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Propane carbonylation on sulfated zirconia catalyst as studied by ^{13}C MAS NMR and FTIR spectroscopy

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Abstract

Using in situ ^{13}C MAS NMR, it has been demonstrated that propane is carbonylated with carbon monoxide to produce isobutyraldehyde and isobutyric acid at 100–150 °C on sulfated zirconia. Isobutyraldehyde represents the intermediate reaction product, which is almost completely converted into the acid at 150 °C. The selective formation of isobutyraldehyde at low temperatures on SZ indicates that principally the secondary C–H bond of propane is activated, rather than its C–C bond. This pathway of the alkane activation can be realized either on Lewis acid sites of SZ or by direct formylation by the formyl cation formed as equilibrated species from the formate. Infrared spectroscopy provides evidence that the sulfate groups of SZ are responsible for the aldehyde oxidation. The formation of surface dithionate species as a result of sulfur reduction is suggested. These dithionate species are readily reconverted into sulfate groups by an oxidizing treatment in an O_2 atmosphere.

Keywords: Propane; Carbonylation; Carbon monoxide; NMR spectroscopy; IR spectroscopy; Sulfated zirconia

1. Introduction

Among the solid catalytic systems that can activate saturated hydrocarbons, sulfated zirconia (SZ) catalysts have received much attention recently [1,2]. This is due to the high activity of these catalysts, revealing the capability of catalyzing the isomerization of C_4–C_5 alkanes at low temperatures [3,4].

Another promising application of SZ is the reaction of alkane carbonylation with CO. It has been shown recently that alkanes (n-pentane, isobutane) can be easily carbonylated on pure sulfated zirconia to produce valuable products such as aldehydes, ketones, and carboxylic acids [5–7]. In this respect, it is of interest to perform a direct carbonylation with CO of propane, which is more inert than C_4–C_5 alkanes, using sulfated zirconia as the solid acid catalyst.

Propane carbonylation with CO has been reported to occur in liquid superacids [8,9], in the presence of strong Lewis acids ($AlCl_3$) [10] or acidic zeolite H-ZSM-5 [11], the reactions presuming the generation of intermediate carbenium ions and their trapping by CO. It has been established recently that SZ catalyzes propane conversion at 200–450 °C by a dimerization–isomerization-cracking process, i.e., via a classical carbenium-ion mechanism [12,13]. Thus, carbenium ions formed in the course of propane activation on SZ are likely trapped with CO to form a carbonyl group-containing compound.

Besides the observation of the carbonylation products themselves, the next point that should be addressed concerns the mechanism of acid formation. Indeed, it is expected that the interaction of an alkane with CO should result in the formation of an aldehyde (or ketone). However, the formation of the acid was also observed when only alkane and carbon monoxide were reacted on SZ [6,7]. Thus, an additional oxidation of aldehyde to produce the acid seems to occur on SZ [6,7]. In this respect, the sulfate groups of SZ could have an oxidative role and should be reduced in the course of the reaction. The reduction of sulfate groups results in a deactivation of the SZ catalyst [14,15]. To restore the catalytic activity of SZ it would be necessary to provide reoxidation of the reduced sulfate group.

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In this paper we report the direct spectroscopic measurements of the carbonylation of propane with CO, using a pure sulfated zirconia as the solid acid catalyst. We also show that the sulfate groups of SZ are indeed responsible for the aldehyde oxidation and can be regenerated by a molecular oxygen treatment.

2. Experimental

2.1. Materials

A sample of sulfated zirconia was synthesized according to the procedure described earlier [16] by treatment of $Zr(OH)_4$ on filter paper with 0.5 M H_2SO_4 aqueous solution and subsequent drying and calcination in air at 600 °C. The zirconia crystallized in the tetragonal phase, the SO_3 content of the sample after calcination was 9.9% (wt), with a surface area of 130 $m^2\,g^{-1}$. Either propane, labeled with ^{13}C isotope in the CH_2 group, [2-^{13}C]propane (82% ^{13}C isotope enrichment), or ^{13}CO (90% ^{13}C isotope enrichment) was used in NMR experiments. [2-^{13}C]Propane was prepared from [1-^{13}C]ethanol (82% ^{13}C isotope enrichment) via a four-step synthesis. Isobutyraldehyde (purity 99%) and isobutyric acid (purity 99.5%) were purchased from Fluka and used without further purification.

