JOURNAL OF CATALYSIS **146**, 317–319 (1994)

NOTE

Characterization of the Acidic Properties of Niobia-Containing Aerogels with [^{18}O]Ethanol Dehydration

DeCanio *et al.* (1, 2) have recently reported the results of a novel mass spectral temperature-programmed reaction study (TPRS) of the dehydration of isotopically labelled ethanol ([^{18}O]ethanol) adsorbed on γ-alumina and flouride-modified alumina. Their key finding is that there are two isotopomeric ether products, $(C_2H_5O)_2{}^{18}O$ and $(C_2H_5O)_2O$, in addition to ethene. This result suggests that adsorbed ethoxide can form via two routes: (i) by dissociative adsorption on Lewis acid site giving rise to the ^{18}O-containing ethoxide and (ii) by the nucleophilic attack of the surface oxide on ethanol which is probably activated toward C–O bond cleavage by interacting with a Brønsted acid site. Thus, the product distribution following the adsorption of [^{18}O]ethanol provides useful information on the acidic properties of oxides, especially with respect to the nature of Lewis versus Brønsted acid sites. In this note we present results which show that in using this technique to study a series of niobia-containing aerogels, we found evidence of stronger Brønsted acid sites on supported niobia than on bulk niobia.

The preparation and characterization of samples used in this study have been described elsewhere (3, 4). Briefly, a niobia gel was prepared by mixing niobium ethoxide, *s*-butanol, doubly deionized water, and nitric acid. The gel was extracted in a standard autoclave with supercritical carbon dioxide to obtain an aerogel, denoted as A-Nb_2O_5. A silica aerogel was similarly prepared with a two-step acid–base catalyzed procedure using silicon ethoxide as a precursor. Niobia was then placed onto the surface of this support via incipient wetness impregnation with a hexane solution of niobium ethoxide and subsequent heat treatments. By adjusting the amount of niobium ethoxide, we prepared three silica-supported niobia samples containing 0.05, 0.1, and 0.25 monolayer of niobia (corresponding to 5.2, 9.6, and 23.7 wt%). Since the silica aerogel has a very high surface area (about 900 m^2/g before the deposition of niobia), even low fractional surface coverages of niobia correspond to high weight loadings. This is in fact the key advantage of a high-surface-area support in that it can accommodate a larger amount of dispersed species than a support with a lower surface area. These samples are denoted as A-NS(x) where x represents the coverage calculated by assuming each $NbO_{2.5}$ unit occupies an area of 0.16 nm^2. All samples were calcined in flowing oxygen at 773 K for 2 h and dried at 383 K for 12 h before TPRS.

In TPRS, adsorption of [^{18}O]ethanol was achieved by vapor deposition: approximately 0.1 g of sample was exposed to the vapor of about 10 μl of the alcohol for 15 min in an air-tight container. Approximately 0.1 mg of each dosed sample was then placed into a glass insertion tube that was loaded into the temperature-programmed probe of the mass spectrometer and immediately inserted into the source chamber with minimal exposure to air. The mass spectrometer was a Finnigan-MAT TSQ70 instrument. The detector was scanned from 12 to 170 Daltons every 0.5 s, and the source was operated at 423 K using a 70-eV ionizing potential with an ion current of 200 μA under electron impact conditions. The pressure of the mass spectrometer source chamber is 1×10^{-7} Torr. The temperature of the sample was increased from 298 to 723 K at a rate of 25 K/min. The probe is within 1 mm of the ionizing electrons, which ensures that the desorbed species are analyzed immediately upon desorption from the sample surface. This arrangement minimizes diffusion losses and time delay and is, therefore, much more sensitive than typical temperature-programmed experiments.

Figure 1 shows that following the adsorption of [^{18}O]ethanol on A-Nb_2O_5, the major dehydration products are labelled diethyl ether ($(C_2H_5O)_2{}^{18}O$, monitored by $m/z = 61$), diethyl ether ($(C_2H_5O)_2O$, $m/z = 59$), and ethene (C_2H_4, $m/z = 26$). As shown by DeCanio *et al.* (1, 2), the labelled ether is produced from the interaction of the alcohol with Lewis acid sites, whereas the unlabelled one is produced with Brønsted acid sites. Their appearance thus confirms the presence of both Lewis and Brønsted acid sites on the surface, in agreement with previous infrared results of adsorbed pyridine (3). Ethene is a dehydration product that can come from both labelled and unlabelled alkoxides.

