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Characterization of Ruthenium Catalysts as Studied by Temperature Programmed Reduction

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The oxidation and subsequent reduction of ruthenium have been investigated by means of temperature programmed reduction (TPR). Ru/SiO_2 prepared by direct reduction of $RuCl_3/SiO_2$ showed surface oxidation followed by "bulk" oxidation upon exposure to air at room temperature. The oxidation/reduction behavior of these catalysts differed substantially from that of Ru/SiO_2 prepared by reduction of RuO_2/SiO_2 obtained by calcination of $RuCl_3/SiO_2$ in air. Application of higher reduction temperatures (up to 973 K) of $RuCl_3/SiO_2$ was found to increase the active metal surface area of the Ru/SiO_2 formed due to the removal of traces of chlorine from the Ru surface. Reduction of RuO_2/SiO_2, obtained by calcination of $RuCl_3/SiO_2$ in air, resulted in lower dispersed Ru/SiO_2. The present results explain the effect of the activation procedure of Ru/SiO_2 catalysts on the activity for benzene hydrogenation. Measurement of H_2 desorption by means of the TPR apparatus gave rapid and useful information about the Ru metal dispersion.

INTRODUCTION

Among the Group VIII metals, Ru occupies an intermediate position between Fe, Co, Ni, and noble metals, as may be demonstrated by the metal–oxygen interactions for Pt, Ru, and Ni (Table 1).

When exposed to oxygen at room temperature, a freshly formed surface of Ru becomes covered by a film of oxide, which will thicken at higher temperature (*6*). The formation of oxides on the Ru surface causes the induction phenomena as found in Ru-catalyzed liquid-phase hydrogenation reactions (*7*).

The oxidation of Ru in the temperature range 293–1670 K has been studied with thermogravimetric analysis (*8*). The interaction between Ru and oxygen at ambient temperature has been investigated by volumetric adsorption determinations (*9–13*), field emission spectroscopy (*14*), EXAFS (*15*), and cyclic voltammetry (*16, 17*). In studies on the adsorption of oxygen on supported Ru the adsorption stoichiometry was determined by oxygen adsorption on Ru black. The O/Ru values thus determined were found to vary from 1 (*9, 10*) to 2 (*11–13*). Taylor (*10*) found a rapid oxygen uptake at room temperature on Ru/Al_2O_3 with small Ru crystallite size (<2.5 nm); in some experiments the oxygen uptake exceeded the Ru content of the catalyst if it is assumed that the adsorption stoichiometry is 1. The oxygen adsorption at 200 K was less than that at room temperature (*10*). Bortner and Parravano (*2*) derived enthalpies of oxygen adsorption on Ru by means of the adsorption and decomposition equilibrium of water in the temperature range 470 to 670 K and found that the heat of oxygen chemisorption is increased by oxidic supports.

With respect to our work on the activation of Ru catalysts (*7, 18*), which revealed the importance of the activation history, and in connection with the literature reports mentioned above it would seem of importance to study the oxidation/reduction behavior for a number of unsupported and silica-supported home-made Ru catalysts. Use was made of the temperature programmed reduction (TPR) technique, which consists of increasing the

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TABLE 1

Metal–Oxygen Interaction for Pt, Ru, and Ni

	Pt	Ru	Ni	Ref.
Heat of formation of oxide (kJ mol^{-1})	−134	−220	−243	(*1*)
Heat of chemisorption of oxygen (kJ mol^{-1})	−109	−176	−235	(*2–4*)
Reduction temperature of oxide (K)	293	433	573	(*5*)

temperature of the partly oxidized catalyst at a slow uniform rate and measuring the rate of hydrogen consumption. In addition the TPR apparatus was successfully used for hydrogen desorption measurements in order to determine the Ru dispersion of the reduced catalysts.

