

THE INTERACTION OF RUTHENIUM WITH A MgO MATRIX

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Ruthenium samples supported on MgO have been prepared and investigated by Thermal Programmed Reduction. Several TPR peaks have been observed and their assignment to chemical species containing reducible ions has been discussed.

Numerous physicochemical and catalytic investigations have shown that ruthenium particles interact with oxide supports [1-8]. The interaction between Ru and SiO₂ is weak and easily destroyed under reducing conditions [1, 4, 5], while the Ru-Al₂O₃ interaction is much stronger, giving rise to species reducible with difficulty [1, 2, 5]. Recent studies provide theoretical evidence of the presence of a strong metal-support interaction for highly dispersed metals [9, 10]. Ru supported on MgO also gives rise to some interaction, as indicated by the different catalytic behaviour, mainly in CO activation [7, 8], observed between samples heated in vacuo at 637 K before reduction and those reduced directly with hydrogen. According to some authors [11], Ru supported on MgO is partially proof against reduction, although reducible in the long run [12]. The existence of a stable Ru-Mg-O surface complex under oxidizing conditions has already been suggested on the basis of thermogravimetric measurements [13].

The aim of this work is to investigate the influence of the different thermal treatments on the occurrence of Ru-MgO interactions and to test their stability. An easy and suitable technique for studying highly dispersed systems containing a low metal loading is temperature-programmed reduction (TPR), which gives the amount of hydrogen consumed in the reduction of a sample with increasing temperature [14-17].

Samples were prepared by impregnating MgO with an aqueous solution of Ru nitroso nitrate (Pfalz & Bauer), RuNO(NO₃)₃ [1]. The N/Ru atomic ratio found by chemical analysis of samples dried at 343 K was 2.7, suggesting a complete loss of the NO groups during the preparation. The Ru content of the samples was 5.03 wt%, and the total specific surface area was 200 m²g⁻¹. The results were confirmed by examination of samples from different preparation batches.

The TPR experiments were performed with a mixture of 5% H₂ in argon, and the flow was regulated with a Matheson mod. 8240 Mass Flow Controller. Nitrogen cannot be used as carrier gas, due to the possible catalytic synthesis of ammonia. The test-tube had a diameter of 4 mm and was heated at a linear rate of 4 degree min⁻¹ from room

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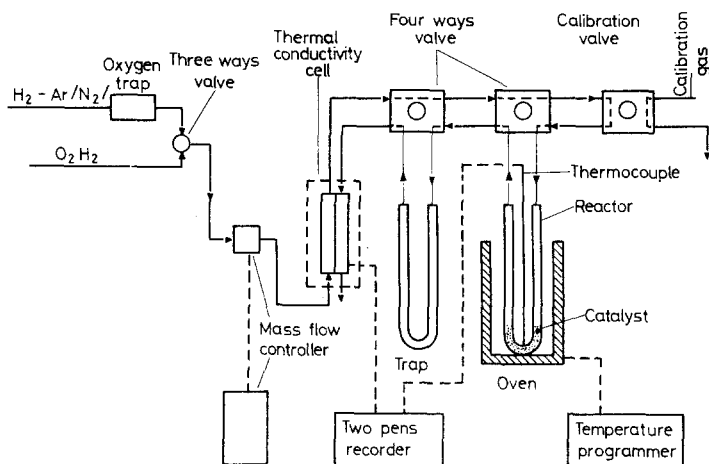


Fig. 1 Scheme of the temperature programmed reduction

temperature to 1073 K. The amount of catalyst was in the range 0.05–0.1 g. A cold trap was placed between the test-tube and the thermal conductivity (TC) detector. Before each run the TC detector response was calibrated by means of the injection of pure argon in the gas mixture. The TPR system is sketched in Fig. 1.

The different treatments of samples are summarized in Fig. 2. The temperatures of the peak maxima in the TPR profile and the number of hydrogen atoms consumed per ruthenium atom are shown in Table 1.

The TPR peaks are classified into five types (I–V), depending on their temperature maximum.

Table 1 Occurrence of TPR peaks, temperatures of the maxima and hydrogen consumptions (in H atoms per Ru atom) of samples described in Fig. 2 and some standards

Sample	I	II	III	IV	V	H/Ru
A			553		673	16–19
B1			513–518			0.8–1.4
B2		488		613		4
B3a	398	473				3.0
b	368–388					3.1
c	363					3.2
d	358					3.6
C			548–558	628–633		14, 19, 23
D		453	543		673	14
RuO ₂		443				4
Ru/MgO*	358					2.5