2.2. NMR experiments

For solid-state NMR analysis a sample of SZ was heated in a glass tube at 400 °C under vacuum (10^{-3} Pa) for 2 h. Then equal amounts of propane and CO (ca. 300 µmol g^{-1} of each coadsorbate) were adsorbed on the sample under vacuum at the temperature of liquid nitrogen. After the glass tube was sealed off at low temperature from the vacuum system, the sample was warmed to room temperature and heated at 100–150 °C for 1 h for the reaction to proceed.

^{13}C NMR spectra with high-power proton decoupling and magic-angle spinning (MAS), with or without cross-polarization (CP), denoted below as ^{13}C CP/MAS NMR and ^{13}C MAS NMR, were recorded at 100.613 MHz (magnetic field of 9 T) on a Bruker MSL-400 spectrometer at room temperature. The following conditions were used for recording spectra with CP: proton high-power decoupling field was 11.7 G (5.0 µs length of 90° ^{1}H pulse), contact time was 5 ms at a Hartmann–Hahn matching condition of 50 kHz, delay time between scans was 3 s. Single-pulse excitation ^{13}C MAS spectra were recorded with 45° flip angle, ^{13}C pulses of 2.5-µs duration, and 10-s recycle delay, which satisfied a $10T_1$ condition. High-power proton decoupling in these experiments was used only during the acquisition time. This eliminates nuclear Overhauser enhancement of the signal areas and allows quantitative assessment of the signals [17]. ^{13}C chemical shifts for carbon nuclei of adsorbed organic species were measured with respect to TMS as the external reference with accuracy $\Delta\delta = \pm 0.5$ ppm. The temperature of the samples during acquisition of NMR spectra was controlled with a BVT-1000 variable-temperature unit.

2.3. FTIR experiments

For IR analysis, 15–20 mg of the SZ sample was pressed into a 2 cm^2 self-supported wafer. The wafer was then placed into an infrared cell, allowing heating of the sample and introduction of the reagents. The sample was activated under vacuum (10^{-3} Pa) at 400 °C for 1 h. The vapor of isobutyraldehyde (or isobutyric acid) was then introduced into the cell at room temperature. The sample was then heated at 100–150 °C for 1–4 h. Afterward it was evacuated at 400 °C for 1 h. Infrared spectra were recorded at room temperature with a Nicolet Magna 550 spectrometer with a DTGS detector, 128 scans, and a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Carbonylation of propane as studied by ^{13}C solid-state NMR

Fig. 1 shows the ^{13}C CP/MAS NMR spectra recorded after heating of the SZ sample with coadsorbed propane and CO for 1 h at 100 °C. The spectra obtained clearly indicate that carbonylation of propane with carbon monoxide occurs at this temperature. Indeed, using ^{13}C-labeled carbon monoxide and unlabeled propane, two intense signals appear (Fig. 1a) in the range of the spectrum typical for the carbonyl groups [18]. The signal at 232 ppm belongs to the carbonyl

