Journal of Thermal Analysis, Vol. 30 (1985) 611–618

TEMPERATURE-PROGRAMMED REDUCTION. METAL-SUPPORT INTERACTION ON SUPPORTED MONOMETALLIC Ru AND Cu CATALYSTS

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(Received October 24, 1984)

Ru and Cu samples supported on SiO_2, Al_2O_3 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 were found to be strongly dependent on the support used, indicating different degrees of interaction between the metal and the support, which can be ranked as $MgO \gg Al_2O_3 > SiO_2$. It is suggested that the interaction occurs through the formation of surface complexes difficult to reduce. The decrease in hydrogen consumption observed on the Ru samples with the number of TPR cycles is attributed to the difficulty in oxidizing large Ru particles.

In this paper we report results obtained in a temperature-programmed reduction (TPR) investigation on monometallic Ru and Cu supported on SiO_2, Al_2O_3 and MgO. TPR is a valuable technique for the acquisition of information on the states of the catalysts, such as the valency of the active species and the nature of the metal-support interaction. Even though some papers have been published on the TPR of Ru [1–5] and Cu [5–10], the need for a detailed study on the monometallic samples arises for two reasons: first of all, an accurate comparison with literature data cannot be performed due to the different experimental conditions used [11]; moreover, the published results are generally limited to the TPR of the unreduced impregnated salts and very little information is available on the redox cycle of the samples.

The data obtained in this study can be used for a better understanding of the behaviour of supported bimetallic Ru–Cu systems. Results on Ru–Cu will be reported in a forthcoming paper.

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Akadémiai Kiadó, Budapest

Experimental

Commerical hydrated ruthenium trichloride (Rudi Pont $RuCl_3 . H_2O$, Reagent grade) and $Cu(NO_3)_2$ (Baker, Analyzed reagent) were used as precursor compounds. The support materials were MgO (Carlo Erba RPE–ACS) with a surface area of 15 m^2/g; SiO_2 (Davison 951 N) with a surface area of 650 m^2/g; and Al_2O_3 (Ketjen, grade A) with a surface area of 160 m^2/g.

Catalysts were prepared by impregnating the support with freshly-prepared aqueous solutions of above salts. The obtained solids were dried for 4 h at 110°. The contents of Ru (Table 1) and Cu (Table 2) in the samples were measured by atomic absorption spectroscopy. 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_2 after calcination at 700° for 1 h were used as reference samples for quantitative analysis. The gas used in the TPR was a mixture of 5 vol.% H_2 in Ar, and the oxidizing gas was air. Before the reducing mixture (20 cm^3/min) was passed 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 of the fresh catalyst sample from 35 to 500° (TPR–1), cooling to 300° in a H_2/Ar mixture, and oxidation of the sample in air from 300 to 500° at 5 deg/min and 30 min at 500°. After cooling to room temperature, a second TPR (TPR–2) was performed. TPR–3, TPR–4, etc. were carried out using a similar procedure.

Table 1 Hydrogen atoms consumed per ruthenium atom in the TPR experiments for supported (SiO_2, MgO and Al_2O_3) ruthenium catalysts

Support	Ru, wt%	H/Ru			
		TPR-1	TPR-2	TPR-3	TPR-4+TPR-7
SiO_2	2.1	4.6	3.7	2.6	
MgO	4.5	6.2	1.8	1.3	
Al_2O_3	2.2	4.4	3.4	2.4	1.8–1.6–1.4–1.4

Table 2 Hydrogen atoms consumed per copper atom in the TPR experiments for supported (SiO_2, MgO and Al_2O_3) copper catalysts

Support	Cu, wt%	H/Cu		
		TPR-1	TPR-2	TPR-3
SiO_2	1.9	3.1	1.9	2.0
MgO	4.2	8.0	1.1	1.1
Al_2O_3	2.5	6.8	1.7	1.8

