

Influence of sulfur dioxide adsorption on the surface properties of metal oxides

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Received 16 February 1996; accepted 27 May 1996

Abstract

The effect of SO₂ chemisorption at 623 K on various metal oxides (CeO₂, MgO, Al₂O₃, ZrO₂, TiO₂ anatase and rutile) has been studied by IR spectroscopy and catalytic tests: cumene cracking and isopropanol decomposition. IR spectroscopic studies of lutidine and pyridine adsorbed on SO₂ treated metal oxides surfaces show the increase or the creation of Brønsted acidity. Test reactions evidence that the strength of such sites depends on the metal oxide, being very weak on MgO and important on TiO₂. Formation of hydrogensulfite species or modification of the redox character of surface properties explains the SO₂ chemisorption effects.

Keywords: Acid–base properties; SO₂ adsorption; Metal oxides; IR spectroscopy; Catalytic activity

1. Introduction

The aim of this study was to discuss the influence of the chemisorption of sulfur dioxide on the surface properties of various metal oxides. The effect of H₂S adsorption on metal oxides was studied in a previous paper [1] by comparison of the activity of metal oxides before or after H₂S adsorption towards two reactions:

(i) the cumene cracking to propene and benzene which is widely applied as a test reaction for strong Brønsted acidity [2]. If the reaction

proceeds via a radical mechanism, styrene and/or α -methylstyrene are formed [3].

(ii) the isopropanol decomposition which leads to the formation of propene with the participation of acidic sites, even weak Brønsted acid sites [4], or to acetone on basic or redox centres [5].

In the same manner, the activity of SO₂ pretreated metal oxides towards both reactions must give information on the influence of sulfur dioxide adsorption on surface properties of catalysts. Moreover, the IR study of probe molecules adsorption must allow to specify the nature of the modifications. It is the reason why basic molecules such as pyridine or 2,6-dimethylpyridine (lutidine), which are generally used to evidence Lewis and/or Brønsted acidity, were

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adsorbed to compare the catalysts acidity in presence or not of SO₂ [6].

2. Experimental

The characteristics of the metal oxides used in this study are reported in Table 1.

Catalysts were granulated (0.5–1 mm) and activated in helium flow at 673 K for 2 h before SO₂ adsorption and catalytic reactions. SO₂ (Fluka) adsorption was carried out in the flow reactor. A mixture containing 1 cm³ min⁻¹ of SO₂ and 39 cm³ min⁻¹ of deoxygenated helium was passed through the catalyst bed (0.2 g) at 623 K for 1 h. Then the weaker held species were desorbed by flowing helium at 623 K for 15 min. The amount of sulfur deposit on catalysts after SO₂ adsorption and short desorption was measured using elemental analysis.

The pulse technique was applied in studies of isopropanol decomposition and cumene cracking; 0.1 g of catalyst and 3 μl pulses of reactants were used. The cumene cracking was carried out at 673 K and isopropanol decomposition at 523 K.

The gas chromatographic analyses were applied for studies of reactants and products amounts. The results presented in the tables correspond to the first pulse of the reactants to determine the influence of the SO₂ pretreatment. In the case of isopropanol decomposition, the results obtained for the sixth pulse are also

reported to study the effect of an eventual SO₂ desorption.

For IR studies, the catalysts were pressed into disks of ca. 10 mg cm⁻². They were activated at 673 K. Two types of experiments were performed: either SO₂ was first adsorbed for 2 h and shortly desorbed at 473 K and then pyridine or lutidine was introduced at room temperature (rt) or SO₂ was added at rt after the adsorption of the probe molecule. The spectra were recorded at rt using a Nicolet MX-1 spectrometer. The scale of absorbance was chosen in such a way that the same surface sample area (100 m² g⁻¹) was taken into account.

3. Results

3.1. SO₂ adsorbed amount

The total amount of sulfur dioxide adsorbed at 623 K after 1 h of SO₂ flow on various metal oxides, measured by chromatography, and the amount remaining after the short desorption (S elementary analysis) are reported in Table 2. The difference between the amount of SO₂ adsorbed for 1 h at 623 K and the remaining SO₂ amount after 15 minutes of desorption at 623 K is presented in the table as % of SO₂ desorbed. It indicates the strength of chemisorption. The following order of the strength of SO₂ chemisorption can be presented on the basis of that statement: CeO₂ >> MgO > ZrO₂ > TiO₂(R) > γ-Al₂O₃ > TiO₂(A).