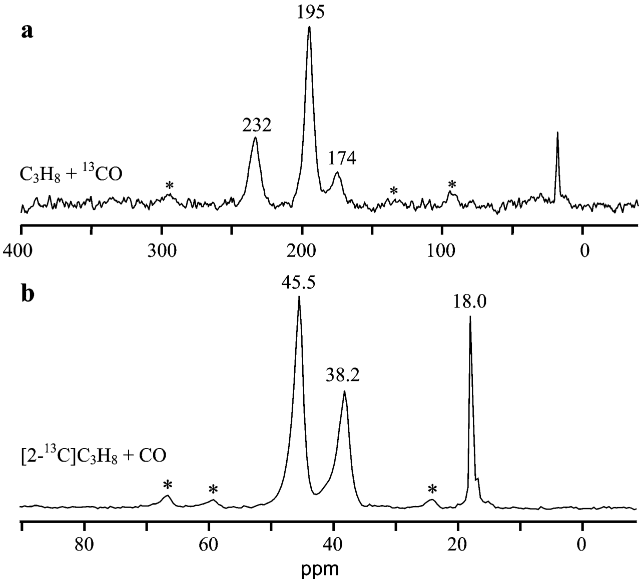
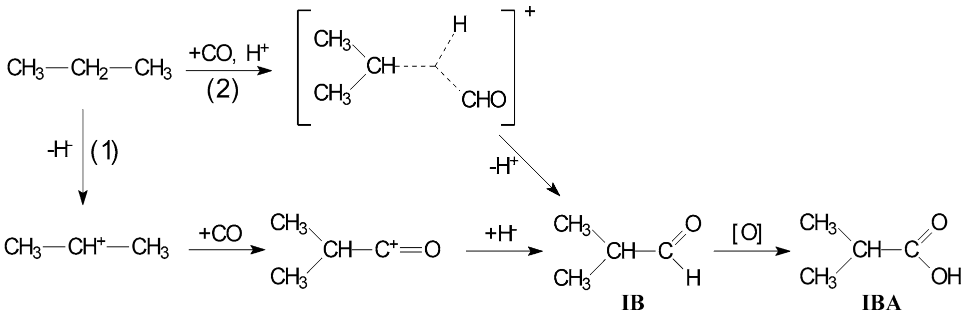


Fig. 1. ^{13}C CP/MAS NMR spectra of the products formed from propane and CO on sulfated zirconia at 100 °C: (a) coadsorption of the unlabeled propane and ^{13}CO (90% ^{13}C enrichment); (b) coadsorption of the [2-^{13}C]C_3H_8 (82% ^{13}C enrichment) and unlabeled CO. Asterisks denote spinning side bands.



Scheme 1. Propane carbonylation on sulfated zirconia at 100–150 °C.

moiety of aldehyde [7], while the signal at 195 ppm points to the formation of a carboxylic acid [5,7,11].

The use of propane, selectively enriched with ^{13}C isotope in the CH_2 group, [2-^{13}C]C_3H_8, allowed us to ascertain the carbonylation products accurately. Note that if propane with a ^{13}C-labeled methylene group is used for the reaction, the signals from the labeled CH_2 group of the initial C_3H_8, as well as from the carbons in the products where the label migrates in the course of the reaction, should be observed in the spectra. Two signals at 45.5 and 38.2 ppm become clearly visible in the ^{13}C CP/MAS NMR spectrum, besides the signal from the CH_2 group of unreacted [2-^{13}C]C_3H_8 at 18.0 ppm [11], when the sample with coadsorbed [2-^{13}C] C_3H_8 and unlabeled CO was heated at 100 °C (Fig. 1b). The appearance of these signals can be readily interpreted in terms of the formation of isobutyraldehyde (**IB**) and isobutyric acid (**IBA**) from propane and CO on SZ. Indeed, the most intense signal appearing at 45.5 ppm can be attributed to the labeled CH group of **IB**, its position being close to that for liquid isobutyraldehyde at 41.2 ppm [19]. The position of the second signal at 38.2 ppm is close to that for liquid **IBA** at 34.8 ppm [20], and, therefore, it is attributed to the labeled CH group of isobutyric acid adsorbed on SZ. It should be emphasized that isobutyraldehyde and isobutyric acid were the only products formed from propane and CO on SZ at 100–150 °C; no other products were identified in the ^{13}C and ^{1}H MAS NMR spectra. The conversion of propane at 100 °C, determined from the ^{13}C MAS NMR spectrum of the sample of Fig. 1b, was 8%, **IB** and **IBA** being formed with 76 and 24% selectivity, respectively. At 150 °C, 16% of propane was converted, the selectivities for **IB** and **IBA** being 7 and 93%, respectively. It should be noted that the order of addition of CO and propane does not influence noticeably the product distribution observed.