Results and discussion

Figure 1 shows TPR profiles of Ru samples supported on SiO_2, Al_2O_3 and MgO, obtained in the range of temperature 35–500°. The TPR spectra of unreduced impregnated $RuCl_3$ (TPR–1) show large differences depending on the support used. Ru/SiO_2 and Ru/Al_2O_3 show a broad reduction peak between 100 and 200°, with a weaker signal at higher temperature, which can be attributed to a Ru species interacting more strongly with the support. The higher temperature of this second peak for Ru/Al_2O_3 with respect to Ru/SiO_2 suggests a stronger interaction of the metal with Al_2O_3 in agreement with previous findings [3, 12].

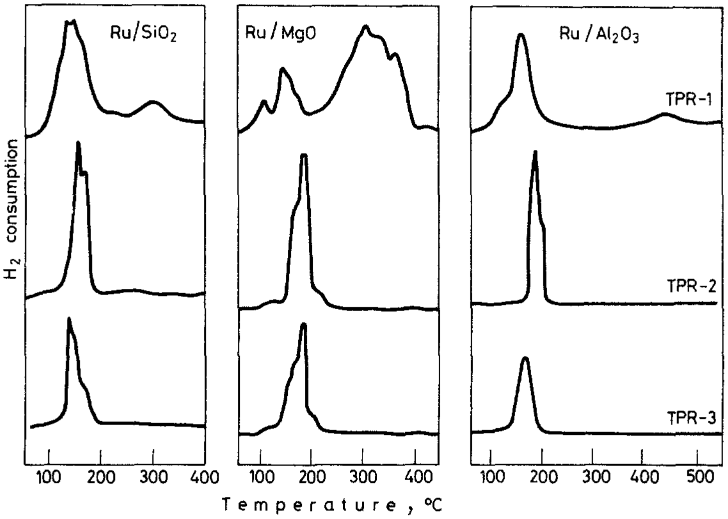

Fig. 1 TPR spectra of Ru samples supported on SiO_2, MgO and Al_2O_3

The H/Ru ratios (atoms of hydrogen consumed per atom of ruthenium) reported in Table 1 are 4.4 and 4.6 for Ru/SiO_2 and Ru/Al_2O_3, respectively. A H/Ru ratio of 4.7 has previously been reported for a 3.86 wt% Ru/SiO_2, found using a different apparatus and different experimental conditions (namely a reduction mixture with 36% H_2 in Ar and a heating rate of 20 deg/min) [13]. The hydrogenation of $RuCl_3$ should lead, according to the following scheme:

$$RuCl_3 + 3/2\,H_2 \rightarrow Ru + 3\,HCl \qquad (1)$$

to a H/Ru ratio = 3. The higher values measured are probably related to the formation, during the impregnation, of hydrolysis products for which a higher hydrogen consumption can be envisaged [13].

Profile TPR–1 for Ru/MgO shows (Fig. 1) a strong broad peak between 200 and 400° (besides the reduction peaks of Ru at 100–200°), comparable to that previously reported on a similar sample [13]. A series of experiments carried out on MgO reference samples alone and on MgO physically mixed with Pt/Al_2O_3 or with unsupported RuO_2 have previously suggested that the high-temperature peaks should be attributed to hydrogen spillover from the metal to the MgO support [13].

The H/Ru ratio reported in Table 1 for Ru/MgO (H/Ru = 6.2) is similar to that reported in ref. 13 and is much lower than that previously determined by Berté et al. [12] (H/Ru = 18). In the latter case the higher hydrogen consumption has to be ascribed to reduction of the nitrogen compound used as precursor (Ru nitrosonitrate).