EXPERIMENTAL

RuO_2 was prepared by treatment of $RuCl_3$ hydrate (Alfa) with air at 101 kPa and 673 K for 2 h; Ru powder by treatment of $RuCl_3$ hydrate with hydrogen at 101 kPa and 473 to 623 K for 2 h. The 5% Ru/SiO_2 was prepared by impregnation of silica (Akzo F2, surface area 345 m^2 g^{-1}) with a solution of $RuCl_3$ hydrate in acetone (*18*), followed by drying in air at 393 K for 2 h. The following activation procedures were used: (i) calcination in air for 2 h at 673 K, giving RuO_2/SiO_2, followed by treatment in H_2 (101 kPa) for 2 h at a fixed temperature; (ii) treatment in H_2 (101 kPa) for 2 h at a fixed temperature.

The TPR apparatus was constructed according to a description by Robertson *et al.* (*19*). The degree of oxidation of the Ru samples was determined using the following procedure. A sample, e.g., 50 mg 5% Ru/SiO_2, was heated in flowing N_2 at 20 K min^{-1} to 673 K, held for 10 min at 673 K, cooled to ambient temperature, and then analyzed by TPR, i.e., heating in 5% H_2 (N_2) stream at 10 K min^{-1}. After the TPR measurement the sample was cooled to room temperature, oxidized at a fixed temperature for 2 h, purged with N_2 at the same temperature, cooled to room temperature, and then analyzed by TPR as given above. In the next cycle the sample was reoxidized at a higher temperature, etc.

The desorption of H_2 from a reduced catalyst was measured as follows. After the TPR treatment the catalyst was cooled to ambient temperature in 5% H_2 (N_2) and subsequently heated at a rate of 200 K min^{-1} to 673 K, while the H_2 desorption was recorded.

The H_2 adsorption measurements were carried out in a conventional glass vacuum system. The chemisorption data were obtained at 336 K after *in situ* re-reduction in H_2 and subsequent evacuation at 673 K.

The thermogravimetric analysis was carried out with a symmetrical thermobalance (Sartorius 4104) in flowing gas.

Ru particle sizes were determined from X-ray line broadening (Philips PW 1050 diffractometer) using the Scherrer equation.

Electron micrographs were obtained using a Philips EM 400-G instrument.

RESULTS

Hydrogen Desorption

Heating of Ru/SiO_2 (from $RuCl_3/SiO_2$, P_{H_2}: 101 kPa, 973 K, 2h) in 5% H_2 (N_2) from 293 K to 673 K at 200 K min^{-1} showed desorption of H_2 (Fig. 1). Subsequent fast cooling showed H_2 adsorption, apparently followed by some slow H_2 desorption; this oversaturation with H_2 was caused, however, by instability of the detection upon fast cooling. This procedure was repeated several times and proved to give reproducible desorption peaks. The metal dispersion, defined as the ratio of hydrogen atoms adsorbed to the total amount of Ru atoms, thus obtained from the desorption peaks is given in Table 2 for differently prepared Ru/SiO_2 catalysts. The data are in good agreement with those from static H_2 chemisorption measurements. The somewhat lower values obtained by H_2 desorption in the TPR apparatus are due to the fact that the H_2 desorption measured at H_2 pressure of 5.05 kPa at 673 K reflects ~90% of the

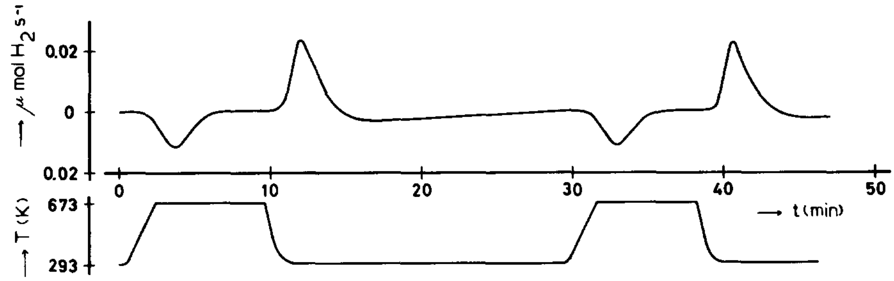

FIG. 1. Desorption and adsorption of H_2 of Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, 973 K, 2 h).

total chemisorbed H_2, as revealed by additional heating to 873 K. This systematic error is of minor importance if relative H/Ru ratios are considered, thus offering a rapid H_2 desorptive TPR method for the determination of Ru metal dispersions. The X-ray diffraction analysis gave Ru particle sizes which were much smaller than those obtained from H_2 ad- or desorption (Table 2). The effect of pretreatment of Ru/SiO_2 catalysts was also determined by means of H_2 desorption and is given in Table 3.