Activation of propane in the presence of CO on H-ZSM-5 zeolite [11] proceeds in full analogy with the process in superacid media [8,9] via C–C bond cleavage to form methane and an ethyl cation. The ethyl cation abstracts a hydride ion from propane to form an isopropyl carbenium ion. The latter interacts finally with CO and water giving rise to isobutyric acid, with methane and ethane being evolved as the other reaction products. In contrast to superacid media and zeolites, propane carbonylation on SZ is consistent with the activation of the secondary C–H bond, rather than the C–C bond. Two mechanisms can provide the activation of the C–H bond. First, Lewis acid sites of SZ can be involved in the alkane activation, via hydride abstraction to form the isopropyl cation, which is further trapped by CO. The reverse hydride transfer to the formed oxocarbenium ion leads to **IB** (Scheme 1, pathway 1). This situation can be similar to the propane carbonylation on Lewis acid catalysts like $AlCl_3$, where isobutyraldehyde and the products of its further transformation were formed [10]. The second possible mechanism for **IB** formation is a direct formylation by formyl cation via pathway 2. Indeed, formate species were shown to be formed upon CO adsorption on SZ [5]. The signal at 174 ppm from formate species can also be detected directly among the products of propane carbonylation with ^{13}CO (Fig. 1a). Thus, formyl cation formed from the formate as equilibrated species can be involved in propane formylation (Scheme 1, pathway 2), with the formation of a three-center two-electron-bonded pentacoordinate carbonium ion as the transition state, similar to the reaction in superacidic solutions [21].

At 100 °C, the aldehyde is the main reaction product (vide supra), **IB** being formed with 76% selectivity. With increasing the temperature up to 150 °C, **IBA** becomes the principal reaction product (93%). These experimental data indicate that isobutyraldehyde is formed as an intermediate product of propane carbonylation. **IB** appears to be oxidized by sulfated zirconia into the acid similar to benzaldehyde [22].

Thus, using solid-state ^{13}C NMR spectroscopy we have demonstrated that propane can be carbonylated with CO on a sulfated zirconia catalyst producing isobutyraldehyde and isobutyric acid. The transformation of **IB** into **IBA** clearly supports that the oxidation step takes place on SZ. To explore the nature of oxidation activity of sulfated zirconia in the reaction studied, we have further examined the conversion of isobutyraldehyde on SZ by IR spectroscopy.

3.2. Oxidation of isobutyraldehyde on sulfated zirconia: IR spectroscopic study

The oxidation activity of sulfated zirconia has already been reported. Farcasiu et al. [14] argued that the oxidizing properties of SZ catalysts are responsible for the light alkane activation via reversible one-electron abstraction. Vera et al.

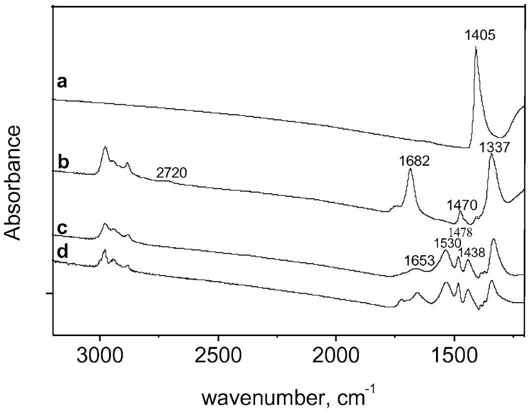


Fig. 2. FTIR spectra recorded after: (a) vacuum activation of SZ sample at 400 °C; (b) room temperature adsorption of isobutyraldehyde (2 Torr of equilibrium pressure in the IR cell) on activated SZ; (c) heating the SZ sample with adsorbed **IB** for 1 h at 150 °C; (d) adsorption of isobutyric acid (2 Torr) on activated SZ.

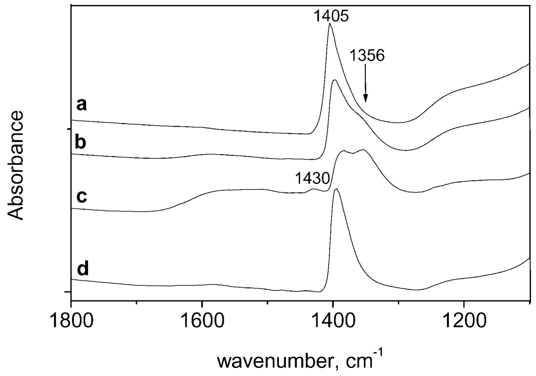


Fig. 3. FTIR spectra recorded after: (a) vacuum activation of SZ sample at 400 °C; (b) room temperature adsorption of isobutyraldehyde (2 Torr) on activated SZ, heating the SZ sample with adsorbed **IB** for 1 h at 150 °C, and decomposition of the acid at 400 °C; (c) adsorption of **IB** (10 Torr) on sample (b), heating the SZ sample with adsorbed **IB** for 4 h at 150 °C, and decomposition of the acid at 400 °C; (d) room temperature adsorption of isobutyric acid (2 Torr) and acid decomposition at 400 °C.