* After reduction with H₂ at 673 K and reoxidation in air at room temperature

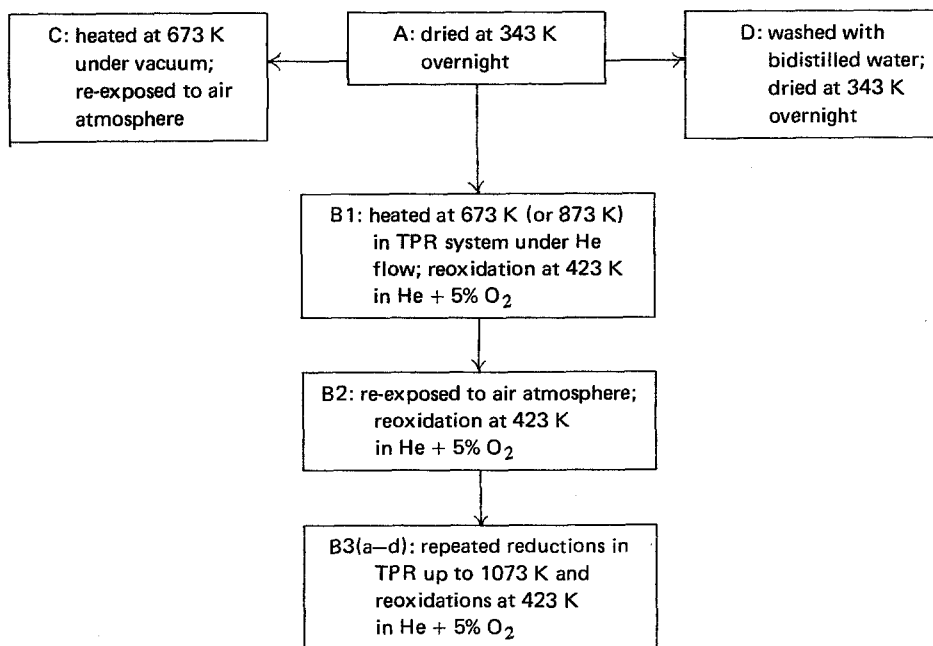
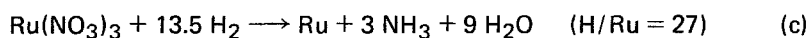
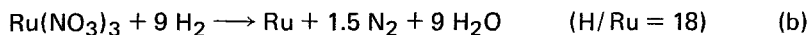


Fig. 2 Different treatments of samples

Figure 3 compares the TPR profiles of samples treated as reported in Fig. 2. For samples dried after impregnation (A), two peaks are observed, near 553 K (type III) and 673 K (type V), the former being much stronger than the latter. The hydrogen consumption is 5–6 times higher than that expected for the reduction of a Ru^{4+} species to metal:



that is 4. Since a N/Ru ratio of 2.7 was found by chemical analysis, the process must also involve the reduction of nitrate ions to N_2 and NH_3 . The presence of NH_3 traces in the outlet gas mixture was actually detected by inserting a Nessler trap after the TPR reactor. The experimental hydrogen consumption assumed a value between those expected for the two limiting equations (b) and (c):



After washing of sample A till nitrate ions could not be detected in the washings, the nitrate content of the sample was reduced by 70% (sample D). Its TPR diagram shows a strong intensity decrease of peak III, and the occurrence of a new peak (type II) at 453 K, while the high-temperature peak V appears unchanged. Peak II at 453 K has a maximum temperature similar to that for pure RuO_2 (Fig. 4).

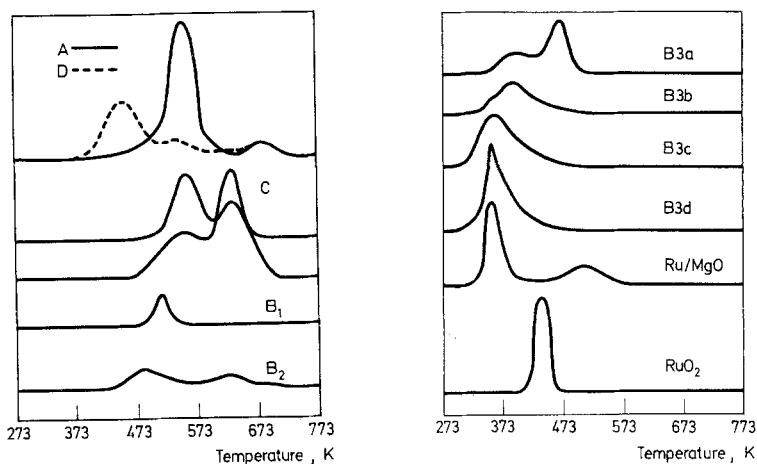


Fig. 3, 4 TPR profiles of samples treated in different ways

We can now attempt to assign peaks type II, III and V, in spite of the limitations of the TPR technique, such as chemical probe and system complexity.