Re-reduction at high temperature of a Ru/SiO_2 catalyst prepared by reduction of $RuCl_3/SiO_2$ at 673 K caused an increase in metal dispersion. The adsorption of chlorine on a Ru/SiO_2 (reduced at 973 K) caused a decrease in dispersion, which could be restored, however, by subsequent high-temperature reduction.

Unsupported Ruthenium (Oxide)

The TPR curve of RuO_2 revealed a maximum rate of reduction at 475 K, i.e., the so-called peak temperature; the reduction was complete at 540 K (curve 1 in Fig. 2). The Ru metal thus formed was reoxidized at 417 K for 2 h and the degree of oxidation was determined by TPR (curve 2 in Fig. 2). In an analogous way the other curves have been obtained successively for the different reoxidation temperatures. The degree of oxidation α of these Ru samples, as determined from the H_2 uptake in TPR, has been calculated using the reaction equation

$$RuO_\alpha + \alpha H_2 \rightarrow Ru + \alpha H_2O.$$

Additional adsorption of H_2 on Ru was not taken into account since no H_2 desorption peaks were found upon heating up to 1000 K. As shown in Fig. 3 (△) α increases with increasing oxidation temperature, although complete reoxidation to RuO_2, the original calcined state, was not reached. The peak temperature of the TPR curves for these reoxidized samples is linearly correlated

TABLE 2

Metal Dispersion of Ru/SiO_2 Prepared by Direct Reduction and Calcination–Reduction

Activation procedure		H/Ru TPR	H/Ru chemisorption	*d* X-ray (nm)
	H_2[a] 663 K	0.037	0.039	3
	H_2 763 K	0.074	0.094	3.5
	H_2 963 K	0.17	0.18	4
Air[b] 673 K	H_2 573 K	0.035		
Air 673 K	H_2 773 K	0.073	0.076	8
Air 673 K	H_2 973 K	0.040		

[a] P_{H_2}: 101 kPa, 2 h.
[b] P_{air}: 101 kPa, 2 h.

TABLE 3

Metal Dispersion of Ru/SiO_2. Effect of Chlorine Adsorption

Activation procedure			H/Ru (TPR)
H_2[a]	673 K		0.12
H_2	673 K, H_2	973 K	0.23
H_2	973 K		0.23
H_2	973 K, Cl_2[b]	293 K, H_2 673 K	0.14
H_2	973 K, Cl_2	293 K, H_2 973 K	0.23

[a] P_{H_2}: 101 kPa, 2 h.
[b] P_{Cl_2}: 101 kPa, 0.5 h.

with the degree of oxidation (△ in Fig. 4). Quite similar results were obtained for Ru, metal dispersion ~0.1, prepared from $RuCl_3$ hydrate by reduction at 473 K for 2 h (▲ in Figs. 3 and 4). The application of a higher reduction temperature (623 K), however, resulted in a less oxidizable Ru metal (metal dispersion ~0.01) (■ in Fig. 3).

Thermogravimetric analysis of Ru, prepared by reduction of $RuCl_3$ hydrate, in air showed that the oxidation started at 400 K and was complete at 1000 K. Subsequent reduction in H_2, after cooling to room temperature, occurred completely at about 440 K (Fig. 5). The oxidation of $RuCl_3$ hydrate in air could be carried out completely at 623 K (*17*).

Silica-Supported Ruthenium (Oxide)

TPR of RuO_2/SiO_2 (calcined $RuCl_3/SiO_2$) showed a peak temperature of 450 K and was complete at 478 K. The reduced Ru/SiO_2 thus formed was submitted to successive oxidation/reduction cycles, going from low to high reoxidation temperature; the degree of reoxidation versus the oxidation temperature is shown in Fig. 6 (○). The effect of the degree of oxidation on the peak temperature of the subsequent reduction curves is shown in Fig. 4. (○).

