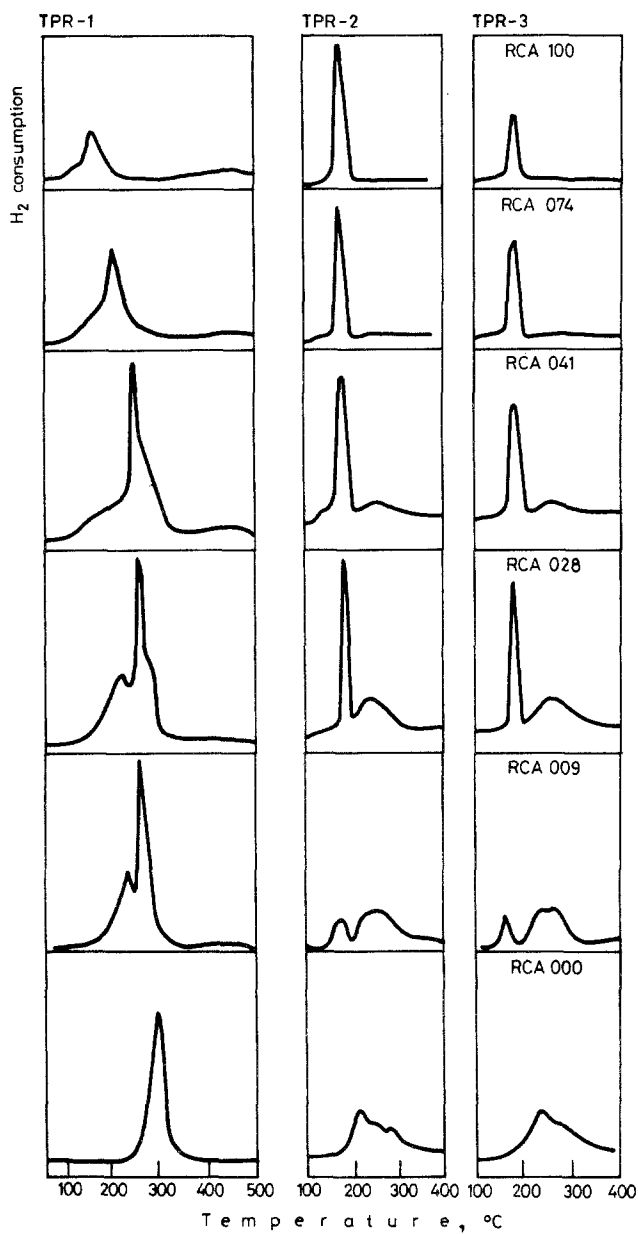


Fig. 5 TPR profiles of Ru-Cu supported on Al<sub>2</sub>O<sub>3</sub>



As observed for the  $\text{SiO}_2$ -supported samples, the presence of Ru decreases the temperature of reduction of copper, but for RCA074 the peak which can be assigned to the simultaneous reduction of the Ru and Cu salts is found in a temperature range significantly higher than that observed for the monometallic Ru/ $\text{Al}_2\text{O}_3$  sample. Samples with higher Cu/Ru ratios (RCA041, RCA028 and RCA009) exhibit a further shift in the maximum of the larger peak, and the appearance of a separate reduction peak for the copper-richest samples.

These results suggest that Ru and Cu interact during the first stages of preparation of the catalyst precursors. In fact, while the lower temperature of reduction of the copper salt could be related to a catalytic effect of Ru (occurring through a spillover of activated hydrogen from the reduced ruthenium [15], the increase in the temperature of reduction of the ruthenium salt has to be attributed to a modification of its chemical nature, due to an interaction between the two metal salts which also involves the  $\text{Al}_2\text{O}_3$  surface.

Figure 5 also shows profiles TPR-2 and TPR-3 obtained after reoxidation of the reduced Ru-Cu/ $\text{Al}_2\text{O}_3$  samples at  $500^\circ$ , following the standard procedure described in the experimental section. It is noted that all bimetallic samples display two main reduction peaks. The first has a maximum at about  $180^\circ$ , which is very close to that observed for unsupported  $\text{RuO}_2$  and in TPR-2 of the monometallic Ru/ $\text{Al}_2\text{O}_3$  sample. The other peak, at higher temperature, is very broad and similar to that found in the same temperature range for Cu/ $\text{Al}_2\text{O}_3$ . It seems that, after the first TPR cycle and oxidation in air at  $500^\circ$ , ruthenium and copper on  $\text{Al}_2\text{O}_3$  form separate oxide particles which are reduced independently.

