

## Behaviour of Neodymia as a Support of Highly Dispersed Rhodium\*

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One of the major problems in interpreting the behaviour of the rare earth oxide-supported metal phases as catalysts is the lack of papers devoted to their characterization [1–4]. In particular, few of them have dealt specifically with the supports [5–8], and this knowledge is required as one of the clues to understanding in depth this interesting group of catalysts.

As far as neodymium oxide-supported metal catalysts are concerned, a few papers have appeared at present [1, 4, 9–12]. Nevertheless, the extent of the characterization studies carried out in the above papers should be considered rather limited.

The present work investigates the behaviour of lanthanide oxides as supports. Our major concern here is the study of the evolution undergone by the neodymia support throughout the whole preparation process leading to the dispersed metal catalysts. Results on the preparation of lanthana-, samaria-, ytterbia- and ceria-supported rhodium phases have already been reported in refs. 5 to 8.

## Experimental

In order to work with a well-defined starting support phase, a sample of hexagonal neodymium oxide (prepared by calcination of an air-aged oxide sample in flowing He at 1273 K for 24 h) was treated with H<sub>2</sub>O at 353 K for 24 h, as suggested by Rosynek [13]. The Nd(OH)<sub>3</sub> phase prepared in this way was further exposed to air for several weeks so that partially carbonated Nd(OH)<sub>3</sub> was obtained, which behaved very similarly to the air-aged lanthana samples [14].

The above starting support sample was impregnated with an aqueous solution of Rh(NO<sub>3</sub>)<sub>3</sub>, 36% Rh (Ventron), following the incipient wetness impregnation technique. In order to achieve a final metal loading of 1%, seven successive cycles of

impregnation at 298 K and drying in air at 383 K for 10 h were necessary.

The starting support sample was also submitted to a series of wetting–drying cycles with distilled water, as in the impregnation process. To distinguish the sample thus treated from the true neodymium oxide, it will hereafter be referred to as Nd<sub>2</sub>O<sub>3</sub>(\*).

The BET surface area of the impregnated sample was found to be 17 m<sup>2</sup> g<sup>-1</sup>. This value was not modified by the reduction treatments carried out at both 623 K and 723 K.

The thermogravimetric analysis (TG) and temperature programmed decomposition (reduction) [TPD (R)] experiments were performed in flowing gas, either He or H<sub>2</sub>. The flow rate was always 1 × 10<sup>-6</sup> m<sup>3</sup> s<sup>-1</sup> (60 cm<sup>3</sup> min<sup>-1</sup>), and the heating rate 0.1 K s<sup>-1</sup>. Analysis of the evolved gases was carried out by mass spectrometry (MS).

The X-ray diffraction diagrams were obtained with a Siemens instrument, model D-500, using Cu K $\alpha$  radiation.

## Results and Discussion

The TG diagrams obtained for the decomposition of Nd<sub>2</sub>O<sub>3</sub>(\*) and Rh(NO<sub>3</sub>)<sub>3</sub>/Nd<sub>2</sub>O<sub>3</sub>(\*) samples in flowing helium, as well as for the reduction of the latter in flowing H<sub>2</sub> are available as 'Supplementary Material'. The behaviour of the neodymium samples above is very similar to that already found by us for an analogous series of phases of lanthanum [5]. According to ref. 5, the first two well-defined steps can be interpreted as due to the dehydration of Nd(OH)<sub>3</sub> through oxyhydroxide, NdO(OH). A third step on the other hand, would account for the decomposition to oxide of a dioxy monocarbonate phase, Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. From this third step the total amount of CO<sub>2</sub> taken up by the support sample can be estimated. This amount is found to be ca. 20 molecules per nm<sup>2</sup>. The total weight loss by calcination is 17.0%.

When the decomposition of Rh(NO<sub>3</sub>)<sub>3</sub>/Nd<sub>2</sub>O<sub>3</sub>(\*) is carried out in flowing H<sub>2</sub> the third step completely disappears, which suggests that in the former case elimination of the carbonated phase on the support takes place at a much lower temperature. To confirm this, the reduction of Rh(NO<sub>3</sub>)<sub>3</sub>/Nd<sub>2</sub>O<sub>3</sub>(\*) has also been studied by TPR–MS, see Fig. 1. For comparative purposes, the TPR–MS spectra for *m/e* = 15 (CH<sub>4</sub>), *m/e* = 18 (H<sub>2</sub>O) and *m/e* = 44 (CO<sub>2</sub>) corresponding to Nd<sub>2</sub>O<sub>3</sub>(\*) have also been included in Fig. 1.

When the traces corresponding to *m/e* = 44 in Fig. 1 are analysed, it should be noted that the full scale used to plot the signals is ten times lower than

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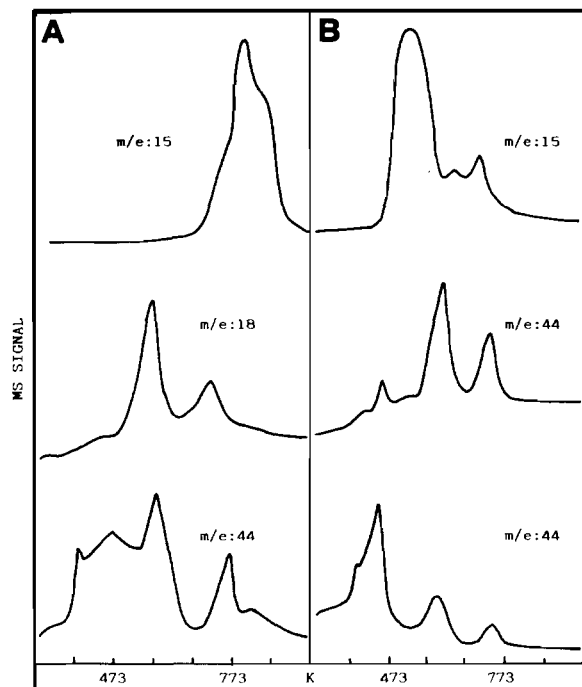