[23] also considered the Zr^{4+}/Zr^{3+} oxidation/reduction pair as the key intermediate in alkane isomerization on SZ.

As to the oxidation of the aldehyde into the acid, the situation seems to be different. The reaction implies irreversible oxygen transfer from the catalyst, so the SZ should be reduced in the course of the reaction. It is worth noting that sulfuric acid possesses well-pronounced oxidative properties. So, the sulfate groups of SZ are the probable source of oxygen for the oxidative step. Indeed, the reduction of surface sulfates of SZ has been already detected in the course of adamantane oxidation [14]. It was also suggested that reduction of the surface sulfates is responsible for the SZ deactivation during *n*-butane isomerization [23,24].

To determine whether the sulfates are the species accomplishing the oxidation of isobutyraldehyde into isobutyric acid, we have used IR spectroscopy, which allows monitoring of the transformation of sulfates in the course of the aldehyde conversion.

Fig. 2 shows the IR spectra of the SZ sample before and after the aldehyde adsorption and reaction at 150 °C. The spectrum of SZ, activated in vacuum at 400 °C, reveals a band at 1405 cm^{-1} (Fig. 2a) characteristic of the asymmetric $\nu_{S=O}$ stretching mode [25]. This resonance shifts to a lower frequency at 1337 cm^{-1} upon room temperature adsorption of isobutyraldehyde (Fig. 2b). In addition, the bands from the adsorbed aldehyde become clearly visible in this spectrum. Besides the aliphatic $\nu_{C–H}$ vibrations (2800–3000 cm^{-1}), a characteristic aldehyde vibration can be detected at 2720 cm^{-1} ($\nu_{C–H}$ of the CHO group), the band at 1470 cm^{-1} is related to the CH_3 deformation, whereas the strong band at 1682 cm^{-1} is attributed to the C=O stretching mode [26]. Heating of the sample with the adsorbed aldehyde at 150 °C for 1 h, i.e., under conditions providing almost complete conversion of the **IB** into **IBA**, (vide supra, NMR data), results in essential changes in the vibration pattern (Fig. 2c). The characteristic signals at 2720, 1682, and 1470 cm^{-1} from the isobutyraldehyde completely disappear from the spectrum. Another pattern of the bands arises in the lower frequency region. Four resonances centered at 1653, 1530, 1478, and 1438 cm^{-1} (Fig. 2c) proved to be very close to the bands observed for isobutyric acid adsorbed on SZ sample in a separate experiment (Fig. 2d) [26,27]. Thus, our IR data further confirm that **IB** can be oxidized by sulfated zirconia to produce **IBA**; i.e., the aldehyde is indeed the intermediate product of propane carbonylation into the acid.

Note, that during the conversion of **IB** into **IBA** the band $\nu_{S=O}$ of SZ remains shifted in comparison with that of the initial activated sample (cf. Figs. 2c and 2a), probably due to the interaction with the adsorbed acid. No visible modification of the $\nu_{S=O}$ band in SZ occurs in the course of aldehyde oxidation, which indicates that the formed acid remains adsorbed on SZ.

To further clarify the fate of the sulfate groups of SZ during the aldehyde oxidation into the acid, we tried to decompose the acid by heating at 400 °C. Fig. 3b shows the IR spectrum recorded after heating the sample of Fig. 2c (i.e., containing the acid formed by the aldehyde oxidation) in comparison with the initial spectrum of SZ after evacuation (Fig. 3a). A new band at 1356 cm^{-1} appears in the region typical for $\nu_{S=O}$ vibrations. This new band is observed as a low-frequency shoulder to the initial signal at 1405 cm^{-1} (Fig. 3b). Introduction of additional amounts of **IB**, followed by its oxidation into **IBA** and decomposition of the acid at 400 °C, results in a further growth of the resonance at 1356 cm^{-1} with simultaneous diminishing intensity of the band at 1405 cm^{-1} (Fig. 3c). In addition to the appearance of the band at 1356 cm^{-1}, a new signal becomes visible in the spectra (Figs. 3b and 3c). According to its position, this broad complex signal centered at about 1500 cm^{-1} is attributed to hydrocarbon deposits of an aromatic (polyenic) nature formed from the acid upon heating at 400 °C, namely, to their C=C stretching vibrations [28–32]. The other band at 1430 cm^{-1} from C–H vibrations in aromatics [29,31,32] appearing in the spectrum of Fig. 3c is