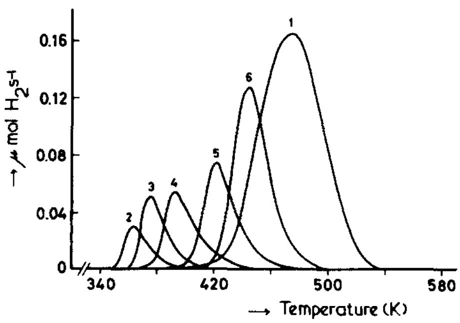

FIG. 2. TPR curves of RuO_2 from $RuCl_3$ hydrate (air 673 K, 2 h) (1) and of RuO_α formed by reoxidation of Ru at 417 K (2), 455 K (3), 499 K (4), 570 K (5), and 673 K (6); 101 kPa.

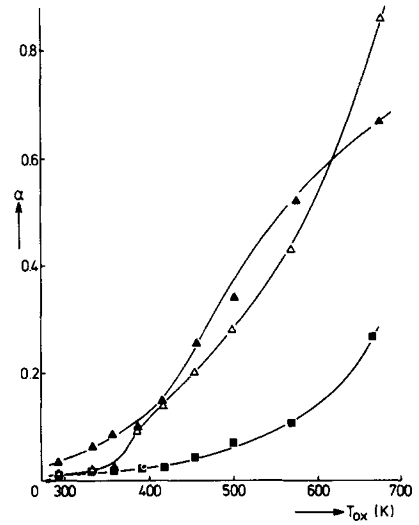

FIG. 3. Degree of oxidation (α) of Ru versus the temperature of reoxidation (air, 2 h); Ru from RuO_2 (curve 1 of Fig. 2) (△), Ru from $RuCl_3$ hydrate (H_2, 473 K, 2 h) (▲), Ru from $RuCl_3$ hydrate (H_2, 623 K, 2 h) (■); 101 kPa.

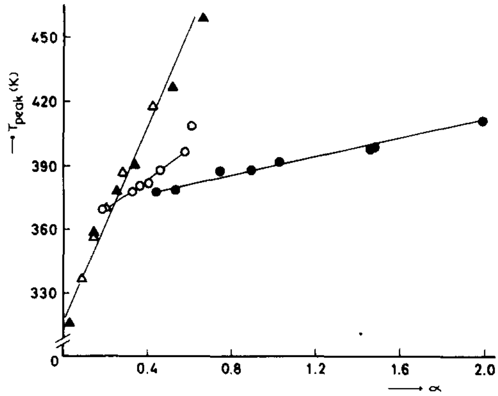

FIG. 4. Peak temperature of TPR of reoxidized (air, 2 h) Ru catalysts versus degree of oxidation (α); Ru from RuO_2 (curve 1 of Fig. 2) (△), Ru from $RuCl_3$ hydrate (H_2, 473 K, 2 h) (▲), Ru/SiO_2 from RuO_2/SiO_2 (5% H_2, 773 K) (○), Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, 873 K, 2 h) (●); 101 kPa.

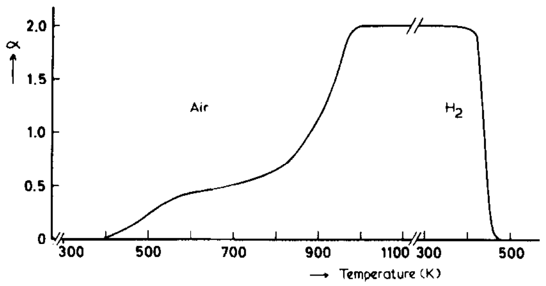

FIG. 5. Thermogravimetric curve of the oxidation of Ru from $RuCl_3$ hydrate (H_2, 498 K, 0.5 h) in air and subsequent reduction in H_2; heating rate 6 K min^{-1}; weight change expressed as the degree of oxidation (α); 101 kPa.