This is confirmed by quantitative analysis of the hydrogen consumed. Figure 6 shows the H/Ru and the H/Cu ratios calculated from the TPR-2 spectra by assigning the peak at lower temperature to the reduction of Ru and the other to the reduction of Cu. Regardless of the Ru/Cu ratio, the amount of hydrogen consumed

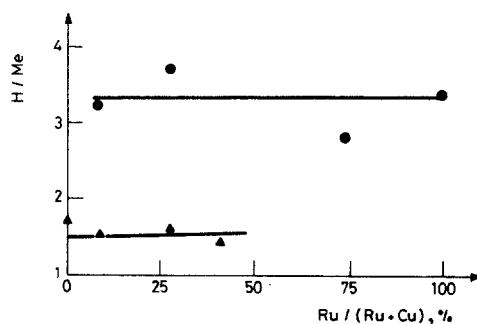


Fig. 6 Hydrogen consumed per metal atom during TPR-2 of Ru-Cu/ $\text{Al}_2\text{O}_3$  samples. ● H/Ru; ▲ H/Cu

per metal atom is very close to that found for the monometallic samples. Similar results have been obtained by examining the TPR-3 spectra.

This higher tendency of Ru and Cu to form separate aggregates on the  $\text{Al}_2\text{O}_3$  support is in agreement with the results obtained after reduction at lower temperature. In these experiments a portion of the unreduced RCA028 sample was subjected to TPR-1 up to only  $300^\circ$ , and it was then oxidized at this temperature for 30 min before the temperature was raised up to  $500^\circ$  in air. Subsequent TPR showed separate reduction peaks. It should be recalled that, with a similar procedure, the RCS034 sample (supported on  $\text{SiO}_2$ ) gave only one reduction peak.

For the alumina-supported samples, it has been observed that the H/Ru ratio decreases with the number of TPR cycles, while the H/Cu ratio remains practically constant. A decrease in the H/Ru ratio has also been observed for the monometallic Ru/ $\text{Al}_2\text{O}_3$  sample and attributed to the formation on this support of larger Ru particles which require a higher temperature to be oxidized [11]. The formation of larger particles on  $\text{Al}_2\text{O}_3$  could explain the higher tendency to form separate Ru and Cu particles on this support. The formation of bimetallic Ru-Cu aggregates is in fact likely to be limited (as a consequence of their low solubility in the bulk) to the outermost layer of the metallic particles. Therefore, only the smaller particles having a high surface/volume ratio will be able to form a significant amount of bimetallic aggregates.

The influence of the support on the formation and stability of bimetallic particles is also evidenced by the results reported in Fig. 7. In this Figure the TPR profiles of the Ru-Cu samples supported on MgO are shown, together with those of Ru/MgO and Cu/MgO. The TPR-1 spectra of the MgO-supported samples display complex profiles, indicating a consumption of hydrogen in a very broad range of temperature. This is observed for all samples, regardless of the Ru/Cu ratio. This behaviour has previously been reported for monometallic Ru/MgO, Cu/MgO [11] and Au/MgO [7], and has been attributed to hydrogen spillover from the metal to the MgO support.

A detailed comparison of the TPR-1 of the Ru-Cu/MgO samples is complicated by the hydrogen adsorbed on MgO. However, it can be observed that, as previously found on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , the reduction of one element is influenced by the presence of the other metal. In particular, the relative increase of the peaks in the range  $100$ – $200^\circ$ , observed following the addition of Cu, indicates that a significant proportion of the Cu and Ru salts are reduced simultaneously, suggesting the formation of bimetallic aggregates. These aggregates, however, are not very stable, as is evidenced by the TPR-2 and TPR-3 profiles. These reduction spectra show in fact two separate peaks, which can be assigned, by comparison with the spectra of the monometallic samples, to the reduction of RuOx (peak at lower temperature) and of CuOx (peak at higher temperature).