Note that the chemisorbed SO₂ amount (Fig. 1) follows the same order. Moreover it is in good agreement with that presented earlier [7,8] for irreversible adsorption of SO₂ at room temperature measured by thermogravimetry. The only differences are noted for TiO₂-rutile and CeO₂. It should be noted that the experimental conditions were not exactly the same. In the present work, the samples were activated under helium flow, treated by SO₂ in the flow reactor and desorption was carried out in helium flow at 623 K. In [8] the samples were activated under

Table 1
Characteristics of metal oxides used in this work

Metal oxide	Specific surface area (m ² g ⁻¹)	Preparation method or origin
MgO	70	Prepared from Mg(OH) ₂
ZrO ₂	80	Prepared from isopropylate
TiO ₂ (R) (rutile)	28	Tioxide Int.
TiO ₂ (A) (anatase)	85	Tioxide Int.
CeO ₂	100	Rhône-Poulenc
γ-Al ₂ O ₃	215	G.F.S. Rhône-Poulenc

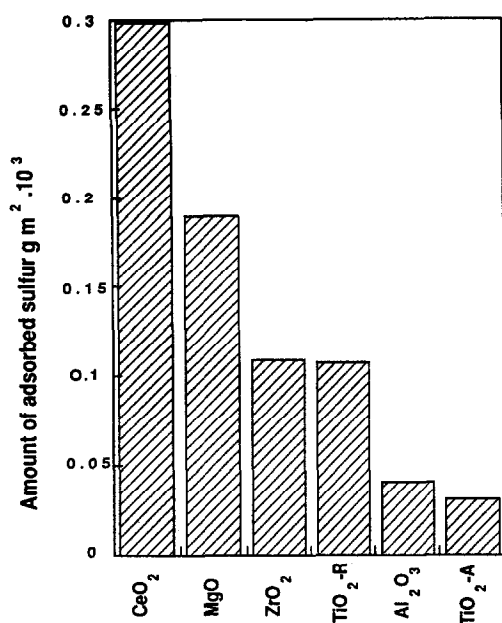


Fig. 1. Amount of adsorbed sulfur (measured by elemental analysis) taking account of the surface area of metal oxides.

Table 2
SO₂ adsorption and desorption at 623 K in a flow of helium

Catalyst	Amount of SO ₂ adsorbed (μmol m ⁻²)		% of SO ₂ desorbed
	after 1 h adsorption	after 15 min desorption	
CeO ₂	9.9	9.3	7
γ-Al ₂ O ₃	4.5	1.3	71
MgO	13.9	5.9	58
ZrO ₂	8.6	3.4	60
TiO ₂ (A)	5.4	0.9	82
TiO ₂ (R)	10.1	3.3	67

Table 3
Influence of SO₂ chemisorption on metal oxides on activity and products distribution of cumene decomposition at 673 K

Catalyst	Pure				After SO ₂ adsorption			
	Cumene conv. (%)	Products distribution (%)			Cumene conv. (%)	Products distribution (%)		
		Propene	propane	Benzene		Styrene	Propene	propane
CeO ₂	70	6	11	83	6	48	32	20
γ-Al ₂ O ₃	1	52	48	–	1	23	15 ^a	–
MgO	0	–	–	–	0	–	–	–
ZrO ₂	0	–	–	–	4	48	52	–
TiO ₂ (A)	3	51	49	–	6	72	270	0.1
TiO ₂ (R)	4	29	31	40	32	60	35	5

^a Ethylbenzene was also produced.

vacuum and SO₂ was adsorbed under static conditions. Then SO₂ was desorbed under vacuum at various temperatures. Moreover, rutile used in this work was from a different origin and has a lower specific area. As for ceria, SO₂ adsorption at 623 K leads to sulfate species. Two types of sulfate have been evidenced (surface and bulk species) [9]. Under flow, it is possible that the bulk sulfate amount could be higher than that formed in static conditions at lower temperatures. Therefore, it should be stressed that the presented above order of the strength of SO₂ chemisorption is valid for desorption at 623 K carried out in helium flow.

3.2. Results of test-reactions

Table 3 shows the catalytic results obtained with the first pulse in cumene cracking on pure samples and after SO₂ adsorption. Pure samples, except ceria, are inactive or very poorly active in the cumene cracking. Preadsorption of SO₂ on ceria gives rise to a high decrease in the cumene conversion which is accompanied by the significant decrease in the formation of styrene. This formation involves electron transfer properties of metal oxides. In the case of MgO and γ-Al₂O₃ no change in the activity after SO₂ adsorption is registered. However, after SO₂ adsorption on alumina, a large amount of ethylbenzene, as the product of a side reaction, was observed. Zirconia, anatase and rutile

Table 4

Influence of SO₂ adsorption on metal oxides on the activity and selectivity in isopropanol decomposition at 523 K

Catalyst	Pure			After SO ₂ adsorption					
	First pulse			First pulse			Sixth pulse		
	Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
		Propene	Acetone		Propene	Acetone		Propene	Acetone
CeO ₂	11	27	73	93	100	–	92	100	–
γ-Al ₂ O ₃	100	100	–	100	99	1	100	97	3
MgO	2	95	5	53	65	32 ^a	27	70	7 ^a
ZrO ₂	21	99	1	84	19	34 ^a	12	22	44 ^a
TiO ₂ (A)	81	99	1	100	100	–	100	100	–
TiO ₂ (R)	43	~ 100	Traces	100	99	–	100	99	–

^a Other products are also formed.

present a higher activity after SO₂ preadsorption which indicates the generation of Brønsted acid sites on their surface. The highest increase in the cumene conversion as a result of SO₂ preadsorption is noted on rutile. On this oxide, similar as on CeO₂, the formation of styrene significantly decreases. This is due to the decrease of the electron transfer properties of the sample. However, contrary to ceria, the activity of rutile increases which indicates that new strong Brønsted acid sites are generated.

Cumene cracking involves strong Brønsted acidic sites. As isopropanol dehydration can occur on weak acidic sites [4], it is expected to be a more sensitive test. Table 4 displays the results obtained for the first pulse of isopropanol and the activity of metal oxides modified with SO₂ for the first and sixth pulse. The activity of the pure samples is the lowest for MgO and the highest for γ-Al₂O₃. The increase in the activity of catalysts is in a good agreement with the decrease of the number of basic sites on metal oxides reported in Ref. [8]. Propene is the main product in the isopropanol decomposition on all the pure metal oxides used, except ceria. The preadsorption of sulfur dioxide, followed by a short desorption, strongly increases the isopropanol conversion. On both titania samples, the increase in the alcohol conversion can be related to the formation of weak Brønsted acid sites because the selectivity to propene is about 100%. One should stress that

on TiO₂ samples both the activity and selectivity do not change up to the sixth pulse of isopropanol, which means that the SO₂ adsorbed species is strongly chemisorbed on both titania samples. The high activity of magnesia and zirconia modified with SO₂ adsorbed is not so stable as on titania samples since a decrease for the sixth pulse is registered. Moreover, on both samples, SO₂ adsorption induces not only Brønsted acidity but also a redox character responsible for acetone formation.

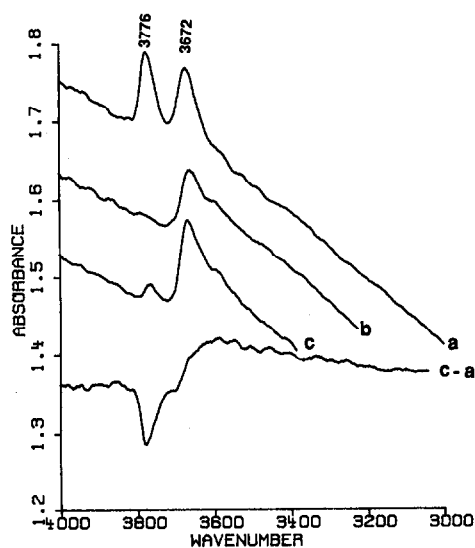


Fig. 2. IR spectra in the ν_{OH} range of ZrO₂. (a) activated at 673 K, (b) after SO₂ addition ($P = 130$ Pa), (c) evacuation at 473 K, (c-a) subtraction.

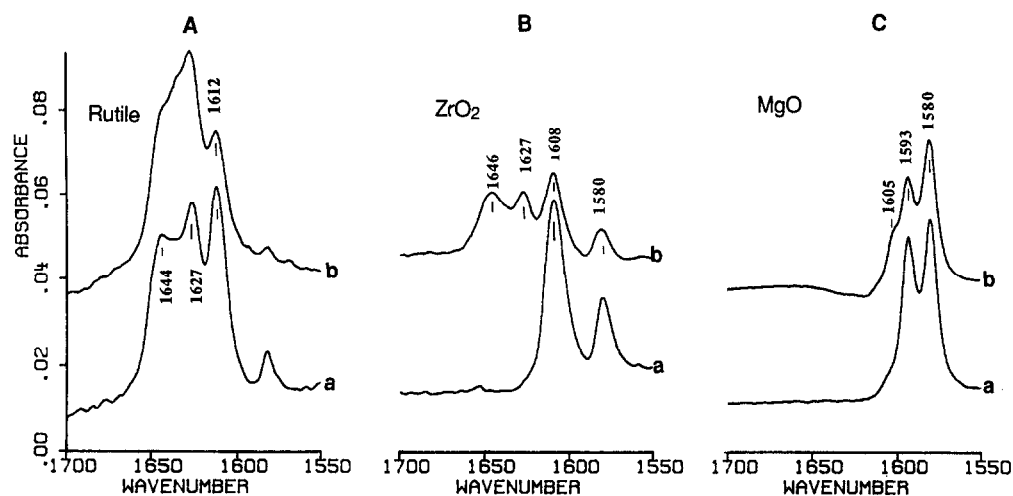


Fig. 3. IR spectra of species formed by lutidine adsorption ($P = 130$ Pa) on pure samples (a) or preadsorbed SO_2 samples (b): TiO_2 -rutile (A), ZrO_2 (B), MgO (C). In the case of TiO_2 and ZrO_2 , the samples have been evacuated at 423 K after lutidine adsorption.

Pure alumina shows a 100% conversion of isopropanol under the conditions used. SO_2 preadsorption does not modify the results.

Ceria which presents a redox character shows a high selectivity for isopropanol dehydrogenation to acetone. The SO_2 adsorption leads to a high increase of its activity and selectivity to propene. Acetone is not formed on ceria modified with SO_2 .

3.3. IR study

As evacuation is more effective than treatment under helium flow for SO_2 desorption, IR

experiments have been performed on the activated samples pretreated with an excess of SO_2 at rt and then evacuated at 473 K. The species formed give rise to bands mainly below 1100 cm^{-1} and were previously assigned to sulfite and hydrogensulfite [8]. The only exception is ceria which presents bands in the $1400\text{--}1350\text{ cm}^{-1}$ range due to sulfate formation as already reported [8,9]. This oxidation occurs with the concomitant reduction of Ce^{4+} into Ce^{3+} [8].

Study of the ν_{OH} range shows that SO_2 specifically interacts with the hydroxyl groups of the highest wavenumber generally considered as monodentate and the most basic. An example