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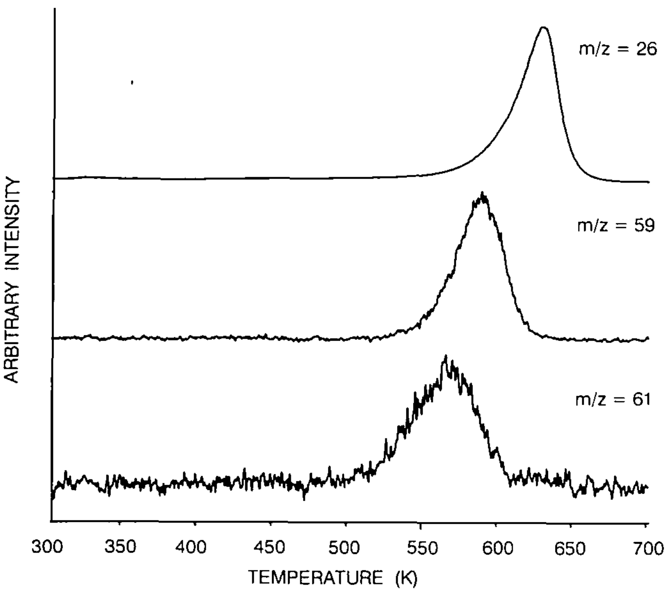

FIG. 1. Temperature programmed desorption products of $C_2H_5{}^{18}OH$ adsorbed on A-Nb_2O_5 (m/z = 26, C_2H_4; m/z = 59, $(C_2H_5)_2O$; m/z = 61, $(C_2H_5)_2{}^{18}O$).

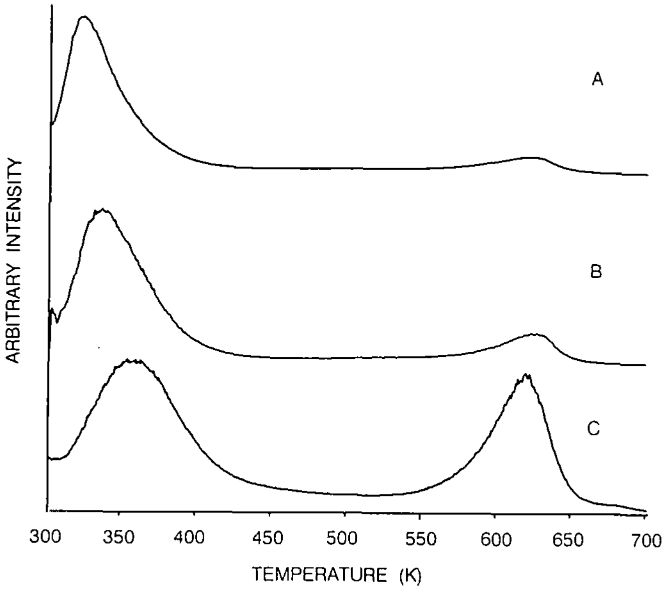

FIG. 3. Desorption of C_2H_4 (m/z = 26 signal) following the adsorption of $C_2H_5{}^{18}OH$ on (A) A-NS(0.05), (B) A-NS(0.1), and (C) A-NS(0.25).

The product distribution for A-NS(0.25) is similar to that for A-Nb_2O_5 with one major exception. As shown in Fig. 2, there is an additional C_2H_4 peak appearing at about 350 K along with a weak $m/z = 59$ signal. This observation points to the presence of new acid sites that are very active for dehydration. As noted earlier, the formation of the unlabelled ether (the $m/z = 59$ signal) involves Brønsted acid sites (1, 2). Our data thus suggest that strong Brønsted acid sites are created by depositing niobia on, in this case, a silica aerogel. Indeed, the low-temperature reaction channel leading to the formation of C_2H_4 exists for the other silica-supported niobia samples (see Fig. 3). Furthermore, the ratio in area of the low-temperature peak (at about 350 K) to that of the high-temperature peak (at about 620 K) decreases with increasing niobia coverage (see Table 1). In other words, as more niobia is deposited onto silica, there is a decrease in the relative amount of strong Brønsted acid sites.