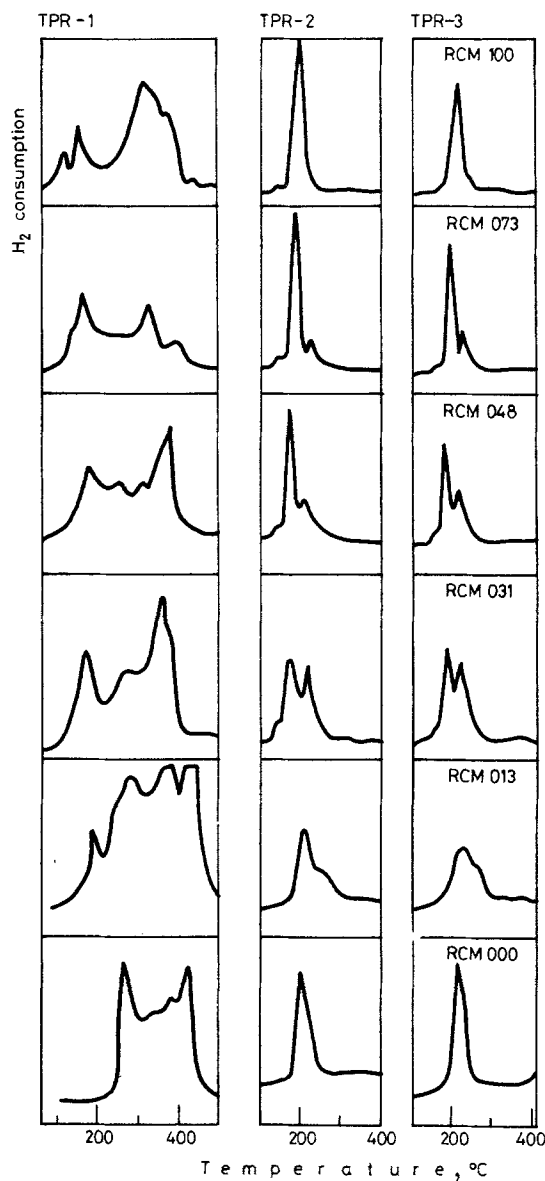


Fig. 7 TPR profiles of Ru-Cu samples supported on MgO

TPR experiments carried out on Ru-Cu/MgO after reduction up to 300° and oxidation in air up to 500° have given results quite different from those obtained on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. On MgO in fact, only the reduction peak of Cu is observed. It seems that under these conditions all the ruthenium atoms interact with MgO,

forming compounds difficult to reduce. With the standard TPR procedure described in the experimental section, only a fraction of the ruthenium was found to interact strongly with the support. The existence of a stable Ru–MgO surface complex under oxidizing conditions has been suggested previously [16, 17]. Tauster et al. [17] have shown that the volatilization of ruthenium in flowing air is strongly retarded by interaction with MgO. Temperatures higher than 1000–1100° were found necessary to decompose the surface complex.

## Conclusions

The TPR profiles show that in the bimetallic samples the reduction of ruthenium and copper precursors occurs within the same range of temperature, even though the Ru and Cu in the monometallic catalysts give reduction peaks which differ by up to 150°. On SiO<sub>2</sub>, the simultaneous reduction of the two salts could be attributed to a catalytic reduction of copper by hydrogen activated on the metallic ruthenium. On Al<sub>2</sub>O<sub>3</sub>, however, the temperature of reduction of the Ru–Cu samples is found in a range which is intermediate between those of Ru/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. This suggests the presence of an interaction between the two metal salts (involving also the support), which occurs even during the stages of preparation and drying. The simultaneous reduction of the two salts could account for the earlier-reported formation of bimetallic aggregates. These aggregates, however, are not in thermodynamic equilibrium and tend to separate.

The results reported in this paper also show that the stability of the bimetallic particles is strongly dependent on the support used, being higher on SiO<sub>2</sub> than on Al<sub>2</sub>O<sub>3</sub> and MgO. On these two latter supports, thermal treatment at 500° leads to separate Ru and Cu crystallites. On SiO<sub>2</sub>, the “demixing” was found to occur readily only if the samples were kept in a reduced state at high temperature for long periods. The different stability could be related to the chemical nature of the support, which would determine a different degree of interaction and/or of agglomeration of the bimetallic particles. In fact, it is likely that larger particles are less stable, due to the bulk immiscibility of Ru and Cu. A TEM study on these Ru–Cu samples is in progress in order to verify this hypothesis.

\* \* \*

The authors thank Dr. G. R. Tauszik for helpful discussion.