Fig. 1. Study by TPR-MS of: (A)  $\text{Nd}_2\text{O}_3(*)$ ; (B)  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$ . The mass/charge ratios,  $m/e$ , are indicated on the diagrams.

in the case of the TPD-MS experiments carried out in flowing He. This means that the amounts of evolved  $\text{CO}_2$  are now much smaller. On the other hand, the shape of the traces for  $m/e = 44$  in Fig. 1 shows that no evolution of  $\text{CO}_2$  occurs at temperatures above 773 K. According to the traces for  $m/e = 15$ , the carbonated phase is reduced by  $\text{H}_2$  with formation of  $\text{CH}_4$ . Comparing the traces obtained for  $\text{Nd}_2\text{O}_3(*)$  and  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$  it is obvious that the reduction of the carbonated phase takes place at a much lower temperature in the presence of rhodium. Quite similar findings have already been reported by us for lanthana-impregnated rhodium nitrate samples [5]. Since the evolution of  $\text{CH}_4$  from  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$  starts at about 473 K, it is very likely that the reduction to metal of the rhodium salt occurs at a lower temperature, which is consistent with the peak observed at 450 K on the TPR-MS trace, i.e.  $m/e = 18$  for the impregnated sample. Furthermore, the temperature mentioned above, 450 K, falls within the range of those previously found by us for the reduction of  $\text{Rh}(\text{NO}_3)_3$  dispersed on several different rare earth oxides [5-8].

In contrast with the reduction of the carbonated phase on the support, no activation by rhodium of its dehydration seems to occur.

According to our thermogravimetric results, also confirmed by the TPR results in Fig. 1, the preparation of a true neodymia-supported catalyst would require reduction temperatures at about 723 K;

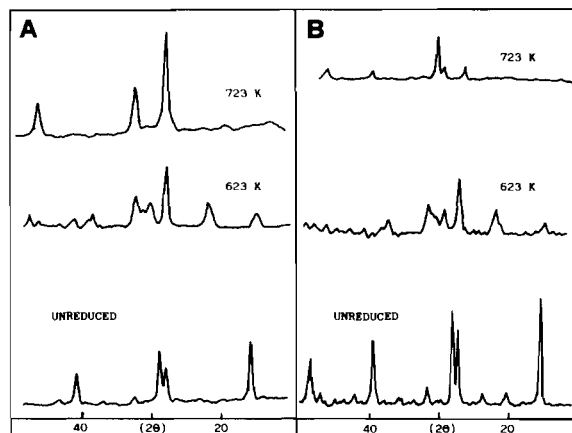


Fig. 2. X-ray diffraction study of: (A)  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$  as well as the phases resulting from its reduction at 623 K and 723 K; (B) the same study on  $\text{Rh}(\text{NO}_3)_3/\text{La}_2\text{O}_3(*)$ .

otherwise, phases other than the sesquioxide would constitute the actual support. It is worth noting, however, that the reduction of  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$  takes place through two well-resolved steps which suggests that if appropriate reduction conditions are selected, well-defined support phases other than the oxide can be obtained.

Based on the results reported here and our previous experience on lanthana-supported phases [5, 6], two reduction temperatures have been selected: 623 K and 723 K. As in refs. 5 and 6, the reduction was carried out in flowing  $\text{H}_2$  at a heating rate of  $0.1 \text{ K s}^{-1}$ . When the reduction temperature was reached, the sample was held for 1 h at that temperature.

The X-ray diffraction patterns of the phases obtained upon reduction, as indicated above, are depicted in Fig. 2, in which the diagram of the unreduced sample,  $\text{Rh}(\text{NO}_3)_3/\text{Nd}_2\text{O}_3(*)$ , has also been included. The diffraction pattern of the latter phase essentially agrees with that of  $\text{Nd}(\text{OH})_3$ , whereas the diffraction lines observed in the diagrams of the samples reduced at 623 K and 723 K can be assigned to  $\text{NdO}(\text{H})$  and  $\text{Nd}_2\text{O}_3\text{-C}$ , respectively. For comparative purposes, Fig. 2 also includes the parallel study carried out on  $\text{Rh}(\text{NO}_3)_3/\text{La}_2\text{O}_3(*)$  [5]. According to Fig. 2, the diagrams of the lanthanum and neodymium samples reduced at 623 K, as well as those of the unreduced phases, are very similar to each other. On the contrary, the diffraction patterns obtained for lanthana and neodymia catalysts reduced at 723 K show notable differences, which can be interpreted in terms of the different structural nature of the 4f oxide phase, cubic in the case of  $\text{Nd}_2\text{O}_3$ , and hexagonal in the case of  $\text{La}_2\text{O}_3$ . This can constitute a significant difference because, as we have recently found [15], the structures of the rare earth sesquioxides have considerable influence on their reactivities.

To summarize, the study of the evolution undergone by a neodymia-supported rhodium nitrate phase, prepared in the usual way, indicates that, as in the previously investigated case of lanthana, the reduction treatment with flowing H<sub>2</sub> induces very strong alterations of the chemical and structural nature of the support, whose dehydration takes place through an oxyhydroxide phase intermediate. Likewise, it has been observed that the presence of rhodium activates the reduction of the carbonated phase on the support, but not its dehydration. In contrast with that found for lanthana-supported rhodium catalysts on reduction at 723 K, the neodymium support phase is constituted by the cubic phase of the oxide.

### Supplementary Material

TG diagrams are available from the authors on request.

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