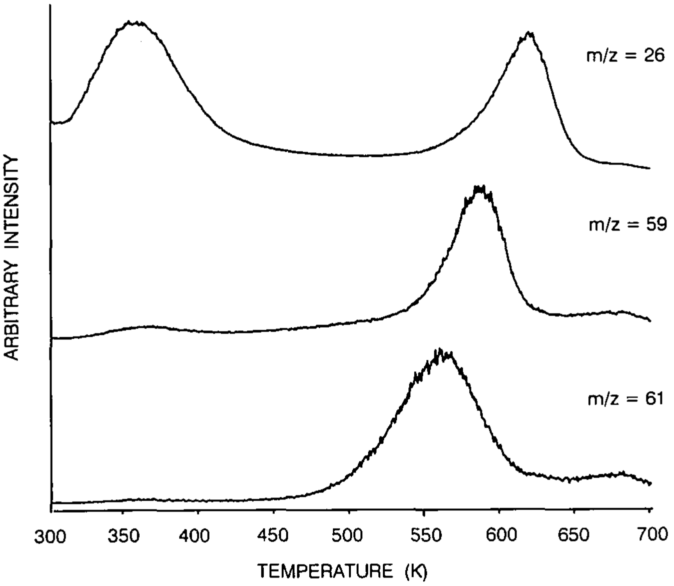

FIG. 2. Temperature programmed desorption products of $C_2H_5{}^{18}OH$ adsorbed on A-NS(0.25) (m/z = 26, C_2H_4; m/z = 59, $(C_2H_5)_2O$; m/z = 61, $(C_2H_5)_2{}^{18}O$).

The presence of both Lewis and Brønsted acid sites on the surface of silica-supported niobia have been previously reported (4–7). Most authors agree that the Lewis acid sites are related to a distorted niobia structure containing a doubly bonded oxygen atom (5, 6), but the nature of Brønsted acid sites remains unclear. Jheng and Wachs

TABLE 1

Alkene Formation Following the Adsorption of $C_2H_5{}^{18}OH$ on Silica-Supported Niobia Samples

Sample	Area of m/z = 26 high-temperature peak (arbitrary units)	Ratio of m/z = 26 areas (low-temperature peak/ high-temperature peak)
A-NS(0.05)	31	9.35
A-NS(0.10)	58	6.83
A-NS(0.25)	237	1.13

(6) found no evidence of Brønsted acidity until a critical niobia loading is reached and suggested that Brønsted acid sites are associated with bulk niobia forming on the surface. On the other hand, Ko and co-workers (4, 5) noted in their infrared results that upon the evacuation of adsorbed pyridine, the ratio of Lewis to Brønsted acid sites increases significantly with evacuation temperature for bulk niobia but remains constant for silica-supported niobia. This difference would be consistent with the presence of stronger Brønsted acid sites on the latter sample to which pyridine is bonded. Our TPRS results with [^{18}O]ethanol support this argument because they identify a reaction channel for the low-temperature formation of C_2H_4 from adsorbed ethanol on silica-supported niobia that is absent for bulk niobia.

We believe the strong Brønsted acidity of silica-supported niobia is associated with hydroxyls bonded to niobium atoms that are doubly bonded to oxygen. In their theoretical calculations on supported transition metal oxide clusters of Ti, Nb, and W, Bernholc *et al.* (8) showed that an increase in Brønsted acidity can come from a terminal oxygen effect and an inductive effect of the support that combine to delocalize the charge upon proton removal. It would thus be possible to stabilize niobia in a structure containing Nb=O bonds on silica with strong Brønsted acidity. With increasing niobia coverage, niobia aggregates on the surface via Nb–O–Nb linkages with the concurrent decrease in the relative amount of terminal hydroxyls. This would explain the qualitative trend shown in Fig. 3. The fact that there is a low-temperature reaction channel for dehydration on A-NS(0.05) also suggests that some Nb–O–Nb linkages already exist at a coverage as low as 0.05 monolayer, as Nishimura *et al.* found no dehydration products from ethanol for isolated niobium monomers (9).

In summary, we have demonstrated the general utility of a new technique, namely, the TPRS of [^{18}O]ethanol, in providing insight into the acidic properties of bulk and supported oxides.

ACKNOWLEDGMENT

One of us (EIK) thanks Niobium Products Company, Inc., for partial support of this work.

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Received August 17, 1993; revised October 19, 1993