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SO_2 Adsorption on Mo-Ni/Al_2O_3 Catalysts

Recently, we have observed by ESR that SO_2 is adsorbed on ZnO in different forms, depending on the temperature at which the oxide is kept after being heated in presence of SO_2 (*1*). If the sample is quenched at 77 K after heating at 573 K in presence of SO_2, a signal due to trapped electrons is detected at 77 K. However, if it is warmed at 293 K the trapped electron signal disappears and the formation of SO_2^- species is observed. This behavior indicates that SO_2 can reduce the ZnO, but under certain experimental conditions it can also oxidize the reduced sample. This particular property of the SO_2 molecule offers interesting possibilities for the study of composed systems containing ions with different reducibilities. To explore these possibilities, in the present work we have used the adsorption of SO_2 as a method to study a supported molybdenum–nickel catalyst. Although several works have been published on the ESR spectra of catalysts of this type, most of the observed signals were originated by the molybdenum ions and almost no information could be obtained concerning the reduction of nickel oxide.

For the present study we have used three samples of oxides supported on γ-Al_2O_3: (A) 14% by weight of MoO_3, (B) 1% NiO, and (C) 14% MoO_3 and 1% NiO. The sample preparation has been described elsewhere (*2*). All the samples underwent a pretreatment at 773 K, first under vacuum and later in oxygen, and were subsequently evacuated at 293 K and put in contact with SO_2 at the same temperature. Afterwards, they were heated at 473 and 673 K for 1 hr in presence of SO_2, and the ESR spectra were registered with a Jeol PE-3X spectrometer at 77 and 293 K.

When sample A was heated at 473 K in the presence of SO_2 and quenched at 77 K, the spectrum at the same temperature was composed of two axial signals, with $g_{\perp_1} = 1.950$, $g_{\perp_2} = 1.941$, $g_{\parallel_1} = 1.896$, $g_{\parallel_2} = 1.871$, and an orthorhombic one with much lower intensity and $g_1 = 2.0149$, $g_2 = 2.0090$, $g_3 = 2.0026$. Both axial signals can be assigned to Mo^{5+} ions in two different environments (*3*), while the parameters of the orthorhombic signal are appropriate for O_2^- species bound to Mo^{6+} ions (*4*). When the sample is warmed at room temperature this last signal disappears irreversibly from the spectrum. As the O_2^- adsorbed on MoO_3, can usually be seen in the ESR spectrum at room temperature, this observation suggests that the species originating this signal should be a modified O_2^-. The spectra at 77 and 293 K of the sample heated at 673 K were similar to those obtained for the sample heated at 473 K at the same recording temperature. The signals, however, presented a higher intensity with a relative larger increase of the oxygen signal a 77 K, which is shown in Fig. 1,a. These results indicate that the SO_2 molecules are adsorbed on lattice oxygens inducing the reduction of the MoO_3, probably by substracting O^{2-} from the lattice and forming SO_3 and/or SO_4^{2-} species, in the same way as has been proposed for ZnO (*1*) and Fe_2O_3 (*5*). The origin of the oxygen adsorbed as O_2^- is not clear; it can come from oxygen impurities in the SO_2 or some leak, although the SO_2 was previously treated to eliminate these impurities and the cell checked for leaks. However, the increase observed in the signal when the sample was heated above 473 K suggests that it could also come from the MoO_3 lattice.

Sample B, heated at 473 K and studied at

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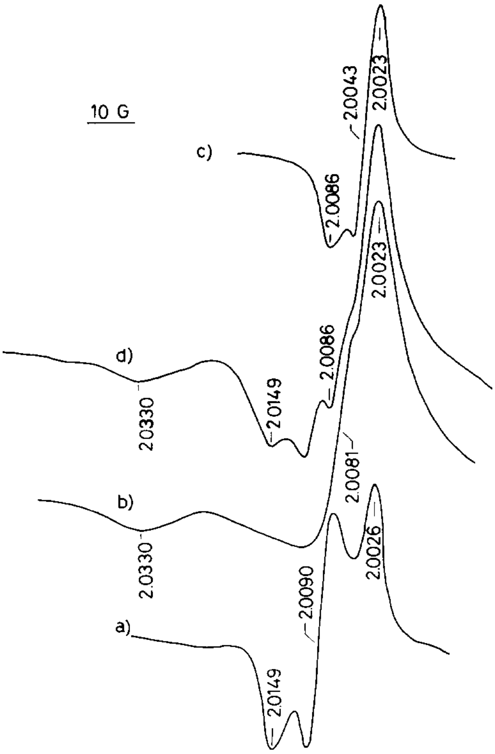