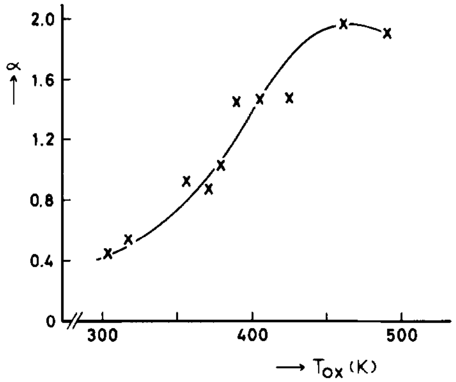

FIG. 7. Degree of oxidation (α) of Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, 873 K, 2 h) versus the temperature of reoxidation; air, 2 h; 101 kPa.

In contrast to these results for Ru/SiO_2 prepared via the calcination method, Ru/SiO_2 obtained by direct high-temperature reduction of $RuCl_3/SiO_2$ gave substantial oxidation at room temperature and almost complete oxidation to RuO_2/SiO_2 at 473 K (Fig. 7). The effect of the degree of oxidation on the peak temperature of the reduction curve is shown in Fig. 4 (●). The effect of the time of reoxidation at 293 and 355 K on the degree of oxidation is shown in Fig. 8.

A series of Ru catalysts, prepared by direct reduction of $RuCl_3/SiO_2$ at 573 to 1073 K for 2 h, were oxidized between 293 and 463 K for 2–1000 h. The degree of reoxidation was almost independent of the catalyst reduction temperature (Fig. 9).

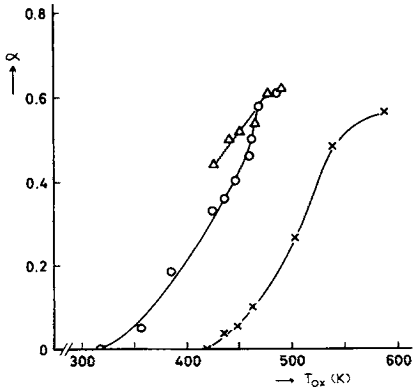

FIG. 6. Degree of oxidation (α), as determined from the H_2 uptake in TPR, of Ru/SiO_2 (5% H_2, 773 K) versus the temperature of reoxidation in air for different times of reoxidation; 0.5 h (×), 2 h (○), and 5 h (△); 101 kPa.

It appeared that the partly reoxidized (293 K) Ru/SiO_2 could be reduced in 5% H_2 (N_2) at room temperature. The Ru/SiO_2 samples oxidized at higher temperatures, however, could only be partly reduced at room temperature (Table 4). This difference in reactivity of the oxidized Ru/SiO_2 samples is further shown by the thermal decomposition in N_2.

DISCUSSION

For unsupported Ru, surface oxidation is followed by subsurface, "bulk" oxidation. Obviously, there is a great influence of the particle size of Ru on the subsurface oxida-

TABLE 4

Reduction and Decomposition of Partly Reoxidized Ru/SiO_2

$T_{oxidation}$[a] (K)	Percentage reduction[b]	Percentage decomposed[c]		
		361 K	460 K	660 K
293	100	51	60	90
361	79	27	47	76
460	5	0	0	0

[a] In air, 2 h; 101 kPa.
[b] In 5% H_2 (N_2), 293 K, 2 h; 101 kPa.
[c] In N_2, 1 h; 101 kPa.

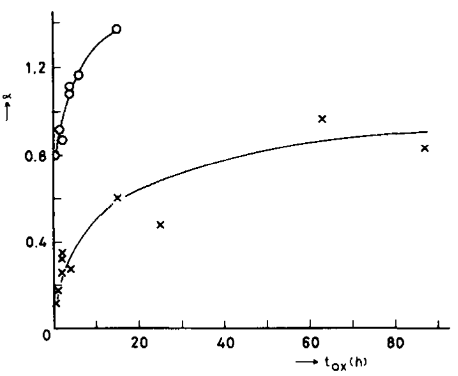

FIG. 8. Degree of oxidation (α) of Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, 873 K, 2 h) versus the time of reoxidation at 293 K (×) and 355 K (○); 101 kPa.

tion as appears from the difficult oxidation of sintered Ru (■ in Fig. 3) in comparison with the other Ru powders (△ and ▲ in Fig. 3). In addition, the reduction of the RuO_α species becomes more difficult with increasing degree of oxidation α as shown by the enhanced peak temperature at higher values of α (Fig. 2 and △, ▲ in Fig. 4).