Figure 1 also shows profiles TPR–2 and TPR–3 obtained after reoxidation at 500° of the reduced samples of the supported catalysts. All three samples examined show only overlapping reduction peaks in the range of temperature 100–230°. If it is considered that the unsupported RuO_2 shows a reduction peak with a maximum at 180° (in agreement with previous findings [12]), it can be suggested that the overlapping peaks in profiles TPR–2 and TPR–3 are related either to different steps of reduction of RuO_2, or to the presence of ruthenium oxide particles of different sizes, or both. It is known that a higher dispersion of oxides not interacting with the support leads to a shift in the reduction peak towards lower temperature. Moreover, TPR profiles with peaks related to different stages of reduction of Ru^{4+} have been reported for Ru/X-zeolites [14].

The amount of hydrogen consumed during TPR–2 (Table 1) is below that expected for the reduction of RuO_2 (H/Ru = 4). The measured H/Ru ratios (3.7 for Ru/SiO_2 and 3.4 for Ru/Al_2O_3) show that on these supports only a small fraction of the Ru does not participate in the redox cycles. The much lower value of H/Ru (1.8) obtained for Ru/MgO seems, instead, to indicate a strong interaction of the metal with the MgO support. The formation of stable and not reducible (under our experimental conditions) surface complexes between Ru and MgO, similar to that reported for Pt/MgO [15], has previously been suggested by Bossi et al. [2].

Table 1 also shows that on all the Ru samples the amount of consumed H_2 decreases with the number of TPR. In particular, for Ru/Al_2O_3 the H/Ru ratio decreases from 4.4 in TPR–1 to 1.4 in TPR–7; afterwards, it remains practically constant. Chemical analysis of the sample used in TPR–7 gave a Ru content of 1.75 wt%, in comparison with 2.2 wt% for the fresh sample. This indicates that a fraction of the Ru volatilizes, probably due to the formation of higher Ru oxides (RuO_3, RuO_4 [16]). However, the decrease in the Ru content (~20%) does not correspond to the larger decrease in the H/Ru ratio, which in TPR–7 is about 70% of that measured in TPR–1. After treatment in air at 600° for 4 h, the H/Ru ratio for Ru/Al_2O_3 rose from 1.4 (TPR–7) up to 3.9. This indicates that the thermal treatment used between two TPR cycles is not sufficient to oxidize all the Ru metal. The decrease observed during subsequent TPR cycles is probably related to the formation of larger particles, which require higher temperatures and/or a longer oxidation time.

On Ru/MgO, oxidation at 600° for several hours did not cause any increase in the H/Ru ratio observed during TPR–2. This rules out the possibility that the low consumption of hydrogen observed on Ru/MgO can be ascribed to larger particles, and therefore confirms that for MgO a strong interaction occurs between the metal and the support. We have also noted that, in the range 100–200°, the areas of the peaks of profiles TPR–1 and TPR–2 are comparable. This suggests that the main interaction between the metal and the support occurs already during the stage of preparation of the precursors.

