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PREPARATION OF CATALYSTS CONSTITUTED BY RHODIUM SUPPORTED ON TWO CERIUM DIOXIDES WITH DIFFERENT SURFACE AREA

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ABSTRACT

The preparation of two ceria-supported rhodium catalysts has been studied by means of XRD, TG, TPD-MS and TPR-MS. The two cerium dioxides used here, from different origins, showed BET surfaces areas of 19 m^2g^{-1} and 110 m^2g^{-1}. According to the TPR-MS study the $Rh(NO_3)_3/CeO_2$ samples, the precursor reduction takes place at slightly lower temperature over the ceria sample with higher surface area. The preparation of rhodium supported on free carbonate ceria samples requires reduction temperatures higher than approximately 600 K. The reduction of the support has been found to occur at about 873 K. The temperature at which this latter process is observed, as well as the intensity of this reaction, was found to be independent both of the ceria sample investigated and of the presence of supporting rhodium. The study by XRD of the reduced and unreduced samples suggests that associated with the reduction treatment in flow of H_2, some sintering of the support occurs. In accordance with our results, upon reduction at 773 K, changes of the surface area from 110 m^2g^{-1} to 20 m^2g^{-1} can be observed.

INTRODUCTION

The cerium dioxide supported metal catalysts started to be studied a few years ago [1-9]. Likewise, some very recent papers have dealt with supported metal catalysts containing ceria as promoter [10-12]. Over some of these phases, quite interesting catalytic properties have been observed [11, 12]. Also, strong metal-support interaction phenomena have been reported to occur on ceria-supported nickel [7] and platinum [1] catalysts. In accordance with this, the papers above have primarily been concerned with the catalytic activity and the characterization of the supported metals. Much less attention has been paid to the investigation of the processes involved in the preparation of these catalysts.

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The study of the evolution undergone by both the precursor metal salt and the support throughout the whole preparation process, however, can contribute to establish experimental conditions for the preparation of ceria supported metal catalysts on a grounded basis.

The present work, which should be inscribed in a general research program aimed at investigating the preparation of rare earth oxide supported metal catalysts [13,14], reports on the preparation of two cerium dioxide supported rhodium catalysts. The two ceria samples used here showed quite different surface areas. In this study, thermogravimetric analysis, in both helium and hydrogen flow, temperature programmed decomposition, temperature programmed reduction and X-ray diffraction techniques have been used.

EXPERIMENTAL

The two ceria samples studied here, both 99.9% pure oxides, were respectively from Ventron (CeO_2-R) and Union Molycorp (CeO_2-MO). Before their use as starting support materials, the oxides were exposed to air until they reached an apparent stabilization. The BET surface area of the aged in air oxides, as determined by nitrogen adsorption at 77 K, was 19 m^2g^{-1} for CeO_2-R, and 110 m^2g^{-1} for CeO_2-MO. Upon impregnation of the supports, their surface areas did not significantly change.

The metal precursor salt was $Rh(NO_3)_3 2H_2O$ from Ventron, of 36% rhodium content. The rhodium nitrate was deposited onto the ceria samples by the incipient wetness impregnation technique, from aqueous solution of the transition metal salt. In order to achieve the final rhodium loading, 1%, six impregnation cycles consisting of wetting the supports followed by drying in air at 383 K, were needed.

The thermogravimetric analysis (TG), temperature programmed decomposition (TPD) and temperature programmed reduction (TPR) experiments were all carried out in flow of either He or H_2, at a flow rate of 1 cm^3s^{-1}, and at a heating rate of 0.1 K s^{-1}. The analysis of the evolved gases was performed by means of mass spectrometry (MS). The X-ray diffraction (XRD) study was carried out with a Siemens instrument, model D-500; the radiation was CuKα and the filter of nickel.

RESULTS AND DISCUSSION

The two cerium dioxide samples used as starting support phases, were studied by XRD, TG and TPD-MS. These ceria samples were then submitted to six succesive cycles of wetting with distilled water and drying in air, as in the true impregnation process, and further characterized by using the same techniques above.

No alterations on the ceria samples could be observed after the simulated impregnation treatment. Figures 1, 2 and 3 account respectively for the results of the XRD, TG and TPD studies carried out on the treated ceria samples.