## References

- 1 I. W. Bassi, F. Garbassi, G. Vlaic, A. Marzi, G. R. Tauszik, G. Cocco, S. Galvagno and G. Parravano, *J. Catal.*, 64 (1980) 405.
- 2 S. Galvagno, J. Schwank, G. Parravano, F. Garbassi, A. Marzi and G. R. Tauszik, *J. Catal.*, 69 (1981) 283.
- 3 S. Galvagno, J. Schwank and G. Parravano, *J. Catal.*, 61 (1980) 223.
- 4 J. Schank, S. Galvagno and G. Parravano, *J. Catal.*, 63 (1980) 415.
- 5 G. R. Tauszik, F. Garbassi and A. Marzi, *Gazz. Chim. Ital.*, 110 (1980) 443.
- 6 J. Schank, G. Parravano and H. L. Gruber, *J. Catal.*, 61 (1980) 19.
- 7 R. G. Tauszik, G. Leofanti and S. Galvagno, *J. Molecular Catalysis*, 25 (1984) 357.
- 8 J. H. Sinfelt, *J. Catal.*, 29 (1973) 308.
- 9 J. H. Sinfelt, L. Y. Lam, J. A. Cusumano and A. E. Barnett, *J. Catal.*, 42 (1976) 227.
- 10 G. C. Bond and B. D. Turnham, *J. Catal.*, 45 (1976) 128.
- 11 S. Galvagno, C. Crisafulli, R. Maggiore, G. R. Tauszik and A. Giannetto, *J. Thermal Anal.*, 30 (1985) 611.
- 12 A. G. Shastri, J. Schwank and S. Galvagno, *J. Catal.*, (submitted).
- 13 G. C. Bond and X. Yide, *J. Molecular Catal.*, 25 (1985) 141.
- 14 S. J. Gentry, N. H. Hurst and A. Jones, *J. Chem. Soc. Faraday Trans. 1*, 77 (1981) 603.
- 15 D. W. Goodman and C. H. F. Peden, *J. Catal.*, 95 (1985) 321.
- 16 A. Bossi, A. Catalani, F. Garbassi, G. Petrini and L. Zanderighi, *J. Thermal Anal.*, 26 (1983) 81.
- 17 S. J. Tauster, L. L. Murrell and J. P. DeLuca, *J. Catal.*, 48 (1977) 258.

**Zusammenfassung** — Auf  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  und  $\text{MgO}$  aufgebrachte bimetallische Ru–Cu-Proben wurden mittels temperaturprogrammierter Reduktion (TPR) untersucht. Experimente wurden sowohl mit unreduzierten, durch Impregnation aufgebrachten Salzen als auch mit nach vorangegangener Reduktion reoxydierten Proben ausgeführt. Die TPR-Profile lassen eine gleichzeitige Reduktion der Ruthenium- und Kupferstufen erkennen, obwohl Ru und Cu in monometallischen Katalysatoren Reduktionspeaks zeigen, die um bis zu  $150^\circ\text{C}$  voneinander entlernt liegen. Es wird angenommen, daß die zwei Metallsalze während des Darstellungs- und Trocknungsstadiums miteinander in Wechselwirkung treten und nach der Reduktion nicht stabile, zum Zerfall tendierende bimetallische Aggregate bilden. Die Stabilität der bimetallischen Partikel ist stark vom Träger abhängig, sie ist an  $\text{SiO}_2$  höher als an  $\text{Al}_2\text{O}_3$  und  $\text{MgO}$ . Es wird angenommen, daß die chemische Natur des Trägers den Grad der Wechselwirkung und/oder Agglomeration der bimetallischen Partikel bestimmt.

**Резюме** — Методом температурно-программного восстановления (ТПВ) изучены биметаллические образцы рутения — медь на подложках из двуокиси кремния, окиси алюминия и окиси магния. Эксперименты были проведены как с невосстановленными пропитанными солями, так и с вновь окисленными ранее восстановленными образцами. Профили кривых показывают одновременное восстановление рутения и меди, тогда как в случае монометаллов пики восстановления рутения и меди отличаются на  $150^\circ\text{C}$ . Это свидетельствует о том, что соли обоих металлов взаимодействуют между собой на стадии получения и высушивания, а после восстановления образуют биметаллические агрегаты, которые неустойчивы и имеют тенденцию к разделению. Установлено, что стабильность биметаллических частиц сильно зависит от характера подложки, являясь более высокой на двуокиси кремния по сравнению с тем, что на окиси алюминия и окиси магния. Предположено, что химическая природа подложки определяет различную степень взаимодействия или агломерации биметаллических частиц.