FIG. 1. EPR spectra of the catalysts heated in presence of SO_2. Sample A heated at 673 K, recorded at 77 K (relative intensity 5.6 a.u.) (a); Sample B heated at 473 K, recorded at 77 (4.8 a.u.) (b) and at 293 K (5 a.u.) (c); Sample C heated at 473 K, recorded at 77 K (6.6 a.u.) (d). The Mo^{5+} signal, present in spectra (a) and (d), is not shown.

77 K, showed only an orthorhombic signal (I) (Fig. 1,b), with $g_1 = 2.0330$, $g_2 = 2.0081$, $g_3 = 2.0023$, that changed reversibly into another one with $g_1 = 2.0086$, $g_2 = 2.0043$, $g_3 = 2.0023$ on warming at 293 K (Fig. 1,c). The parameters of this last signal indicate that it is due to SO_2^- species (*1*). When the sample is heated at 673 K a larger signal of SO_2^- is obtained at both recording temperatures, although at 77 K the signal is not well resolved, probably because strong dipolar interactions produce a line broadening. However, if a small amount of oxygen (~1 Torr) is then introduced in the sample tube the signal (I) is again observed at 77 K. This behavior suggests that the species producing signal (I) contains oxygen, as in the case of the signal found in sample A. The parameters of signal (I) are similar to those of O_2^- species, although the g_1 value is lower than it would be expected for O_2^- bound to an ion with charge +2 (*6*), the maximum oxidation state at which the nickel ion should be present in these conditions. The reversibility of signal (I) at 77 K, converted to SO_2^- at 293 K, together with the fact that this signal is not observed when only oxygen is adsorbed on sample B after reducing pretreatments, suggest that this species also contains SO_2. In fact, its parameters are similar to those assigned by Symons *et al.* (*7*) to a peroxide radical, $O_3SO_2^-$, obtained by uv irradiation of $K_2S_2O_8$ crystals. It could thus be tentatively assigned to a sulfur-containing peroxide-type radical such as $O_2SO_2^-$, formed through the equilibrium

$$SO_2^- + O_2 \rightleftharpoons O_2SO_2^-.$$

In any case, these results indicate that the supported NiO is reduced by SO_2, with introduction of oxygen defects in the NiO lattice, so that the reduced nickel can later be (at least partially) reoxidized by an electron transfer to the adsorbed SO_2 molecules. This fact suggests the possibility of following the process of NiO reduction by examination of the SO_2^- subsequently formed after SO_2 adsorption. Initially the Ni^{2+} ions at the surface should be reduced to Ni^+ or Ni^o, but after SO_2 is adsorbed it will form Ni^{2+}–SO_2^- complexes and no Ni^+ signal will be observed.

When sample C was heated at 473 K and studied at 77 K, it exhibited the spectrum shown in Fig. 1,d. It can be interpreted by the superposition of the signals due to the sulfur-containing peroxide species bound to nickel, O_2^- bound to Mo^{6+}, SO_2^- and Mo^{5+} (the last is not shown in the spectrum). This indicates that by heating at 473 K both constituents of the active phase of the catalyst have been at least partially reduced. The Mo^{5+} signals show the $g_\parallel$ values well resolved but are broader than those found for sample A, indicating the existence of larger dipolar interactions. When the sample is studied at 293 K, only the signals of SO_2^- and Mo^{5+} are visible, but the other signals are recovered if the spectrum is recorded again at 77 K. This reversible formation at 77 K could indicate that the species producing the peroxide signal is also formed by SO_2 as in the case of signal (I) with sample B. When the sample is heated at 673 K, the spectra are similar at 77 and 293 K, showing only the Mo^{5+} and SO_2^- signals. The signal intensity is larger than after treatment at 473 K, but the SO_2^- signal is smaller than for sample B under similar conditions and the Mo^{5+} signal is larger than for sample A. This seems to indicate that the simultaneous presence of MoO_3 and NiO changes the reduction characteristics and/or the exposed active area of both oxides.

In conclusion, the present results show that the SO_2 adsorption can provide a method to study the reducibility of compound catalysts, following not only the reduced ionic species, but also the adsorbed species formed by an electron transfer from the catalyst to the adsorbed SO_2.

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