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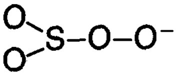
An Electron Spin Resonance Study of Formation of SO_2^- and  Radicals on Nickel/Alumina Catalysts

The interaction of SO_2 with an oxide surface is a preliminary step in the reaction mechanism either in the catalytic oxidation of SO_2 to obtain SO_3 for the sulfuric acid synthesis (*1*) or in the reaction of SO_2 with SH_2 on silica (*2*) or alumina (*3*) in the Claus process that gives elemental sulfur and water as main products.

ESR spectroscopy has been widely used to study the paramagnetic species formed by the adsorption of SO_2 on such oxides (*4–11*), although less attention has been paid to the reactivity of these species with oxygen and to the effect of SO_2 at higher temperatures.

In a previous work on SO_2 adsorption on fully oxidized nickel oxide supported on γ-Al_2O_3, we have observed by ESR two different species at 77 K depending on the adsorption temperature (*12*). Signal I, tentatively assigned to O_2SOO^-, was observed after the adsorption of SO_2 at 473 K and another, corresponding to SO_2^-, when the sample was heated at 673 K in the presence of SO_2.

In order to clarify the formation mechanism of these paramagnetic sulfur species and get more detailed information about the interaction of SO_2 and O_2 on the supported nickel oxide, in this work we have studied the adsorption of SO_2 on NiO/γ-Al_2O_3 at different temperatures between 298 and 773 K and used ^{17}O-enriched oxygen to confirm the assignment of the signal observed at low temperature and ascribed to O_2SOO^- species.

EXPERIMENTAL

A sample containing 1% NiO by weight was obtained by impregnation of γ-Al_2O_3 from Girdler (T-126), specific surface area 118 $m^2\ g^{-1}$, with an aqueous solution of nickel nitrate. A detailed study of this sample is given elsewhere (*13*).

The sample was outgassed in the greaseless vacuum cell used for ESR measurements at 773 K for 1 h and heated under O_2 for 2 h at the same temperature. After this pretreatment the sample had a pale green color. Then it was outgassed at 298 K, contacted with SO_2 (10 Torr) for 30 min at the desired temperature in the range 298–773 K and quenched at 77 K.

Just prior to use the SO_2 was submitted to various freeze–pump–thaw cycles at 77 K to eliminate any trace of oxygen or other impurities. The ^{17}O-enriched oxygen (70%) was supplied by CEA (France) and was used without further purification.

The ESR spectra were recorded with a Jeol PE-3X spectrometer at 77 and 298 K, using a DPPH standard to calibrate the magnetic field.

RESULTS

The initial NiO/γ-Al_2O_3 sample showed no ESR signal. After it contacted SO_2 at 298 K a small signal I with $g_1 = 2.033$, $g_2 = 2.008$, and $g_3 = 2.002$ was recorded at 77 K. The intensity of this signal increased after treatment at growing temperature up to 473 K in the presence of SO_2. If the sample

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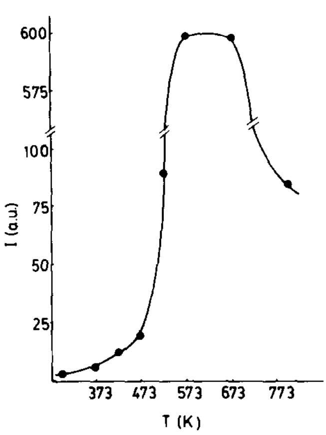


FIG. 1. Intensity of the SO_2^- signal recorded at 298 K against the heating temperature of the NiO/γ-Al_2O_3 sample under SO_2.

heated in the range 298–473 K was observed at 298 K a signal with $g_1 = 2.008$, $g_2 = 2.004$, and $g_3 = 2.002$, previously ascribed to SO_2^- radicals (*12*), was obtained. After treatment at $T > 523$ K only this last signal was present in the spectra taken at either 77 or 298 K, with better resolved components at 298 K and a more symmetrical lineshape at the highest heating temperatures. The intensity of the SO_2^- signal changed with the heating temperature, presenting a maximum at about 573 K as it is shown in Fig. 1. In addition, there were observed modifications in the color of the sample; it became yellow when heated at 473 K < T < 673 K and gray at 773 K. The SO_2^- radical was very stable in all the cases, its signal remaining unchanged after several weeks at 298 K.