Supported Ru is oxidized to a greater extent than unsupported Ru due to smaller metal particle size. In addition, the enthalpy of chemisorption of oxygen on Ru is increased by the support (*2*); i.e., the oxidic support increases the affinity of oxygen towards Ru. Furthermore, the catalyst prepared by direct reduction can be oxidized almost to completion at ~460 K. The effect of metal dispersion for these small particles, as brought about by using different reduction temperatures, on the degree of oxidation is very small (Fig. 9). Up to reoxidation temperatures of ~470 K the oxidation reduction cycles for Ru/SiO_2 can be reproduced; thus no sintering takes place upon this treatment. At reoxidation temperatures above ~470 K the degree of reoxidation decreased. These findings are in agreement with the observation (*20, 21*) that the H_2 chemisorption decreased upon treatment in air.

The oxidation of Ru/SiO_2 with metal dispersion of ~0.2 at room temperature (Fig. 8) indicates serious subsurface oxidation. This shows that great care must be taken when using oxygen chemisorption for the determination of the metal surface of Ru catalysts, even for particle sizes above 4 nm as suggested by Taylor (*10*). The (sub)surface Ru oxides formed upon exposure to air at room temperature can be partly decomposed by nitrogen treatment at higher temperature (Table 4). On the other hand, complete reduction to Ru(0) occurs at room temperature. The reduction started after an induction period, as was also found in the Ru-catalyzed liquid phase hydrogenation (*7*), due to the reduction of surface Ru oxides which originate from exposure of the catalyst to air at room temperature.

A comparison of the behavior of Ru/SiO_2 prepared by direct reduction of $RuCl_3/SiO_2$ with that of Ru/SiO_2 prepared by calcination in air of $RuCl_3/SiO_2$ to RuO_2/SiO_2 followed by reduction shows the following features:

—No oxidation at room temperature occurs for the catalyst obtained by calcination–reduction.

—No complete reoxidation of Ru/SiO_2 prepared from RuO_2/SiO_2 can be reached at the calcination temperature (673 K).

—Reduction of partly reoxidized Ru/SiO_2 prepared from RuO_2/SiO_2 is more

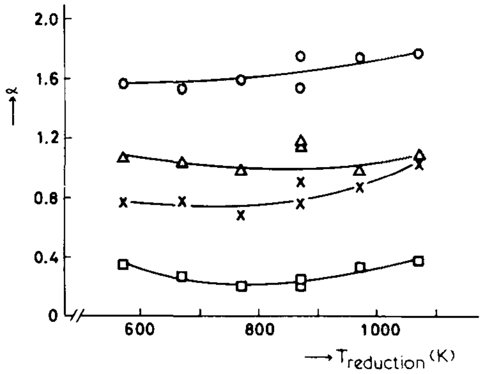

FIG. 9. Reoxidation of Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, various temperatures, 2 h). Plot of degree of oxidation of Ru (α) versus the reduction temperature of $RuCl_3/SiO_2$ for some different reoxidation times and temperatures: 1000 h, 293 K (△); 2 h, 293 K (□); 2 h, 355 K (×); and 2 h, 460 K (○).

difficult than that of Ru/SiO_2 prepared by direct reduction of $RuCl_3/SiO_2$. Partly reoxidized Ru powder, however, shows no difference in reducibility, either calcined or directly reduced.

—The metal dispersion of the Ru of Ru/SiO_2 (from RuO_2/SiO_2) as determined with H_2 desorption is independent of the temperature of reduction of the RuO_2/SiO_2.

—The metal dispersion of the Ru of Ru/SiO_2 (from $RuCl_3/SiO_2$) as determined with H_2 ad- and desorption increases with increasing reduction temperature of the $RuCl_3/SiO_2$.

—The particle size as determined with X-ray line broadening is larger for the Ru/SiO_2 from RuO_2/SiO_2 than for Ru/SiO_2 prepared by direct reduction of $RuCl_3/SiO_2$. This difference in particle size of Ru for the calcined-reduced and the directly reduced catalysts is confirmed by electron microscopy (Fig. 10). The particle size of the Ru/SiO_2 from directly reduced $RuCl_3/SiO_2$ increases slightly at higher reduction temperature.