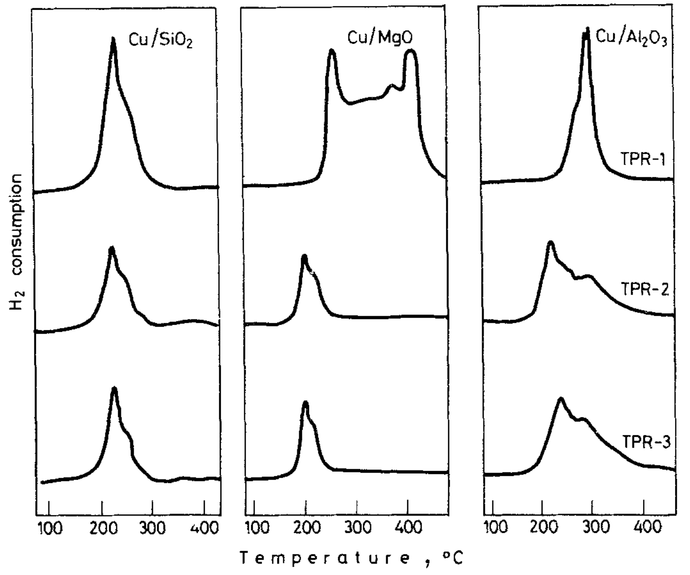

Fig. 2 TPR spectra of Cu samples supported on SiO_2, MgO and Al_2O_3

Figure 2 shows the TPR diagrams of copper samples supported on SiO_2, Al_2O_3 and MgO. Profile TPR–1 for Cu/SiO_2 shows a peak at 240°, with a shoulder at higher temperature. Similar reduction peaks, slightly shifted towards lower temperature, are also noted in profiles TPR–2 and TPR–3. The unsupported $Cu(NO_3)_2$ similarly exhibited two reduction peaks in profile TPR–1, but shifted to higher temperatures (*T*max. = 288° and shoulder at 293°). In the related profiles TPR–2 and TPR–3, a broad peak was observed in the same temperature range as for TPR–1. The lower temperature of reduction of Cu/SiO_2 with respect to the unsupported $Cu(NO_3)_2$ is attributed to the higher dispersion of the Cu species on the support [5].

The hydrogen consumption measured during TPR–1 for Cu/SiO_2 was found to be significantly higher than that observed during TPR–2 and TPR–3 (Table 2), as a consequence of the hydrogen used for the reduction of nitrate:

$$Cu(NO_3)_2 + 9\,H_2 \longrightarrow Cu + 2\,NH_3 + 6\,H_2O \tag{2}$$

$$Cu(NO_3)_2 + 6\,H_2 \longrightarrow Cu + N_2 + 6\,H_2O \tag{3}$$

Since $Cu(NO_3)_2$ decomposes at 170° [17] with the formation of CuO and nitrogen oxides, it may be expected that, during TPR–1, hydrogen is consumed either by the undecomposed nitrate or by CuO. The ratio between the areas of profiles TPR–1 and TPR–2 (about 0.6) indicates that the amount of undecomposed nitrate is 9–14%, depending on the stoichiometry of reduction of $Cu(NO_3)_2$.

The presence of different reduction peaks in profiles TPR–1, TPR–2 and TRP–3 indicates once again a consumption of hydrogen related to different steps of reduction of Cu^{2+} [6] and/or to different degrees of dispersion [5]. Moreover, the value of H/Cu (2) found in steps TPR–2 and TPR–3 indicates that all the Cu present participates in the redox cycles, suggesting a very low interaction between Cu and SiO_2.

Profile TPR–1 for Cu/Al_2O_3 shows overlapping peaks of reduction, with a maximum at 280°, which is significantly higher than that measured with SiO_2. This shift can be attributed either to a lower degree of dispersion of $Cu(NO_3)_2$ on Al_2O_3, due to its lower surface area, or to a stronger interaction with the support. Profiles TPR–2 and TPR–3 show a consumption of hydrogen corresponding to a H/Cu ratio 1.7, which is about 20% less than that expected for CuO. This would indicate the presence of an interaction between Cu and Al_2O_3, with the formation of stable compounds which are not involved in the redox procedure used (at least under our experimental conditions). An X-ray analysis of the reduced Cu/Al_2O_3 sample did not show any formation of bulk compound between the metal and the support, but it has been reported that at low concentrations copper enters the defect spinels of the γ-Al_2O_3 support to yield a well-dispersed phase which is not detected by X-ray diffraction analysis. An aluminate phase was also revealed on samples calcined at 300° [10]. The value of H/Cu (6.8) in step TPR–1 for Cu/Al_2O_3 is much higher than that measured for Cu/SiO_2 ($H/Cu = 3.1$). This can be taken as evidence of an interaction between the precursor nitrate and Al_2O_3 which would stabilize the salt against decomposition to CuO. In this case the amount of undecomposed $Cu(NO_3)_2$ is 22–36%. This is in agreement with the shift to higher temperature of the *T*max. of profile TPR–1 for Cu/Al_2O_3 with respect to Cu/SiO_2.