For all heating temperatures, when O_2 (10^{-1}–1 Torr) was adsorbed at 77 K, the SO_2^- signals was transformed into signal I. As an example, the spectra corresponding to the sample heated in SO_2 at 673 K and posterior O_2 adsorption are presented in Figs. 2a and b, respectively. By prolonged outgassing at 77 K of the sample showing signal I, a slightly modified spectrum was obtained (Fig. 2c) which shows an extra feature at $g = 2.017$. However, by outgassing the sample at 298 K the spectrum of Fig. 2d, corresponding to the SO_2^- signal, was recorded at 77 or 298 K. This adsorption–desorption sequence could be repeated as many times as desired, indicating a complete reversibility of the process.

To determine the structure of species I, ^{17}O-enriched oxygen was adsorbed at 77 K on a sample with preexisting SO_2^- radicals. The resulting spectrum is presented in Fig. 3. It shows a hyperfine structure due to the ^{17}O (nuclear spin, $I = \frac{5}{2}$) formed by two sets of six lines centered at g_3 ($A_{3\perp} = 92.\ 5$ G; $A_{3\parallel} = 51.5$ G; $A_1 \sim A_2 \sim 0.0$).

DISCUSSION

The hyperfine pattern of signal I indicates the presence in the radical of two inequivalent oxygen atoms with a peroxy type structure. However, the radical cannot be assigned to an O_2^- species with inequivalent oxygen atoms adsorbed either on Ni^{2+} or

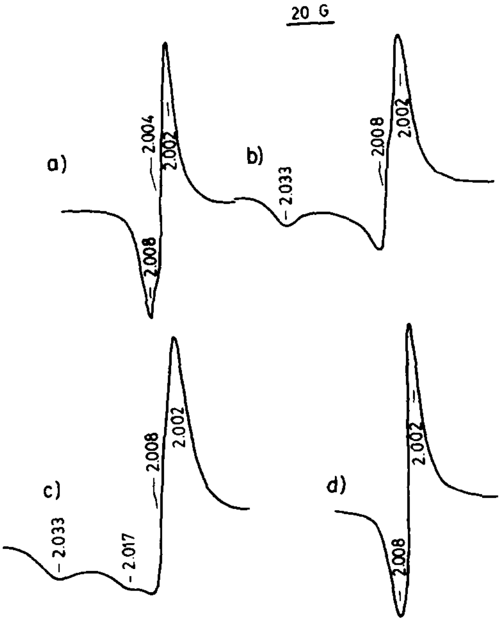


FIG. 2. ESR spectra recorded at 77 K of the NiO/γ-Al_2O_3 sample after SO_2 adsorption at 673 K (a), followed by O_2 adsorption at 77 K (b), outgassing at 77 K (c), and outgassing at 298 K (d).

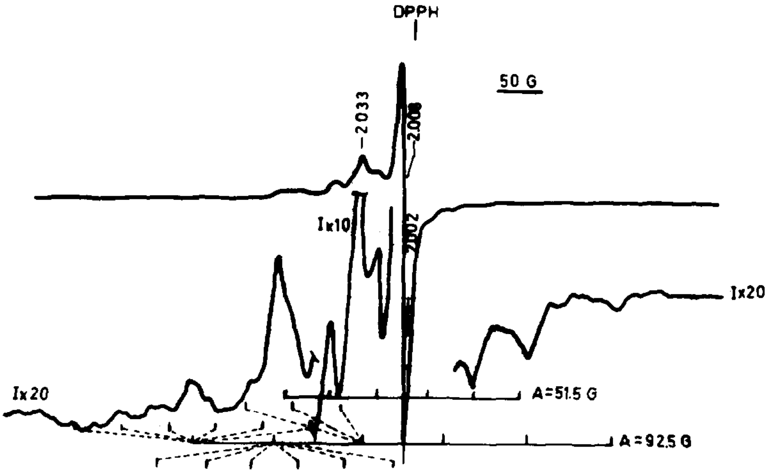
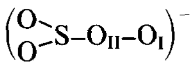


FIG. 3. ESR spectrum recorded at 77 K of the NiO/γ-Al_2O_3 sample heated under SO_2 at 673 K after the adsorption of ^{17}O-enriched oxygen at 77 K.