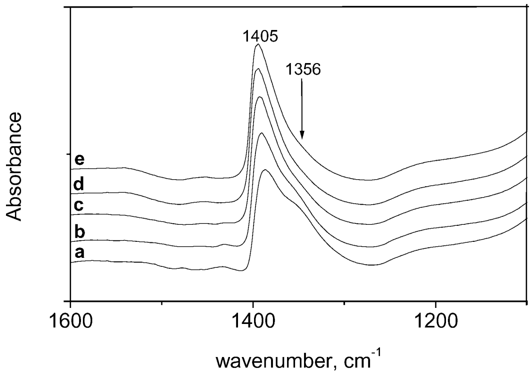


Fig. 4. FTIR spectra obtained after: (a) oxidation of isobutyraldehyde on SZ sample at 150 °C and subsequent decomposition of the acid at 400 °C; (b–d) subsequent oxidative treatment (O_2, 100 Torr, 1 h) of the sample (a) in O_2 atmosphere: (b) at 200 °C, (c) at 350 °C, (d) at 400 °C; (e) the spectrum of initial SZ, activated in vacuum at 400 °C.

indicative of the conversion of polyaromatic (polyenic) deposits (with a very small content of C–H groups) into simple aromatics, similar to the process observed for polyaromatic deposits on zeolites [33].

The following alternative reasons for the appearance of the new signal from the S=O stretching mode at 1356 cm^{-1} are considered. This resonance may belong to either the surface sulfates interacting with the hydrocarbon deposit (coke) or some sulfur species formed in the course of the acid decomposition. This band may also belong to reduced sulfur species formed during the **IB** oxidation into the acid.

To discriminate between these possibilities, the sample containing isobutyric acid adsorbed on SZ (rather than the **IBA** formed from the aldehyde); i.e., the sample of Fig. 2d, was heated at 400 °C. The spectrum obtained (Fig. 3d) reveals the broad resonance at about 1500 cm^{-1} from the hydrocarbon deposits and the band at 1405 cm^{-1} from the initial activated SZ. No noticeable modification of the $\nu_{S=O}$ resonance under the decomposition of adsorbed acid occurred (cf. Figs. 3a and 3d). So, the reaction of **IBA** decomposition, as well as the coke species formed, cannot be responsible for the new signal from the S=O stretching mode at 1356 cm^{-1}. These data allow us to conclude that the resonance at 1356 cm^{-1} is in fact due to some reduced form of sulfur formed during isobutyraldehyde oxidation on SZ.

To clarify whether these changes in the region of S=O vibrations observed during the **IB** oxidation are reversible, the sample prepared similar to that of Fig. 3b, i.e., after the decomposition of the acid formed by the oxidation of 2 Torr of **IB**, has been treated with molecular oxygen at different temperatures (Figs. 4b–4e). The oxidative treatment of SZ at 500 °C in O_2 flow is known to recover completely the catalytic activity of SZ reduced during n-butane isomerization [24]. Fig. 4b shows the IR spectrum obtained after oxidation at 200 °C. As follows from the analysis of this spectrum, the band at 1356 cm^{-1} decreases, and the signal at 1405 cm^{-1} rises in intensity. At the same time, there is no noticeable change in the spectral region between 1400 and 1600 cm^{-1} where hydrocarbon deposits are observed (Fig. 4b). This fact further disclaims that the coke species causes the change of $\nu_{S=O}$. Further treatment of the sample in the O_2 atmosphere at higher temperatures (250–400 °C) results in the gradual growth of the 1405 cm^{-1} band, while the intensity of the resonance at 1356 cm^{-1} decreases further (Figs. 4c and 4d). The sulfate $\nu_{S=O}$ band completely recovers to its initial intensity after oxidation at 400 °C (cf. Figs. 4d and 4e).

