Journal of Alloys and Compounds, 180 (1992) 271–279
JAL 8080

Preparation and characterization of a praseodymium oxide to be used as a catalytic support

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Abstract

This work reports on the preparation and characterization of a praseodymia sample to be used as a support for highly dispersed metals. The oxide sample was prepared by decomposing in a flow of helium, at 973 K, the phase obtained by precipitation with ammonia from a solution of $Pr(NO_3)_3$. The preparation conditions were established after investigating the thermal evolution of the precursor phase by thermogrammetric analysis, temperature-programmed decomposition–mass spectrometry, Fourier transform IR spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Data corresponding to the textural and chemical characterization studies carried out on the oxide are also presented and discussed.

1. Introduction

Rare-earth-oxide-supported (promoted) metals constitute a relatively new class of multicomponent catalytic systems showing rather unconventional behaviours [1–4]. In particular, ceria-containing phases have received very much attention because of their use as three-way catalysts [5, 6].

The characterization of ceria-supported metal catalysts can also be considered a major scientific challenge. In effect, it is generally acknowledged that the chemistry of ceria against some of the classic probe molecules such as CO and H_2 is rather complex [7–12]. Likewise, several workers have reported the occurrence of strong metal support interaction phenomena on a number of M–CeO_2 catalysts [13–16]. At present, the actual nature of this interaction remains unclear [17, 18].

Contrary to the case of M–CeO_2 catalysts, the literature concerning some other reducible rare earth oxides such as praseodymia is rather scarce [19, 20]. In spite of this, it is our opinion that the investigation of M–PrO_x systems, in addition to its intrinsic scientific interest, might well contribute to a better understanding of the characterization problems and metal–support interaction phenomena observed on ceria containing catalysts. This prompted us to initiate this research project the first results of which are presented here.

This work reports on the preparation and characterization of a praseodymium oxide to be used as transition metal support. In accordance with

0925-8388/92/$5.00

the application that we have foreseen for the oxide, we have tried to prepare a sample with a mean surface area value, good textural stability under the reducing conditions used during the preparation of the supported metal catalysts, and an anionic impurity content as low as possible, particularly with respect to carbonates.

2. Experimental details

The praseodymium oxide was prepared from $Pr(NO_3)_3 \cdot 6H_2O$, 99.9% pure, supplied by Fluka. The concentrated aqueous ammonia used here was from Merck.

The thermogravimetric analysis (TGA) experiments were performed in a Mettler model TA-H 20 balance. Our temperature-programmed decomposition (TPD) or reduction studies with analysis of the evolved gases by mass spectrometry (MS) were carried out under the following conditions: flow rate of either helium or H_2 through the reactor, 1 cm^3 s^{-1}; heating rate, 10 K min^{-1}. Details of the experimental set-up have been given elsewhere [21].

X-ray diffraction (XRD) patterns were recorded with a Siemens model D-500 instrument interfaced to a microcomputer. The radiation was Cu Kα, and a filter of nickel was used.

The IR spectra were recorded with a Fourier transform IR (FTIR) instrument from Philips, model PU9800. The sample disks were prepared in a KBr matrix (95% KBr and 5% sample).

The transmission electron microscopy (TEM) images were obtained with a JEOL model 2000 EX instrument, equipped with a top-entry specimen holder and ion pump. The scanning electron microscopy (SEM) study was performed with a JEOL model 820 instrument.

The Brunauer–Emmett–Teller (BET) surface area of both the precursor and the final oxide phases were determined by nitrogen adsorption at 77 K.

3. Results and discussion

The procedure followed by us to prepare the praseodymium oxide consisted of the thermal decomposition, in a flow of helium, of a precursor phase obtained by adding an excess of concentrated ammonia to an aqueous solution of $Pr(NO_3)_3$. The precipitate was washed several times with distilled water, dried in an oven at 383 K and further stored with no special precautions. The specific conditions used for the preparation of the oxide sample were established after investigating the thermal evolution of the precursor phase by TGA, TPD–MS, FTIR spectroscopy, SEM and TEM.