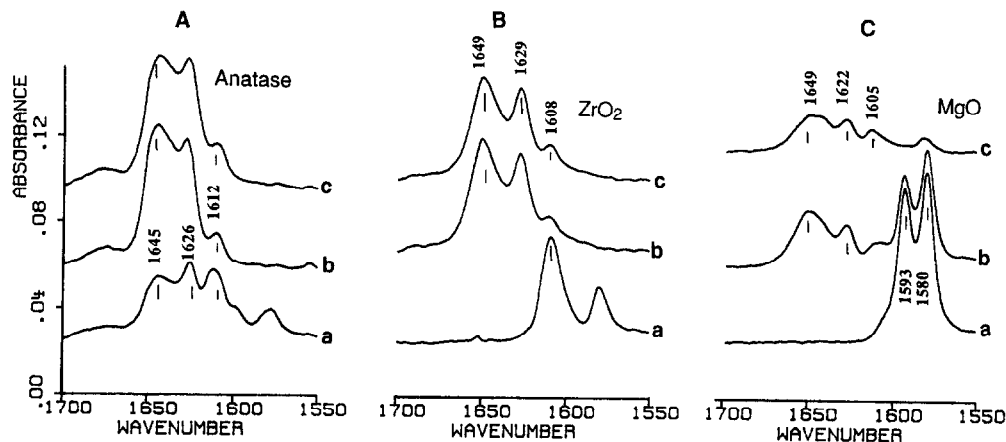


Fig. 4. IR spectra of adsorbed lutidine species on titania (A), zirconia (B), magnesia (C). (a) pure samples ($P = 130$ Pa), lutidine being evacuated at 423 K (A, B), or rt (C), (b) after SO_2 addition ($P = 400$ Pa), (c) after evacuation at rt.

is given in Fig. 2 relative to ZrO_2 . A broad band develops below 3600 cm^{-1} and has been considered as characteristic of hydrogensulfite species as already reported on alumina [10].

Lutidine is generally considered as more sensitive to Brønsted acidity than pyridine and therefore is used in the present study. Let us remain that lutidinium species are characterized by bands between 1620 and 1650 cm^{-1} , while adsorption on Lewis sites gives rise to bands below 1620 cm^{-1} [11].

On pure metal oxides, lutidine addition at rt followed by evacuation at 423 K reveals the presence of a few amount of Brønsted acidic sites on only tioxide surfaces. SO_2 pre-adsorption increases this amount on TiO_2 (Fig. 3A) and creates Brønsted acidity on all other oxides, as for example on ZrO_2 (Fig. 3B), magnesia being excepted (Fig. 3C).

To confirm these results, SO_2 has been introduced at rt on the activated samples on which lutidine has been preadsorbed. On all the samples lutidinium species are created after SO_2 addition (Fig. 4). It is generally at the expense of lutidine species adsorbed on Lewis acidic sites showing a transfer of the probe molecule from Lewis to created Brønsted acidic sites (Fig. 4B). On magnesia, lutidine is slightly chemisorbed and is desorbed after evacuation at 423 K . So, in this case, the sample was not evacuated at 423 K after lutidine addition before SO_2 addition (Fig. 4C). In such conditions,

contrary to those previously used (Fig. 3), SO_2 adsorption also creates Brønsted acid sites on MgO .

As shown on ZrO_2 (Fig. 5), experiments using pyridine as a probe molecule confirm these results. The intensity of the 1443 and 1605 cm^{-1} bands due to coordinated pyridine decreases when SO_2 is introduced whereas bands at 1542 and 1638 cm^{-1} , characterizing pyridinium species, appear.

4. Discussion

SO_2 adsorption on the surface of metal oxides used in this work was studied previously by infrared spectroscopy and gravimetric and temperature programmed desorption techniques [7,8]. It was stated that SO_2 can be coordinatively adsorbed on Lewis acid sites and in such a case SO_2 acts as an electron donor. Such interactions are very weak and most probably do not play a significant rôle in the conditions used in this work. On basic metal oxides, SO_2 acts as an electron acceptor and is adsorbed on either basic O^{2-} sites or OH groups. On O^{2-} sites, strongly adsorbed sulfite species are formed. Adsorption of sulfur dioxide on basic OH groups leads to the formation of hydrogensulfite species. The structure of the hydrogensulfite ions is still discussed. Some authors suggested that hydrogensulfite species are as HSO_3^- ions [12] whereas others rather proposed SO_2OH^- species [8]. EPR results showed that SO_2^- radical species were also formed for instance on Al_2O_3 [13] or on MgO [14].