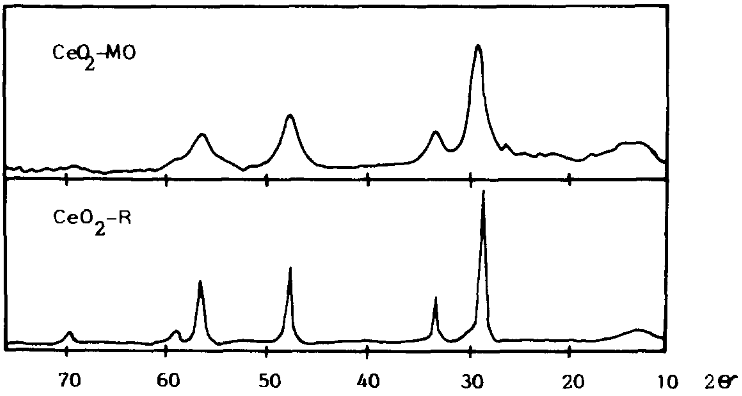

Fig. 1. XRD diagrams of the two ceria samples previously submitted to six wetting-drying cycles with distilled water.

According with Fig. 1, the only diffraction lines that can be observed on the diagrams corresponding to the two ceria samples are those of the cubic phase, fluorite-like structure, of the oxide. It is worth noting, however, that the diffraction lines are much broader in the case of the CeO_2-MO sample, wich suggests that the particle size is smaller in this oxide sample. This observation, wich is consitent with the larger surface area of CeO_2-MO, is also supported by TEM studies.

In contrast with that observed by us on various lanthanide sesquioxides [15-19], the hydration and carbonation phenomena occurring at the two cerium oxides seem to be surface processes. In effect, in addition to the results of the XRD study reported above, the TG diagrams in Fig. 2 suggest that the total weight loss is much smaller in the sample with lower surface area. Furthermore, according to the TPD-MS spectra depicted in Fig. 3, the major peak of H_2O occurs on both oxides at about 373 K, wich would indicate an important contribution of the weakly retained water to the total weight loss.

The oxide samples resulting from the wetting-drying treatment in distilled water have also been studied by TPR-MS. The diagrams corresponding to the evolution of water are reported in Fig. 4.

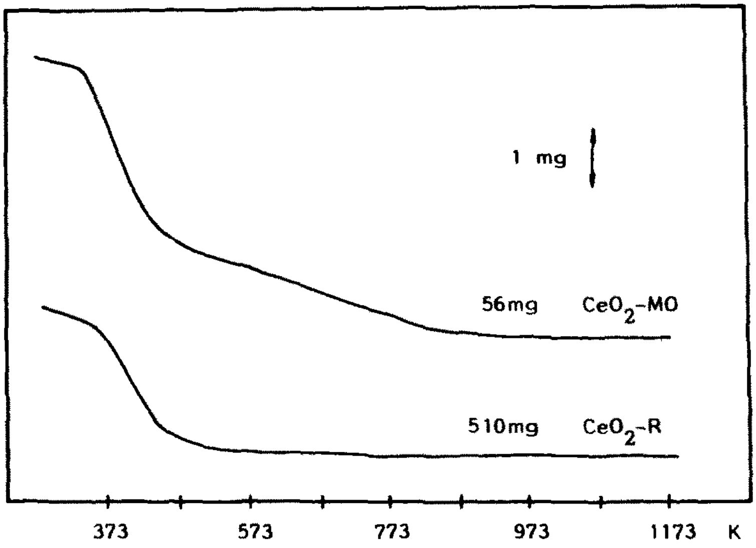

Fig. 2. TG diagrams of the two ceria samples previously submitted to six wetting-drying cycles with distilled water.

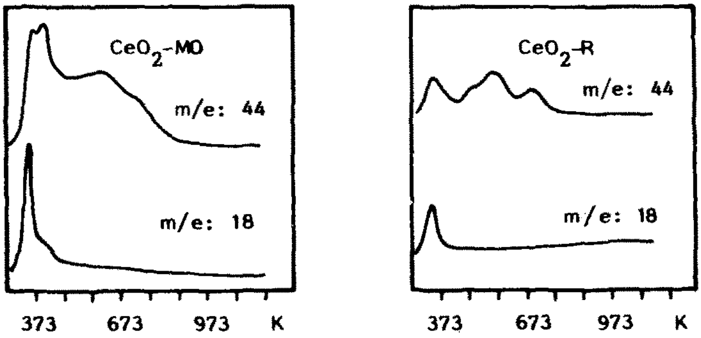

Fig. 3. TPD-MS diagrams of the two ceria samples previously submitted to six wetting-drying cycles with distilled water.