Earlier studies [22] dealing with the preparation of rare earth oxides by means of a method similar to that used here suggest that, in the present case, the precursor phase would consist of partially nitrated and carbonated praseodymium(III) hydroxide. This suggestion is confirmed by the XRD and FTIR characterization studies carried out on the precursor.

According to the TPD–MS diagrams for the precursor phase given in Fig. 1, the main decomposition processes, those involving the elimination of H_2O and NO_x, take place below 773 K. This is also confirmed by TGA. It should be noted, however, that in accordance with the TPD diagram for CO_2 (*m/e*, 44), the complete elimination of carbonates requires much higher decomposition temperatures. Taking also into account the trace for $m/c = 32$, which gives information about the evolution of O_2, *i.e.* on the thermal stability of the different non-stoichiometric praseodymia phases, the following preparation conditions were established. The precursor phase was calcined in a flow of helium (1 cm^3 s^{-1}), at a heating rate of 5 K min^{-1}, up to 973 K; the sample was further held at 973 K for 1 h, and then it was cooled to room temperature, always in a flow of inert gas.

The XRD pattern for the recently prepared praseodymium oxide (Fig. 2(a)) fits well that reported in the ASTM file for Pr_6O_{11}.

The praseodymia sample was also studied by TPD–MS (Fig. 3). As in the case of the remaining characterization studies carried out on the final oxide phase, this TPD–MS experiment was performed within the first 48 h after its preparation. Regarding Fig. 3, some interesting aspects can be outlined. The signals for H_2O and CO_2 are much less intense than those reported for the precursor in Fig. 1. In particular, the trace for water shows a first peak, the most intense one, at around 400 K, which might well correspond to weakly adsorbed molecular water; a second peak occurs at around 525 K, and several other small features spread over a wide range of temperatures. These latter might reasonably be assigned to dissociatively

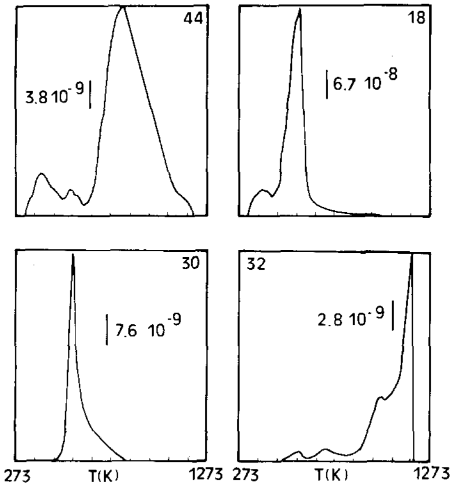

Fig. 1. TPD–MS study of the precursor phase. Traces corresponding to the evolution of CO_2 ($m/e = 44$), H_2O ($m/e = 18$), NO ($m/e = 30$) and O_2 ($m/e = 32$). The ordinate scale, in Torrs, for each of the signals is indicated on the figure.

