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LETTER TO THE EDITORS

COMMENTS ON THE PREPARATION of M/4f OXIDE CATALYSTS

Sirs,

Lanthanide oxide-supported transition metals have become a quite interesting class of heterogeneous catalysts [1-4]. However, papers dealing with their characterization are rather scarce [5,6]. Particularly, little attention has been paid to the investigation of the actual nature of the supports and their evolution throughout the process of preparation of the supported metals.

For the past years, we have been investigating the behaviour of 4f oxides against atmospheric CO_2 and H_2O under the usual pressure and temperature conditions. La_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3 and Yb_2O_3 have been studied. Some of the corresponding results have already been published [7-13].

According to these studies, throughout the lanthanide series the behaviour of 4f oxides shows notable differences. Although for all the sesquioxides investigated hydration and carbonation in bulk has been observed, these reactions are much faster on the lighter oxides of the series [8,11,12].

The phase resulting from the stabilization in air of the 4f sesquioxides are also different. Thus, lanthana thoroughly transforms in a few hours to partly carbonated hydroxide [7,11]. In spite of the carbonation in bulk of lanthana, no difference is observed between the X-ray diffraction patterns corresponding to La_2O_3 stabilized in air and that reported for $La(OH)_3$ in the ASTM file.

At the end of the lanthanide series, i.e. Yb_2O_3, the process is slow, the transformation of the oxide is only partial and, on the other hand, a single hydroxy-carbonate-like phase seems to be the final product. It must also be pointed out that the X-ray diffraction pattern for the ytterbia sample, stabilized in air, correspond to that reported for the cubic phase of the oxide [8].

Contrary to that found for La_2O_3 [11], for samaria, an intermediate oxide in the lanthanide series, the reactivity towards CO_2 and H_2O strongly depends on the origin of the samples [12], some of them resembling lanthana, whereas others behave like ytterbia. As in the case of lanthana and ytterbia, no evidence of the carbonation in bulk of the samaria samples, stabilized in air, could be obtained from X-ray diffraction.

Since the lanthanide sesquioxides undergo strong hydration and carbonation phenomena by simple exposure to the air, their use as transition metal supports has some peculiarities worthy of being noted. First, depending on the reduction conditions selected to prepare the supported metal, phases other than true 4f sesquioxides may constitute the actual support. In other words, some of the catalysts

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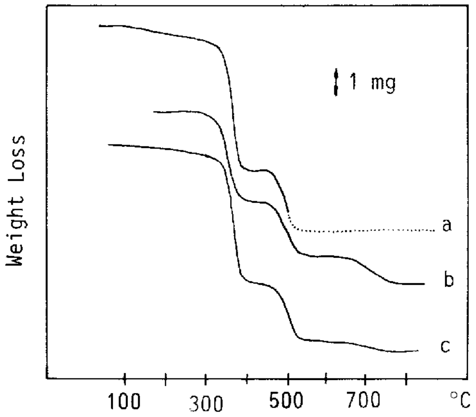

FIGURE 1 (a) TG trace of the decomposition in a flow of helium, up to 500°C, of 40 mg of lanthana stabilized in air (full line), followed by a treatment of 2 h at 500°C in a flow of helium (dotted line). (b) TG trace corresponding to sample proceeding from experiment a, cooled to 120°C in a flow of helium and then exposed to the temperature, at 120°C, for 12 h. (c) TG trace of the decomposition in a flow of helium, up to 850°C, of 40 mg of lanthana stabilized in air.

reported in the literature as M/4f oxide phases are improperly described by this term. Secondly, throughout the process of preparation of the supported metals, strong structural rearrangements of the supports must take place, and therefore, overcoating of the metal particles by the supports might well occur.

In order to prevent the latter of the effects mentioned above, in a recent paper [5] a preparation method of Pd/4f oxide catalysts consisting of heating the supports in air for 2 h at 500°C, and carrying out the impregnation of the palladium precursor in nonaqueous media has been reported. The conditions of pretreatment of the lanthanide oxides were selected on the basis of the results reported by Rosynek for lanthana [14]. However, as can be deduced from the results previously reported by us, and those included in Figure 1 (compare drawings a and c), the above mentioned treatment, which allows the dehydration of the support, does not permit decomposition of the dioxomonocarbonate phase formed when lanthana, stabilized in air for a few hours, is heated. The amount of CO_2 picked up by lanthana is, on the other hand, much higher than that corresponding to a simple surface process.

In the case of the heavier 4f sesquioxides, the possibility of obtaining partly carbonated phases, when treated as in ref. [5], cannot be ruled out [8,12]. In any case, X-ray diffraction data cannot be used to exclude such a possibility.

When $Rh(NO_3)_3/La_2O_3$ (stabilized in air) samples are reduced in flowing hydrogen, the elimination of CO_2 takes place at temperatures lower than 500°C [13]. A rather similar effect on the reduction of the carbonated phase has been observed in [15] for Pd/La_2O_3 phases. Accordingly, the preparation method followed in ref. [5] does not guarantee the absence of structural rearrangements of the supports associated to the reduction of the carbonated phase, at least in the case of the lighter oxides.

It should also be mentioned that, unless rigorous absence of CO_2 and H_2O is used, other steps of the procedure followed in ref. [5] to prepare lanthanide oxide-supported palladium catalysts may also induce hydration and carbonation of the supports. Thus, trace b on Figure 1 accounts for the TG diagram corresponding to the lanthana sample heated up to 500°C and then exposed to the air at 120°C overnight. As can be deduced from this trace the sample is extensively rehydrated and the carbonation in even a little more intense than in the case of the sample stabilized in air, at ambient temperature, trace c on Figure 1.

Furthermore, the simple manipulation of the lanthana phases obtained after each of the preparation steps followed in reference [5] in air at room temperature for a few hours may induce the rehydration and recarbonation of the support.

In summary, it is our opinion that, when the preparation method of M/4f oxide catalysts suggested in ref. [5] is followed, overcoating of the metal particles by the support, occurred during the process of reduction of the precursors, should not be excluded.

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