It is particularly noteworthy the appearance on both ceria samples of a feature, centered at around 873 K, not found on the corresponding TPD-MS diagrams shown in Fig. 3. This peak, also observed on the TPR-MS traces for $Rh(NO_3)_3/CeO_2$ included in Fig. 5, can be interpreted as due to the reduction of the cerium dioxides [20]

The XRD diagrams of the two ceria impregnated rhodium nitrate samples did not revealed any substantial difference with respect to those reported in Fig. 1.

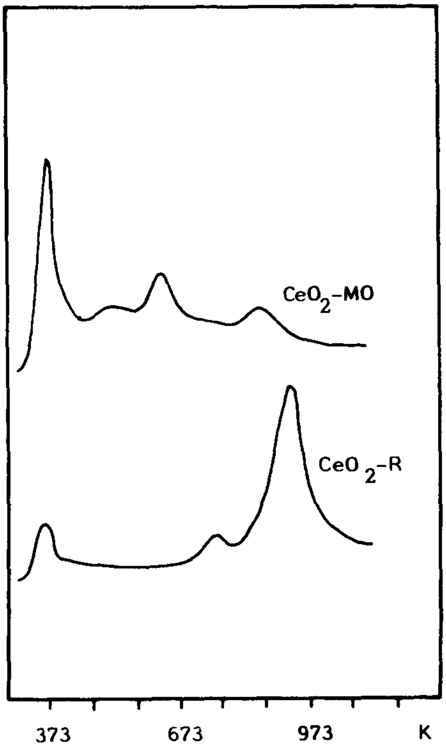

Fig. 4. TPR-MS traces for m/e: 18 (H_2O) corresponding to the two ceria samples submitted to six wetting-drying cycles with distilled water.

Two aspects will be distinguished in the analysis of the TPR-MS diagrams obtained for the two $Rh(NO_3)_3/CeO_2$ samples, (Fig. 5), on the one hand the reduction of the rhodium precursor salt, and on the other hand the evolution undergone by the support. In order to carry out this analysis, the signals corresponding to m/e: 14 (CH_4 and NH_3), m/e: 17 (NH_3 and H_2O) and m/e: 18 (H_2O) are reported in Fig. 5.

The reduction to ammonia of the rhodium nitrate, as deduced from the comparison of the traces for m/e: 14, 17 and 18, occurs at slightly different temperatures on the two samples. The lowest reduction temperature, 373 K, was found on the CeO_2-MO supported sample. In this case, the ammonia peak is very narrow, which would indicate that the reduction of the rhodium nitrate takes place very rapidly. Since the surface area of CeO_2-MO is much higher than that of CeO_2-R, the results above suggest that the higher dispersion of the precursor salt, the faster the reduction process. A quite similar effect has been observed

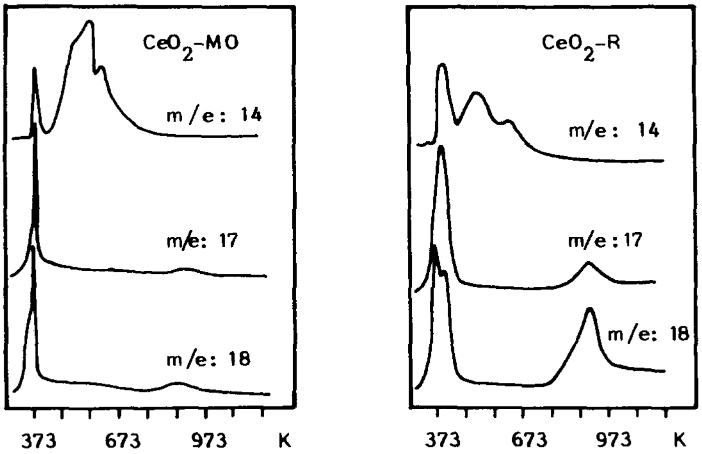

Fig. 5. TPR-MS diagrams of the two ceria supported rhodium nitrate samples.

by us on two lanthana supported $Rh(NO_3)_3$ samples with 1% and 10% metals loadings [14].

Upon comparison of the reduction temperatures deduced from Fig.5 to those found by us for several lanthana, samaria and ytterbia supported rhodium nitrate samples [14], and even to that deduced from the TG study reported in reference [21] for $Rh(NO_3)_3/Al_2O_3$, it can be concluded that in all these cases, the reduction of the rhodium nitrate takes place within a relatively narrow range of temperatures, which suggests that the reducibility of this rhodium salt is not significantly modified by the nature of the support. In fact, our results suggest that the reducibility of the rhodium nitrate is more influenced by the dispersion of the precursor salt than by the support. This contrasts with the results reported in reference [7], according to which the nature of the support can strongly modify the temperature at which the reduction of the transition metal precursor occurs.