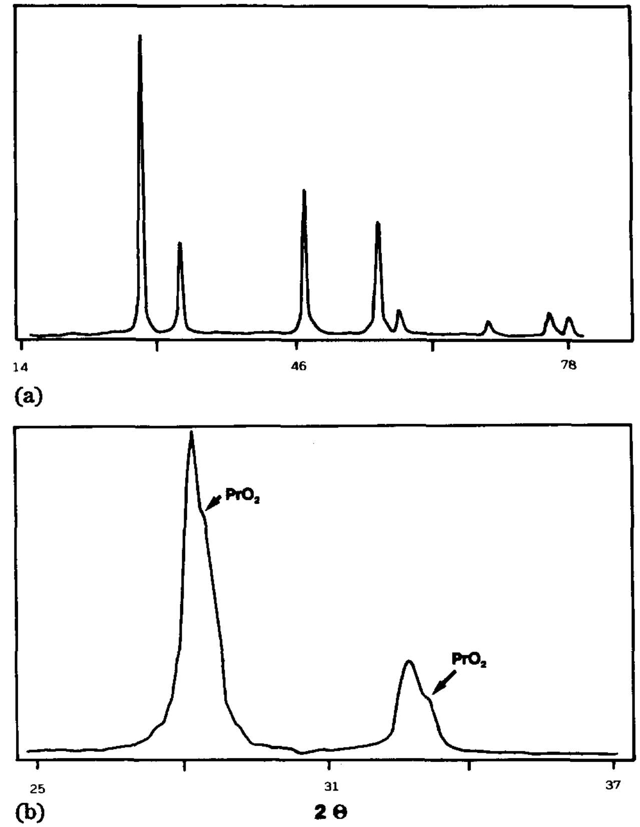

Fig. 2. XRD diffraction patterns of the praseodymia sample prepared in this work: (a) recently prepared; (b) aged in air, at 298 K, for 6 months.

chemisorbed water. The trace for CO_2 in Fig. 3 is about three times less intense than that shown in Fig. 1. In spite of its complexity, two main regions can be distinguished in it. Peaks appearing in the lower temperature region, *i.e.* below 873 K, can be assigned to surface carbonate species formed upon exposure of the oxide to air, at room temperature; the feature peaking at about 1073 K, on the contrary, might well correspond to residual inner carbonate species not decomposed during the calcination treatment, leading to preparation of the oxide. In other words, the high temperature peak can be used as a rough indication of the carbonate content intrinsically associated with the preparation procedure followed by us. The residual content of nitrate species was found to be negligible; the signal reported in Fig. 3 is about 200 times less intense than that obtained for the precursor in Fig. 1; furthermore, the temperature at which the peak is observed in Fig. 3, 725 K, would indicate that it can proceed from surface contamination occurred after the preparation. Regarding the evolution of oxygen ($m/e = 32$), Fig. 3 shows the occurrence of a narrow peak at 800 K, well below the temperature reached during the calcination treatment (973 K). This suggests that, upon

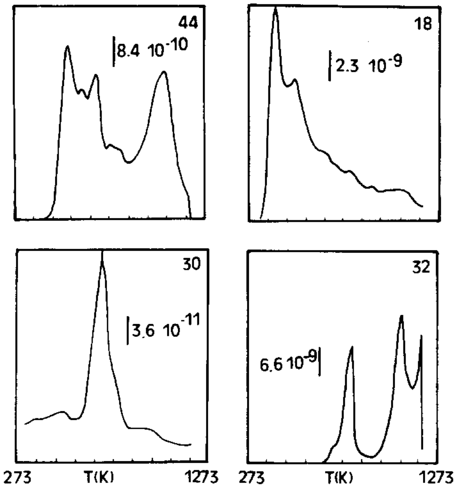

Fig. 3. TPD–MS study of the recently prepared praseodymia sample. Traces corresponding to the evolution of CO_2 ($m/e = 44$), H_2O ($m/e = 18$), NO ($m/e = 30$) and O_2 ($m/e = 32$). The ordinate scale, in Torrs, for each of the signals is indicated on the figure.

exposure to air at room temperature, some sample reoxidation does occur. This prompted us to investigate the effects on the praseodymium oxide prepared by us of the long-term exposure to air, at room temperature.

Figure 2(b) depicts the XRD pattern recorded for the praseodymia sample after exposure to air for approximately 6 months. Compared with the XRD diagram for the recently prepared sample (Fig. 2(a)), that for the oxide aged in air shows a broadening of its main diffraction lines. Finally, after aging for several months, the broadened peaks become sufficiently resolved as to suggest the coexistence of two different praseodymia phases. In accordance with the data reported in the ASTM file, the phase resulting from aging might well be PrO_2. In addition to the segregation of a phase richer in oxygen, the XRD for the aged phase shows some weak diffraction lines which can be assigned to praseodymium(III) hydroxide. This proposal is also supported by FTIR spectroscopy. In effect, the spectrum reported in Fig. 4, corresponding to the praseodymia sample which had been aged in air shows, in addition to a series of bands at 1496, 1391 and 849 cm^{-1} typically associated with carbonate species, two features at 3607 and 664 cm^{-1} which in accordance with the literature [23] can be interpreted as due to praseodymium(III) hydroxide. The observation of at least two well-defined phases, PrO_2 and $Pr(OH)_3$, suggests that the aging process can induce the disproportionation of the mixed-valence praseodymium oxide prepared by us. The occurrence of solvolytic disproportionation of praseodymia phases under mild conditions has recently been discussed in ref. 24.

We have also investigated by TPR–MS the behaviour of the recently prepared praseodymia sample under reducing conditions (Fig. 5). First of all, the trace for water shows a major very intense peak centred at 673 K. This feature can be assigned to the reduction of the starting oxide to Pr_2O_3,

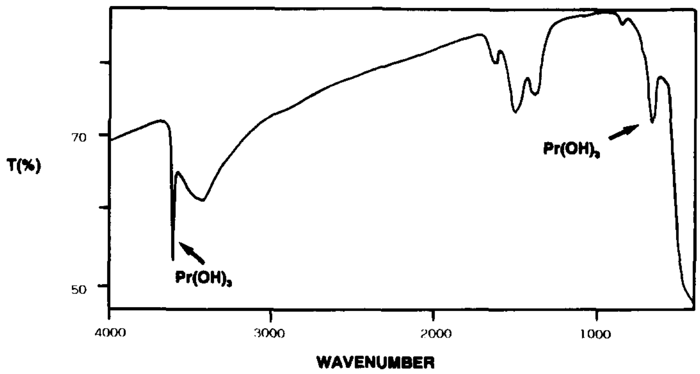

Fig. 4. FTIR spectrum for the praseodymia sample after being exposed to air, at 298 K, for 6 months.

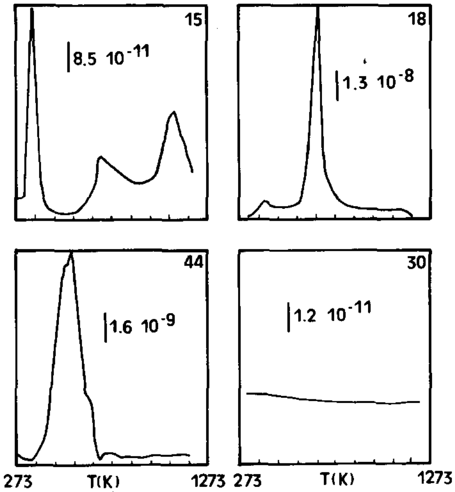

Fig. 5. TPR–MS study of the recently prepared praseodymia sample. Traces corresponding to the evolution of CH_4 ($m/e=15$), H_2O ($m/e=18$), CO_2 ($m/e=44$) and NO ($m/e=30$). The ordinate scale, in Torrs, for each of the signals is indicated on the figure.

the final oxide phase that we have found to occur. This suggests that, in contrast with that observed in the TPD–MS experiments, where the evolution of oxygen takes place through several well-resolved steps (Fig. 3); when we operate in a flow of H_2, the reduction to the sesquioxide phase occurs through a single step at a fairly low temperature. The trace for CO_2 in Fig. 5 is quite different from that depicted in Fig. 3. It can be noted that at 673 K the signal for $m/e=44$ in the TPR experiment abruptly falls to the background level, which would suggest that, from this temperature upwards, reduction of the carbonate species does occur. This is confirmed by the trace for $m/e=15$, in accordance with which CH_4 is formed in the high temperature range of the TPR spectrum.

An important property of the oxides to be used in catalytic applications is their textural stability. Table 1 reports the BET surface area of both the precursor phase and the praseodymium oxide submitted to a number of different treatments similar to those usually applied for the preparation of supported metal catalysts. According to Table 1, the preparation procedure used here does not induce strong surface area reduction of the sample, compared with that of the precursor phase. This rather modest effect of the calcination treatment at 973 K on the textural properties of the sample can reasonably be understood by comparing the SEM and low magnification TEM images obtained by us for both precursor and final oxide phases. Figure 6 shows an example of our TEM study. It can be deduced from the analysis of these two figures that, under the conditions used here, decomposition of the precursor phase takes place without significant morphological modifications of the material. This means that the method that we have followed leads to a praseodymium oxide with a mean surface area value very convenient