—The activation procedure has a great effect on the activity of the Ru catalysts for the liquid-phase hydrogenation of benzene (*18*). Ru/SiO_2 obtained from direct reduction of $RuCl_3/SiO_2$ showed an increase in activity at increasing reduction temperature, whereas the activity of Ru/SiO_2 prepared from RuO_2/SiO_2 was independent of the reduction temperature applied. Using the metal dispersion as determined from H_2 desorption the activity expressed as turnover number is hardly dependent on the activation procedure.

The question arises as to the origin of these differences in behavior of Ru/SiO_2 from directly reduced $RuCl_3/SiO_2$ and calcined-reduced $RuCl_3/SiO_2$. The increase in metal dispersion for directly reduced $RuCl_3/SiO_2$ as determined from H_2 ad- and desorption may be due to a decrease in particle size at higher reduction temperatures. This is not in agreement with the X-ray line broadening analysis, which gives small particles (3–4 nm, which corresponds to H/Ru of 0.36–0.27) irrespective of the reduction temperature applied. This indicates that not the metal dispersion itself but the active metal surface increases with increasing reduction temperature. This must then be due to a progressive removal of surface impurities, possibly chlorine (*22*). This is demonstrated by the effect of chlorine adsorption on the "metal dispersion" (H/Ru ratios in Table 3). Here, the Ru surface chlorine impurities have been simulated by treatment of a high temperature (973 K) activated "clean" Ru/SiO_2 with chlorine. Activation of the chlorine-treated Ru/SiO_2 at 673 K and 973 K gives the same

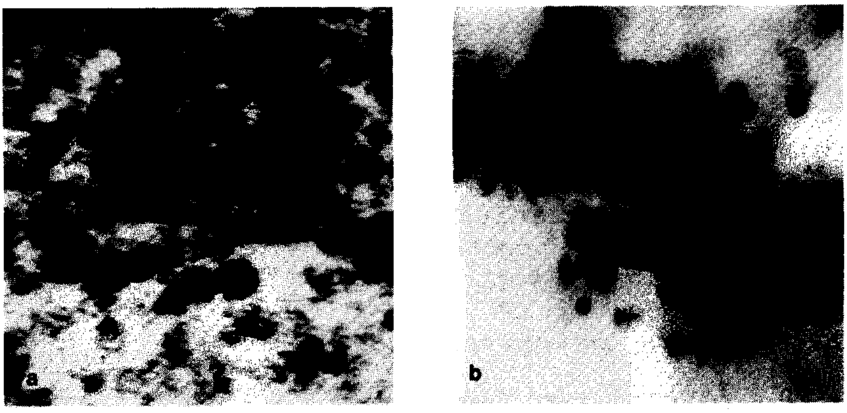

FIG. 10. Electron micrographs of Ru/SiO_2 from RuO_2/SiO_2 (H_2, 773 K, 2 h) (a) and Ru/SiO_2 from $RuCl_3/SiO_2$ (H_2, 763 K, 2 h) (b); scale: 1 mm = 2.5 nm.

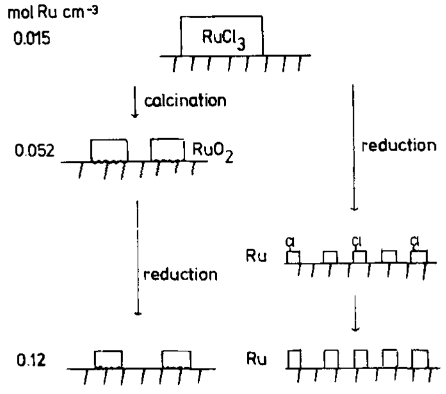

FIG. 11. Scheme of the activation of Ru/SiO_2.

H/Ru ratios as those found for Ru/SiO_2 prepared by direct reduction of $RuCl_3/SiO_2$ at these temperatures.