Thus, on the basis of our IR data we conclude that the oxidation of isobutyraldehyde to isobutyric acid on sulfated zirconia is accompanied by an appreciable alteration in the region of sulfate vibration. The sulfate group with the band at 1405 cm^{-1} is converted into the species, exhibiting a resonance at 1356 cm^{-1}. These species must be some reduced form of sulfur, which can be completely recovered to sulfates under oxidative treatment in O_2.

It should be noted that an analogous effect has already been observed for sulfated zirconia reduced in an H_2 atmosphere [34]. The reduction causes a diminishing of the intensity of the $\nu_{S=O}$ resonance; this signal shifting to low frequencies as well [34]. However, subsequent treatment in an oxidizing atmosphere of O_2 did not reproduce the original spectral features of sulfates, presuming evolution of sulfur in the form of SO_2 during the reduction in H_2 [34]. In comparison with molecular hydrogen, isobutyraldehyde seems to produce a milder reducing atmosphere, by which the reduced sulfur species remain on the surface of the catalyst. So, it becomes possible to recover the initial amount of surface sulfates.

The question arises as to the nature of the reduced sulfur species formed during the conversion of **IB** to **IBA**, appearing at 1356 cm^{-1}. Morterra et al. [34] argued that sulfite species were formed under reducing treatment of SZ in H_2. The surface sulfites, if formed, creates a resonance in the lower frequency region of the spectrum at 1000–900 cm^{-1} [35], but not in the vicinity of the observed band at 1356 cm^{-1}. Therefore, we believe that the observed signal (1356 cm^{-1}), which undoubtedly belongs to some reduced sulfur species, may be attributed to SO_x species, in which the sulfur atom possesses an intermediate oxidation state between 6+ and 4+, e.g., to dithionate species. Indeed, the formation of dithionate species cannot be excluded since the surface area and SO_3 content of the SZ sample used in the present study allow two sulfates to find each other in a proximity sufficient for S–S bond formation. In fact, according to the literature data [35,36], the $\nu_{S=O}$ moiety in dithionate is characterized by the resonance in the range of 1400–1250 cm^{-1}, i.e., in the region close to the one typical for sulfates [35]. However, one cannot exclude completely the possibility of the formation of sulfites in addition to dithionates during the reduction of sulfate groups, since the nontransparency of the catalyst did not allow analysis of the lower frequency range of the spectra at 1000–900 cm^{-1} typical for sulfites [35].

Thus, we have demonstrated that the sulfate groups are indeed responsible for the oxidation of the intermediate product of propane carbonylation on sulfated zirconia, isobutyraldehyde. Surface dithionate is likely to be the product of sulfate reduction; an oxidizing treatment in O_2 atmosphere completely restores the sulfate moiety.

4. Conclusions

From in situ ^{13}C MAS NMR and IR spectroscopy studies of the hydrocarbon products formed on sulfated zirconia, the following conclusions are drawn on the conversion of propane in the presence of carbon monoxide.

Propane is carbonylated with CO on sulfated zirconia catalysts at 100–150 °C to produce isobutyraldehyde and isobutyric acid. Isobutyraldehyde represents the intermediate product and is almost completely converted into the acid at 150 °C. Thus, the first evidence has been obtained for the propane carbonylation on sulfated zirconia into the valuable chemical products.

The distribution of the observed reaction products, different from that formed from propane in the presence of solid Brønsted acid catalysts [11] and superacidic media [8, 9,37], indicates that the activation of propane by SZ is performed primarily toward the secondary C–H bond of the alkane rather than its C–C bond. This can be realized by either the Lewis acid sites of SZ or by direct formylation by the formyl cation formed as equilibrated species from the formate.

The intermediate product isobutyraldehyde is oxidized by sulfated zirconia into the isobutyric acid. The sulfate groups of SZ are responsible for the aldehyde oxidation, surface dithionate species being suggested to form as a result of sulfur reduction. The latter are readily transformed to sulfates via an oxidizing treatment in O_2 atmosphere, and thus the activity of SZ can be restored.

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References

[1] X. Song, A. Sayari, