Isomerization of *n*-butane on sulfated zirconia: evidence for the dominant role of Lewis acidity on the catalytic activity

F. Pinna [1], M. Signoretto, G. Strukul

Department of Chemistry, University of Venice, Calle Larga St. Marta 2137,
I-30123 Venice, Italy

G. Cerrato and C. Morterra

Department of Inorganic, Physical and Materials Chemistry, University of Turin,
via P. Giuria 7, I-10125 Turin, Italy

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The catalytic activity of a ZrO_2/SO_4 catalyst in the isomerization of *n*-butane at 423 K is reversibly suppressed by addition of CO. IR analysis of the adsorption of CO indicates that the only σ-coordination of CO onto coordinatively unsaturated surface Zr^{4+} cations occurs in the 300–473 K interval.

Keywords: sulfated zirconia; *n*-butane isomerization; CO IR spectroscopy

1. Introduction

It is known that, when prepared and activated under particular conditions, sulfated zirconia catalysts may possess superacidic sites capable to promote the isomerization of light paraffins under mild conditions [1,2].

The exact nature and the role of the acidic sites responsible for this behaviour is not clearly established and is still a matter of discussion. In fact, two different views have been proposed: on the one hand the catalytic activity has been correlated with the presence of Brønsted acid sites [3], while on the other hand only the existence of strong Lewis acid sites has been evidenced on some active catalysts by spectroscopic investigations [4]. In addition, Vedrine et al. have proposed that acid sites of both Brønsted and Lewis type must be present on the surface in order to induce superacidic properties [2]. Lately, through a quantum mechanical study

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[1] To whom correspondence should be addressed.

performed on molecular models of sulfated zirconia, Babou et al. [5] have reported that the superacidity computed for this model is essentially of the Brønsted type, the presence of some residual water being essential in the behaviour of the chemical system. Clearly, a better understanding of this crucial point seems very important for a more rational preparation of catalysts with a better performance.

In a recent study of the effect of hydration on the catalytic activity of sulfated zirconia catalysts in *n*-butane isomerization [6], we have found a correlation between activity and surface concentration of strong Lewis acid sites. In fact, a partial rehydration of the working catalyst leads to an increasing loss of activity that can be completely recovered only after calcination, which converts the newly formed Brønsted acid sites into Lewis ones.

In order to shed more light on this crucial point, in this work we report the effect of a typical Lewis acidity probe, carbon monoxide, on the catalytic activity of *n*-butane isomerization and a parallel investigation of the catalyst surface with IR spectroscopy.

2. Experimental

A ZrO_2/SO_4 catalyst containing a nominal amount of 2.8 SO_4 groups/nm^2, designated ZS8, was prepared by suspending into an aqueous $(NH_4)_2SO_4$ solution amorphous $Zr(OH)_4$, previously prepared by use of the sol–gel technique [6] from a Zr propoxide precursor. The mixture was stirred for 2 h, slowly evaporated to dryness and finally calcined in dry air at 823 K for 3 h.

The isomerization of *n*-butane was performed in a continuous flow reactor at 423 K and 1 atm by feeding a mixture of *n*-butane and dry helium (*n*-butane/helium = 3; space velocity = 200 h^{-1}) and the products were analyzed on line by gas chromatography. Prior to reaction, the catalyst was activated in a dry air stream at 723 K for 2 h, and then cooled to the reaction temperature (423 K).

FTIR spectra were obtained in a strictly in situ configuration at resolution 2 cm^{-1} with a Bruker 113v spectrophotometer, equipped with an MCT detector. The samples were prepared from an aqueous suspension in the form of thin-layer deposition (10 mg cm^{-2}) on a pure Si platelet, then activated in vacuo at 723 K. CO differential spectra were computer-subtracted of the gas contribution, in order to obtain semi-quantitative data.

3. Results and discussion

The isomerization reaction of light *n*-alkanes is known to occur to a negligible extent on regular acidic catalyst systems, whereas it proceeds with high yield on superacidic catalysts also at room temperature [7].

The catalyst ZS8, activated at 723 K, has been tested in the isomerization of *n*-butane in a continuous flow reactor at 423 K. In fig. 1 a total conversion versus

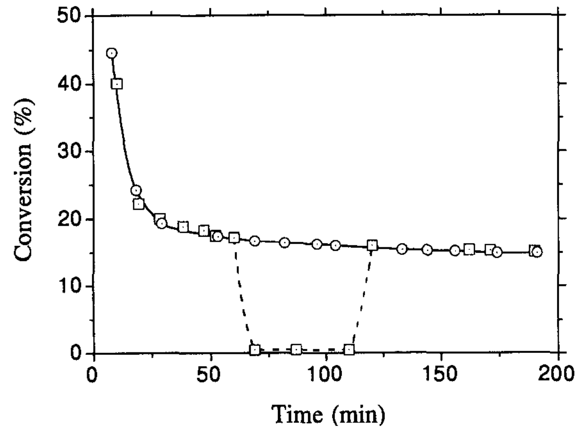

Fig. 1. Circles: catalytic conversion of *n*-butane as a function of time on stream; squares: effect of CO addition and release (dashed-line) on the same reaction after reactivation of the catalyst.

time on stream plot is reported, which shows a rapid decrease of the activity at the beginning of the catalytic run, probably due to a partial deactivation process suggested by the observation of some cracking products. After about 50 min the conversion stabilizes around 15–18% and remains practically constant for at least 300 min. The initial activity can be completely recovered after reactivation of the sample in dry air at 723 K. When, after 60 min, the He present in the reactant stream is replaced with CO, the dramatic effect shown in fig. 1 can be observed. The catalytic activity drops almost to zero (0.4–0.5% conversion) in a few minutes and remains constant as long as CO is present in the feed. When CO is released and replaced with He, the conversion suddenly rises and the catalyst recovers its normal steady state activity.

Since a similar effect on the catalytic activity has been observed upon addition of H_2O and H_2O was observed to poison selectively the sites active towards CO adsorption [6], the results of fig. 1 seem to suggest that the same type of catalytically active sites are poisoned in both cases.

CO is known to chemisorb around ambient temperature on d^0 oxidic systems through a σ-coordination to coordinatively unsaturated surface (cus) cations, acting as strong Lewis acid sites. Sulfated zirconia systems are no exception in this respect: at ambient temperature CO adsorbs in small amounts [8] yielding CO band(s) centered at 2200 cm^{-1}, i.e. at frequencies higher than in the case of non-sulfated ZrO_2 [9], because of the strong inductive effects from surface sulfates.

Fig. 2a reports the background IR spectrum of the ZS8 catalyst activated at 723 K, and the effects on the IR spectrum caused by CO uptake at beam temperature (b.t. $\approx$ 340 K). The background spectrum presents discrete bands in the 4000–3000 cm^{-1} range, due to residual surface hydroxyl groups (see the inset to fig. 2a); the adsorption of CO at b.t. yields a single broad and structureless band centered at 2210–2200 cm^{-1} (see fig. 2b; the dashed-line curve represents the inter-

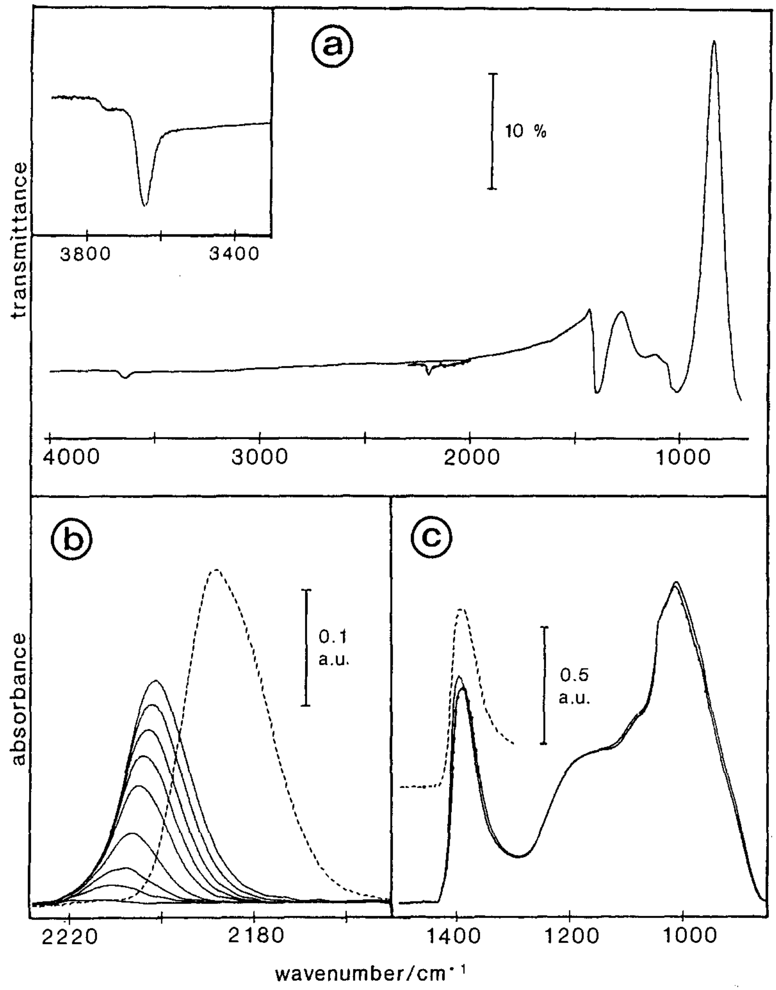

Fig. 2. IR spectra of the ZS8/CO system. (a) The background transmittance spectrum of ZS8 activated at 723 K, and (dotted-line segment) the effect of dosing 100 Torr CO at beam temperature. Inset: Blown-up detail of the OH stretching region. The OH spectra coincide before and after the allowance of 100 Torr CO at beam temperature and after heating in CO at 473 K. (b) Differential absorbance spectra of CO adsorbed at beam temperature on ZS8 activated at 723 K (solid-line curves; P_{CO} in the range 1.0×10^2–1.2×10^{-2} Torr), and on non-sulfated ZrO_2 activated at 723 K (dashed-line curve; P_{CO} 1.0×10^2 Torr). (c) Solid-line: absorbance IR spectrum of surface sulfate on ZS8 activated at 723 K. The spectrum is reproduced after CO uptake and evacuated at beam temperature. Dotted-line: the spectrum of sulfates after the allowance of 100 Torr CO at beam temperature. Dashed-line: segment of the spectrum of sulfates after heating ZS8 into 100 Torr CO at 473 K and subsequent evacuation of CO at ambient temperature.

action with a non sulfated ZrO_2 surface), while it does not produce any perturbation on the spectrum of surface OH groups. In fact it is necessary to lower the adsorption temperature to 77 K to observe a weak perturbation of the OH bands, due to CO molecules interacting via H-bonding with the free hydroxyls.

Notably, after a prolonged heating in the presence of 100 Torr CO at temperatures as high as 473 K (i.e., at temperatures equal to or slightly higher than that of the isomerization reaction of fig. 1), the OH spectrum of ZS8 remains unchanged.

In the spectral region below 1800 cm^{-1}, the background IR spectrum of ZS8 presents two main absorptions at $\sim 1400\ \mathrm{cm}^{-1}$ (the $\nu_{\mathrm{S=O}}$ mode) and $\sim 1000\ \mathrm{cm}^{-1}$ (the $\nu_{\mathrm{S-O}}$ mode), due to surface sulfates that, on the activated material, display a covalent configuration [6]. The adsorption of CO at b.t., shown in fig. 2b, causes a minimal perturbation on the spectrum of sulfates (see the details in fig. 2c): the $\nu_{\mathrm{S=O}}$ mode at 1400 cm^{-1} is lowered by 10 cm^{-1}, due to weak inductive effects originated by the presence of the charge-releasing CO adspecies and acting on the force constant of the charge-withdrawing S=O oscillators. Evacuation of CO eliminates the band at 2210–2200 cm^{-1} (see the desorption pattern in fig. 2b) and reproduces the starting spectrum of surface sulfates.

Heating in the presence of 100 Torr CO at temperatures as high as 673 K neither modifies the spectrum of sulfates (see the dashed-line curve in fig. 2c), nor causes the formation of any other spectroscopically detectable surface species. In fact formate-like surface species, that form at $T \geqslant 423$ K on pure ZrO_2 [10], do not form on sulfated zirconia.

CO σ-coordination to cus Zr^{4+} cations is thus the only effect produced by CO uptake on ZS8 at temperatures in the 300–473 K range. Gas-volumetric and microcalorimetric measurements are in progress, to evaluate both the amounts and the adsorption heats of CO on the surface of ZS8.

4. Conclusions

Carbon monoxide uptake at temperatures around ambient temperature brings about a plain σ-coordination to surface cationic sites, and thus is a specific probe for strong acidic sites of the Lewis type.

The adsorption of CO on the working catalyst ZS8 poisons selectively and reversibly the active sites for the isomerization of *n*-butane. The present results do not exclude that, in the isomerization of light *n*-alkanes over SO_4/ZrO_2 systems, some protonic (Brønsted) acid sites may actually play some role, but certainly constitute the first unambiguous evidence that the presence of abundant Lewis sites (made superacidic by the presence of surface sulfates and inductive effect therefrom) is vital for the occurrence of catalytic activity under mild conditions, typical of superacidic systems.

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