With regard to the evolution undergone by the support, it can be noted that only negligeable amounts of CO_2 could be detected in the TPR-MS experiments; instead, the evolution of methane, starting below 473 K, could be observed. This suggests that, as in the case of several other rare earth oxide supported rhodium nitrate phases [14], the presence of the transition metal activates the reduction of the carbonate species on the support. According to Fig. 5, the preparation of rhodium supported on free-of-carbonate ceria samples requires reduction temperatures around 623 K.

A second aspect of the TPR-MS diagrams depicted in Fig. 5 which deserves some further comments is that concerning the evolution of water. According to the traces for m/e: 17 and m/e: 18 the two ceria impregnated samples show a peak at about 873 K, which should be adscribed to the reduction of the support. Since in the case of $Rh(NO_3)_3/CeO_2$-MO sample the traces for m/e ratios above show a very narrow peak at 373 K, assigned to the reduction of the nitrate, that at 873 K appears as a tiny feature. Nevertheless, the TG experiments performed in flow of H_2 have demonstrated that the weight loss associated with the high temperature peak commented on above is just the same for the two ceria supported samples, 0.9%, which suggests that a reduction process affecting the bulk of the oxides has occurred [20] . If the TPR-MS traces for m/e: 18 reported on Fig. 4 and 5 are compared, it can de deduced that the temperature at which the reduction of the cerium oxides takes place is not affected by the presence of rhodium. Furthermore , the study by TG of the reduction process indicates that the weight loss associated with the high temperature step is the same, no matter if rhodium is present or not. No influence on the reducibility of ceria due to platinum supported on it has been observed earlier [20].

The phases resulting from the reduction of the two ceria supported samples has been studied by XRD. The only diffraction lines that could be observed were those corresponding to the cubic phase of the cerium dioxide. Accordingly, no evidences for the existence of metallic rhodium could be obtained from the XRD diagrams. This was so even in the case of samples reduced at temperatures as high as 973 K, (Fig. 6) which

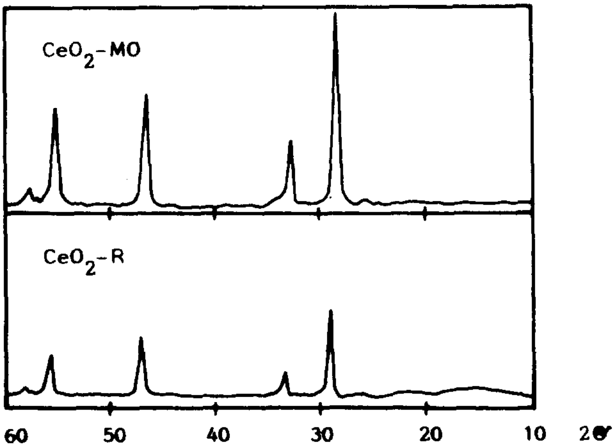

Fig. 6. XRD diagrams obtained upon reduction at 973 K the two ceria supported rhodium nitrate samples.

would indicate that the rhodium particles are well dispersed, and, on the other hand, that no sintering of the metal crystallites has occurred.

If the XRD patterns reported in Fig. 6 are compared to those depicted in Fig. 1, it can be observed that the diffraction lines obtained for the reduced phases are narrower than those corresponding to the ceria supported rhodium nitrate, specially in the case of CeO_2-MO. This can be interpreted assuming that, associated with the reduction treatment, some sintering of the support occurs. In agreement with this interpretation, the BET surface area values determined for $Rh(NO_3)_3/CeO_2$-MO reduced at 623 K and 773 K were found to be, respectively, 50 m^2g^{-1} and 20 m^2g^{-1}.

CONCLUSION

It can be concluded from our study of the processes involved in the preparation of the two ceria supported rhodium catalysts that, by contrast to that found on several <u>4f</u> sesquioxides [15-19], the ceria samples impregnated with aqueous solutions of the rhodium nitrate do not seem to exhibit alterations of their bulk structures. In particular, from the TPR-MS study some interesting conclusions can be obtained. The surface area of the starting support oxides seems to slightly affect the reducibility of the precursor salt. The carbonate species on the ceria samples can only be eliminated upon reduction at temperatures around 623 K. When the ceria supported samples are treated in flow of hydrogen, reduction which affects the bulk of the oxides seems to occur at about 873 K. Neither the temperature nor the intensity of this reduction process is significantly modified by the presence of the supported rhodium. The temperature above can be considered a reference in studies aimed at investigating the ocurrence of strong metal-support interaction phenomena over ceria supported metal catalysts.

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