Al^{3+} cations. In the first case it would present a larger g_1 value, in agreement with the adsorption of the radical on a twofold cation, while in the second case the spectrum would have a superhyperfine structure due to aluminum (^{27}Al has nuclear spin, $I = \frac{5}{2}$) (*14*).

Another possibility is to assume that the O–O bond is polarized by a SO_2 molecule in a sulfoperoxide radical,  $\left(\begin{smallmatrix}O\\O\end{smallmatrix}\!>S\text{–}O_{II}\text{–}O_{I}\right)^-$. Similar A and g tensor values have been obtained by several authors for other peroxide radicals stabilized on different oxides such as $(O_2COO)^-$ on MgO (*15*), $(O_2COO)^-$ on MoO_3/SiO_2 (*16*), $RCH_2OO^{\cdot}$ on TiO_2 (*17*), or $(OCOO)^-$ on TiO_2 (*18*). Recently we have also reported another sulfoperoxide species stabilized on TiO_2 with g and A values similar to those of signal I (*19*).

The formation of species I by adsorption of O_2 on SO_2^- strongly support its assignment to a sulfoperoxide radical. This result is similar to that found by Ben Taarit *et al.* (*15*), and González-Elipe *et al.* (*16*), which, on MgO and MoO_3/SiO_2, respectively, were able to stabilize a $(O_2COO)^-$ radical by reaction of CO_2^- with molecular oxygen at 77 K. In our case, the following equilibrium can be proposed to explain the formation of the sulfoperoxide radical:

$$SO_2^- + O_2 \rightarrow (O_2SOO)^-, \qquad (1)$$

where the reversibility of the reaction is a particular characteristic of this system that has not been found in other cases with CO_2^- and SO_2^- (*16, 17, 20*).

The generation of the shoulder at $g = 2.017$ by prolonged outgassing at 77 K of the sample with the sulfoperoxide radical is a result similar to that found for O_2COO^- on MgO obtained by γ-irradiation at 77 K in the presence of CO_2 and then contacted by O_2 at the same temperature (*15*). This extra peak has been explained by Schlick and Kevan (*20*), assuming a jumping of the O–O set around its bond to the carbon. In our case a similar explanation would be valid, being likely to assume that this modified signal is produced by O_2SOO^- species adsorbed on certain sites where, in the absence of the excess of physisorbed O_2, this jump would be possible.

The formation of sulfoperoxide radicals by UV irradiation of TiO_2 at 77 K in the presence of SO_2 and O_2 has been accounted for by a mechanism similar to (1) (*19*). However, its behavior against temperature is different on TiO_2 than that on NiO/γ-Al_2O_3. While on TiO_2 it decomposes irreversibly at 298 K producing adsorbed O_2^- species, on NiO/γ-Al_2O_3, SO_2^- species are produced at this temperature in a reversible way. This different reactivity can be related to the stabilization of O_2^- and SO_2^- on both systems. Thus, while O_2^- species once formed on TiO_2 are stable at 298 K, SO_2^- radicals, obtained by quenching at 77 K a sample heated at 673 K in the presence of SO_2, are unstable at 298 K (*19*). On the contrary, on NiO/γ-Al_2O_3 the SO_2^- is very stable at 298 K; meanwhile no O_2^- species are observed by ESR.

The different stability of SO_2^- adsorbed on TiO_2 or NiO/γ-Al_2O_3 is also reflected by the spin density distribution through the structure of the sulfoperoxide radical. Following the method reported by Che and Tench (*14*) the values obtained for the two oxygen atoms of the peroxy group, ($-O_{II}-O_I$) are 0.69 for O_I and 0.27 for O_{II} on TiO_2, and 0.60 for O_I and 0.34 for O_{II} on NiO/γ-Al_2O_3. These values are very different than those found for O_2^- species with inequivalent oxygen nuclei (typical values are, for example, 0.55 and 0.42, (*14*)) and indicate that the polarization of the O–O group is greater on NiO/γ-Al_2O_3 than on TiO_2, suggesting that the bond of the sulfur dioxide with the surface is stronger on the nickel catalyst.

The reaction between sulfur dioxide and dioxygen species has been previously studied by ESR on different systems. Thus Ono *et al.* (*21*) reported that in a Y type zeolite with SO_2^- species, O_2^- is formed after prolonged contact with molecular oxygen. A similar reaction has been reported by Che *et al.* (*22*) on SnO_2 and by us on TiO_2 (*19*). SO_4^- radicals also been shown to be a product for this kind of reaction. Ono *et al.* (*11*) found this species when molecular oxygen interacted with SO_2^- on the surface of CaO, while Rao and Lunsford (*7*) got a similar radical on V_2O_5 from SO_2^- and O_2^- species. In both cases no hyperfine splitting could be detected by using ^{17}O-enriched oxygen, and a sulfate type structure was assumed on the basis of the *g* values of the radicals. According to the present results all these reactions are likely to occur via a sulfoperoxide species, which stress the importance of this intermediate in the reaction between SO_2 and O_2 on metal oxides.

Turning to the NiO/γ-Al_2O_3 system, the question remains whether the formation of SO_2^- species is related to the support or to the nickel phase. The formation of SO_2^- upon heating γ-Al_2O_3 in the presence of SO_2 at 723 K has been reported by Khulbe and Mann (*9*), while its formation by adsorption of SO_2 at 298 K on a vacuum activated alumina has been recently studied by Datta *et al.* (*10*) and previously by Ono *et al.* (*8*). In our case, with a sample that has been heated under oxygen at 773 K, SO_2^- (or O_2SOO^- at 77 K) is already formed at 298 K. This, together with the variation profile of the concentration of this species against temperature, that does not fit that reported by Datta *et al.* (*10*) and Ono *et al.* (*8*), supports the participation of the nickel phase in the generation of these radicals.

In the previous results three different temperature ranges can be distinguished (298–473 K, 473–673 K and >673 K), for which changes in the color of the sample are also observed. For these ranges various reactions can be proposed to explain the formation of SO_2^-. For $T < 473$ K,

$$2SO_2 + O_2^{2-} \rightarrow 2SO_2^- + O_2, \qquad (2)$$

where the formation of O_2^{2-} ions in the NiO/γ-Al_2O_3 sample is likely after the heating of the sample under oxygen. Thus, in NiO annealed in air at high temperature this species has been detected by Roberts and coworkers (*23*) using XPS, being stable under vacuum only below 473 K. Also for $T < 523$ K, Lalauze, Thiesse, and co-workers (*24*) have observed that adsorption of SO_2 on

NiO is related to O^-, species that can also be described as peroxide ions.

While for $T > 473$ K the following reactions can be invoked:

$$SO_2 + Ni^{2+} \rightarrow Ni^{3+} + SO_2^- \quad (3)$$

or/and

$$SO_2 + O^{2-}_{latt.} \rightarrow SO_3 + 2e^- \quad (4)$$

$$SO_2 + e^- \rightarrow SO_2^-, \quad (5)$$

where e^- designates a reduced nickel species (Ni^0 or Ni^+).

On silica Ni^{3+} ions can be extensively generated by heating a nickel–silica catalyst under oxygen at high temperature (*25*). In our system, reaction (3) is not unlikely since SO_2 has greater electron affinity than O_2 (1.093 eV (*26*) compared to 0.43 eV in the case of oxygen (*27*)), so that it can be the most important source of SO_2^- between 573 and 673 K, when the sample became yellow, color observed for the Ni^{3+} on silica (*25*). Finally, reactions similar to (4) and (5) have been previously proposed by us on the basis of ESR results to explain the formation of SO_2^- on ZnO (*28*) and by Kim and Choi (*29*) to justify their electrical conductivity measurements with TiO_2 and Fe_2O_3 heated under SO_2. On $NiO/\gamma\text{-}Al_2O_3$ these reactions must be more important at the highest temperature, when the sample became gray, indicating a certain reduction of the nickel.

In conclusion, the previous results support that SO_2 can react with the surface of oxide catalysts in several ways, according to the temperature and that SO_2^- radicals and molecular oxygen can interact giving a sulfoperoxide radical that can play an important role in the oxidation of SO_2 on these catalysts.

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