A scheme of the activation of Ru/SiO_2 catalysts is presented in Fig. 11. After the impregnation of the silica with a solution of $RuCl_3$ the surface of the silica is covered with $RuCl_3$ crystallites upon drying. Subsequent H_2 reduction at "low" temperature gives small ruthenium crystallites with surface contamination of chlorine, which is removed at higher reduction temperatures. Accordingly, a small and gradual H_2 consumption in TPR was observed between 673 and 973 K. The formation of small particles may be due to the substantial shrinking during the conversion of $RuCl_3$ to Ru. At high reduction temperature there is only a small increase in particle size due to sintering, which points to a strong metal–support interaction leading to thermally stable crystallites (*23*). A difference between directly reduced $RuCl_3/SiO_2$ and calcined-reduced $RuCl_3/SiO_2$ is a one-step versus a two-step shrinking of the ruthenium precursor, resulting in larger particles for the Ru/SiO_2 formed via the calcination procedure (8 nm). In addition the intermediately formed RuO_2/SiO_2 may result in less mobile ruthenium particles due to ruthenium–oxygen–silica interactions.

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REFERENCES

1. Samsonov, G. V. (Ed.), "Oxide Handbook," IFI/Plenum, New York, 1973.
2. Bortner, M. A., and Parravano, G., *Engelhard Ind. Tech. Bull.* **3**, 23 (1962).
3. Gonzalez, O. D., and Parravano, G., *J. Amer. Chem. Soc.* **78**, 4533 (1956).
4. Madey, T. E., Engelhardt, H. A., and Menzel, D., *Surface Sci.* **48**, 304 (1975).
5. Jenkins, J. W., McNicol, B. D., and Robertson, S. D., *CHEMTECH.*, 316 (1977); McNicol, B. D., and Short, R. T., *J. Electroanal. Chem.* **92**, 115 (1978).
6. Chaston, J. C., *Platinum Met. Rev.* **9**, 51 (1965).
7. Koopman, P. G. J., Kieboom, A. P. G., and van Bekkum, H., *Colloids and Surfaces* **3** (1981), in press.
8. Bayer, G., and Wiedemann, H. G., *Thermochim. Acta* **11**, 79 (1975).
9. Buyanova, N. E., Karnaukhov, A. P., Koroleva, N. G., Ratner, I. D., and Chernyavskaya, O. N., *Kinet. Catal.* **13**, 1364 (1972).
10. Taylor, K. C., *J. Catal.* **38**, 299 (1975).
11. Kubicka, H., *React. Kinet. Catal. Lett.* **5**, 223 (1976).
12. Kubicka, H., and Kuznicka, B., *React. Kinet. Catal. Lett.* **8**, 131 (1978).
13. Corro, G., and Gomez, R., *React. Kinet. Catal. Lett.* **12**, 145 (1979).
14. Kraemer, K., and Menzel, D., *Ber. Bunsenges. Phys. Chem.* **78**, 591 (1974).
15. Lytle, F. W., Via, G. H., and Sinfelt, J. H., *J. Chem. Phys.* **67**, 3831 (1977).
16. Michell, D., Rand, D. A. J., and Woods, R., *J. Electroanal. Chem.* **89**, 11 (1978).
17. Hadzi-Jordanov, S., Angerstein-Kozlowska, H., Vukovic, M., and Conway, B. E., *J. Electrochem. Soc.* **125**, 1471 (1978).
18. Koopman, P. G. J., Kieboom, A. P. G., and van Bekkum, H., *React. Kinet. Catal. Lett.* **8**, 389 (1978).
19. Robertson, S. D., McNicol, B. D., de Baas, J. H., Kloet, S. C., and Jenkins, J. W., *J. Catal.* **37**, 424 (1975).
20. Dalla Betta, R. A., *J. Catal.* **34**, 57 (1974).
21. Clausen, C. A., and Good, M. L., *J. Catal.* **38**, 92 (1975).
22. Ott, G. L., Delgass, W. N., Winograd, N., and Baitinger, W. E., *J. Catal.* **56**, 174 (1979).
23. Fiedorow, R. M. J., Chahar, B. S., and Wanke, S. E., *J. Catal.* **51**, 193 (1978).