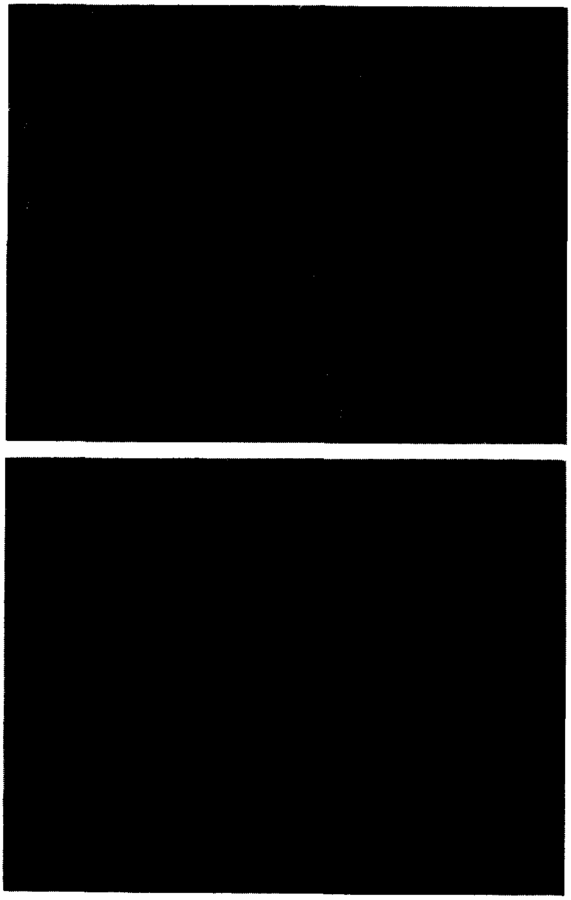

Fig. 6. TEM images corresponding to (A) the precursor phase and (B) the recently prepared praseodymium oxide.

TABLE 1

Textural stability of the praseodymia sample prepared by us using the Brunauer–Emmett–Teller surface area data after a number of different treatments

Sample	Treatment			Surface area (m^2 g^{-1})
	Atmosphere	Temperature (K)	Time (h)	
Precursor	–	–	–	46
Precursor	He	973	2	32
Pr_6O_{11}	Vacuum	623	1	31
Pr_6O_{11}	Vacuum	773	1	34
Pr_6O_{11}	Vacuum	973	1	31
Pr_6O_{11}	H_2	623	1	33
Pr_6O_{11}	H_2	773	1	30
Pr_6O_{11}	H_2	995	1	25

for the specific application foreseen for it — the use as a support of highly dispersed transition metal catalysts.

Regarding the effect on the surface area of the oxide of further thermal treatments carried out under high vacuum and hydrogen, the results given in Table 1 indicate that the textural stability of our sample is very good. In effect, our study shows that, even under strong reducing conditions, at a fairly high temperature (995 K) the surface area of our praseodymia sample decreases very slightly.

4. Conclusions

To summarize, we have carried out the preparation as well as the chemical and textural characterization of a praseodymia sample to be used as support of highly dispersed metal catalysts. Upon exposure to air at room temperature, the praseodymia sample prepared by us undergoes significant disproportionation into PrO_2 and $Pr(OH)_3$. This can be an important factor in determining the catalytic behaviour of the starting oxide phase. The textural properties of the oxide that we have prepared are also very interesting for its applications as a support. Its resistance to sintering could be very useful for investigating the actual nature of the so-called strong metal–support interaction phenomenon [25], notably disturbed by this side effect in the case of M–CeO_2 systems [17].

Acknowledgments

This work has received financial support from the Comisión Interministerial de Ciencia y Tecnologia under the contract PB87-0961. We wish to acknowledge Professor L. Eyring for his material help and stimulating discussions.

We also thank Dr. A. Justo and Mrs. G. Blanco for recording respectively the XRD diagrams and FTIR spectrum included in this work.

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