It is known that MgO undergoes considerable transformation to hydroxide during impregnation, and that nitrate ions react with it [18]. We can reasonably assume that on sample A some sort of Ru hydroxide nitrate is present, and that some NO_3^- ions are now bonded to magnesium, for example giving rise to $\text{Mg}(\text{OH})\text{NO}_3$. The assignment of peaks III and V, respectively, to such species is supported by the results of TPR experiments carried out on pure Ru nitroso nitrate and on MgO previously treated with a dilute solution of HNO_3 .

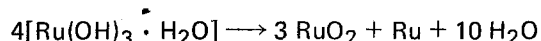
Washing would cause a more complete hydrolysis of Ru hydroxide nitrate, with formation of $\text{Ru}(\text{OH})_3$ or $\text{Ru}(\text{OH})_4$, which are stable solid phases. In solution, Ru hydroxide is easily oxidized to a Ru^{4+} species [19], which is highly probable in our case. Peak II for sample D, the growth of which clearly depends on the decrease of peak III, can be assigned to this species.

In previous work [8] we observed different catalytic behaviour in the activation of CO by Ru/MgO samples heated at 673 K under vacuum with respect to those directly reduced in the reactor. For this reason, a sample treated in this way (sample C) was taken into account. With respect to sample A, peak V disappeared in the TPR profile, peak III was maintained with reduced intensity, and a new peak occurred near 623 K (type IV). In repeated runs, the relative intensities of III and IV varied widely, as shown in Fig. 3. Nitrates are still present in the sample, as indicated by chemical analysis (about 35% of the initial amount) and a high H_2 consumption by TPR.

As this variability of the TPR profiles was initially attributed to experimental difficulties in managing the thermal treatment (i.e. temperature control, transfer of sample from vacuum bottle to TPR apparatus, etc.), new samples were prepared,

heating being performed directly in the TPR tube. Vacuum was substituted by an inert He flow. Surprisingly enough a very different results were obtained (sample B1): a single small peak III, associated with a very low hydrogen consumption. At the same time the nitrogen content was reduced to less than 10% of the initial amount.

Very similar results were obtained by varying the heating temperature up to 873 K and also by inserting a soft oxidizing step (5% O₂ in He for 2 h) between the heating and reduction. This latter allows exclusion of the occurrences of a partial reduction due to H₂ traces in the He, or to a disproportionation reaction [19]:



A possible relation between samples C and B1 was found by exposing the latter, after TPR, to an air flux for 2 h, followed by reoxidation with 5% O₂ in H₂ at 423 K and a new TPR run (sample B2). A peak of type IV again occurred (near one of type III) and the hydrogen consumption increased by a factor of almost 4. The residual nitrate content did not change with respect to B1.

This leads to an important conclusion, which must be confirmed by a more extensive investigation. In B2, the Ru, although in a non-metallic state does not seem available for reduction. On heating in an inert atmosphere, the formation of a Ru-O-Mg complex stable under reducing conditions is suggested. On this basis the TPR profile of sample C can also be interpreted. The contact of the sample with atmosphere humidity causes the fast hydroxylation of MgO, and destroys this complex. A surface compound between Ru, Mg, OH⁻ and possibly NO₃⁻ ions is formed, peak IV originating on reduction. When sample B2 was subjected to several reduction-oxidation cycles, a gradual shift of the peaks towards lower temperatures was observed (samples B3a-d and Fig. 4). A H/Ru ratio approaching the value expected for the reduction of RuO₂ was found. The final peak maximum temperature is 360 K, much lower than that for pure RuO₂, but similar to that found for sample A after reduction at 673 K and reoxidation at room temperature. In the latter case, a small residual peak III is present.

Similar low-temperature peaks (type I) were obtained on SiO₂-supported Ru samples [17, 20], a system where metal-support interactions are weak [8]. It can be inferred that RuO₂ in small particles, not interacting with the support, is more easily reduced than bulk RuO₂. The progressive temperature shifts in samples B3a-d represent the progressive destruction of such interactions in the Ru/MgO system.

TPR has proved a powerful technique for study of the interactions between precursors, metals and supports during the preparation of supported catalysts. The cooperation of other physicochemical techniques is necessary, for the complete identification of species giving rise to the TPR peaks.

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Zusammenfassung – Proben von auf MgO aufgebrachten Ruthenium wurden hergestellt und durch temperaturprogrammierte Reduktion untersucht. Es wurden verschiedene TPR-Peaks beobachtet und deren Zuordnung zu reduzierbare Ionen enthaltenden chemischen Species diskutiert.

Резюме — Получены и исследованы методом термического программированного восстановления (ТПВ) образцы рутения на подложке из MgO. Обсуждено отнесение наблюдаемых ТПВ-пиков к химическим частицам, содержащих восстанавливаемые ионы.