Cu/MgO shows a complex profile TPR–1, indicating a consumption of hydrogen in a very broad range of temperature (240–500°). This behaviour is similar to that found for Ru/MgO (Fig. 1) and Au/MgO [13]. The first peak at 260° can be assigned to the reduction of the copper precursor, and the hydrogen consumption at higher temperatures to hydrogen spillover onto the MgO support [13].

Profile TPR–2 for Cu/MgO displays a shift of the reduction peak of copper towards lower temperatures, which can be attributed to a higher degree of dispersion. It has recently been shown that air treatment of CuO on MgO leads to a spreading out of the metal on the support [8].

The H/Cu ratio measured for the Cu/MgO sample during step TPR–2 is about 1.1, which is about half that measured for Cu/SiO_2. It can therefore be suggested that in this case too (as for Ru/MgO) the metal interacts strongly with the support, leading to stable surface complexes which are difficult to reduce under our experimental conditions. During the subsequent redox cycles (TPR–3, TPR–4, etc.) there was no change in the H/Cu ratio, suggesting that the interaction between Cu and MgO occurs during the preparation of the precursor and/or during the first reduction of the metal salt.

Conclusions

The TPR profiles and the H/metal ratios for Ru and Cu show 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 can be ranked as:

$$MgO \gg Al_2O_3 > SiO_2$$

For the Cu samples the H/metal ratios have been found to remain constant during the subsequent redox cycle, while for the Ru samples a decrease is observed.

Oxidation of Ru samples at higher temperatures and/or for a longer time have shown that, under the experimental conditions used between two TPR cycles, the oxidation of ruthenium is not complete, probably due to a slow diffusion of oxygen from the surface into the core of the metal particles. The decrease in the H/Ru ratio with the number of TPR cycles is attributed to the formation of larger crystallites.

The TPR profiles of Cu and Ru samples show several reduction peaks, mostly overlapping, which indicate a reduction through different steps and/or a non-uniform distribution of the metal particles.

Our data lend further support to the hypothesis that the interaction between the metal and the support occurs through the formation of surface complexes which are difficult to reduce.

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Zusammenfassung — Auf SiO_2, Al_2O_3 und MgO aufgebrachte Ru- und Cu-Proben wurden mittels temperaturprogrammierter Reduktion (TPR) untersucht. Experimente wurden sowohl an unreduzierten Salzimprägnierungen als auch nach Oxydation von bereits reduzierten Proben ausgeführt. Die TPR-Profile sind stark vom benutzten Trägen abhängig, was auf unterschiedliche Grade der Wechselwirkung zwischen Metall und Träger hindeutet; die Reihenfolge ist $MgO \gg Al_2O_3 > SiO_2$. Es wird vermutet, daß das Wesen der Wechselwirkung in der Bildung von schwer reduzierbaren Oberflächenkomplexen zu suchen ist. Die bei Ru-Proben mit der Zahl der TPR-Zyklen beobachtete Verminderung des Wasserstoffverbrauchs wird mit der Schwierigkeit, große Ru-Partikel zu oxydieren, in Zusammenhang gebracht.

Резюме — Методом температурно-программируемого восстановления (ТПВ) изучены образцы меди и рутения на подложках из SiO_2, Al_2O_3 и MgO. Эксперименти были проведены как с невосстановленными импрегнированными образцами, так и с окисленными, но предварительно подвергнутих восстановлению, образцами. Найдено, что профили ТПВ сильно зависят от используемой подложки, показывая тем самым различные степени взаимодействия между металлом и подложкой в следующей последовательности $MgO \gg Al_2O_3 > SiO_2$. Предположено, что такие взаимодействия протекают с образованием на поверхности комплексов, трудно подвергающихся восстановлению. Наблюдаемое в случае образцов рутения уменьшение расхода водорода от числа циклов ТПВ, объяснено трудностью окисления больших частиц рутения.