SO_2 adsorption on metal oxides depends on the strength of both types of basic sites and on the number of these sites. On the basis of data collected in Table 2 and Fig. 1, the order of the strength of SO_2 chemisorption was written above. From literature results [7] the sequence of the number of basic sites is as follows:

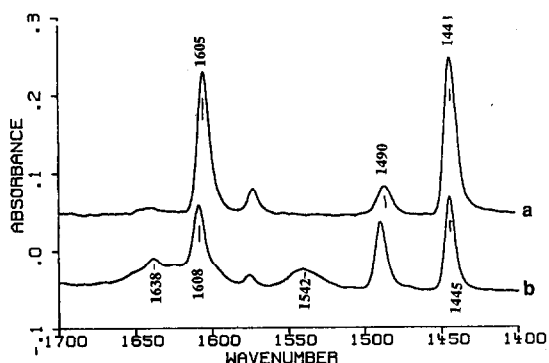
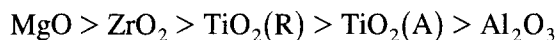


Fig. 5. IR spectra of adsorbed pyridine. (a) on pure ZrO_2 sample evacuated at 423 K , (b) effect of SO_2 addition ($P = 400\text{ Pa}$).

The order of the Lewis basicity strength slightly depends on the probe molecule which is used [7]. On the basis of various literature descriptions, one can propose the following order for the Lewis basicity strength:



Ceria is not included since its redox character causes difficulties in the measurement of its basicity [7].

IR results clearly show that SO_2 addition leads to creation of Brønsted acidic sites certainly due to hydrogensulfite species formation. This indicates that they could correspond to the monoanion of the sulfite acid, i.e. HSO_3^- . This increase of acidity is in agreement with the increase of activity in isopropanol decomposition and selectivity to propene observed for both titania samples. Cumene cracking results specify that SO_2 adsorption on the rutile form leads to the highest increase of the strong Brønsted acidity. This can be related to the amount of SO_2 adsorbed species, calculated by m^2 (Fig. 1, Table 2) which is higher on rutile than on anatase. As for alumina, the very high activity of the pure sample towards isopropanol dehydration does not allow one to detect any SO_2 effect on its acidity but cumene cracking shows that the created Brønsted acidity is not strong.

Among the metal oxides used, MgO is a typical basic oxide [15]. Isopropanol dehydrogenation is often considered as a reaction test for basicity [4]. However, the very low activity of pure MgO under the conditions used rather suggests, as already mentioned [5], that acetone formation is more likely related to the sample redox properties. SO_2 adsorption increases its acidity since the propene yield is higher. However the created Brønsted acidic sites are weak since IR spectroscopy is not able to detect them on the SO_2 pretreated sample (Fig. 3). Moreover no activity for cumene cracking is noted (Table 3). Since SO_2 adsorption mainly occurs on O^{2-} basic sites, it should decrease the basic character of the sample. In spite of that, the

acetone yield is increased by SO_2 adsorption (Table 4). It could be due to generation of redox properties. Similar effects of SO_2 adsorption are observed on zirconia. Comparison of results obtained for the first and the sixth pulses of isopropanol shows that the SO_2 effects tend to decrease with time in the cases of MgO and ZrO_2 . This indicates the progressive desorption of SO_2 with time, the surface properties tending to those of the pure samples.

The amount of SO_2 adsorbed on ceria is the highest. It is known from literature [16,17] that SO_2 causes the reduction of Ce^{4+} to Ce^{3+} whereas it is oxidized to sulfate species. Taking into account the radical mechanism proposed for cumene cracking [3] the presence of Ce^{4+} sites explains the high activity of ceria for this reaction. Their partial conversion into Ce^{3+} after SO_2 oxidative adsorption reduces the number of potential active sites leading to a decrease of the catalytic activity and selectivity towards styrene. It is confirmed by results obtained by isopropanol decomposition considering that SO_2 adsorption drastically decreases acetone formation due the modification of ceria redox properties. On the other hand, propene formation strongly increases indicating creation of Brønsted acidic sites as shown by IR spectroscopy.

5. Conclusion

The chemisorbed SO_2 amount on metal oxides follows quite the same order than the Lewis basicity strength. SO_2 chemisorption leads on all metal oxides studied to the creation of Brønsted acidic sites as shown by IR spectroscopy. Catalytic results show that the strength of these acid sites depends on the metal oxide: it is quite weak on MgO, more pronounced on $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 and TiO_2 anatase and high on rutile. The creation of such sites on ceria is accompanied by a drastic modification of its redox properties.

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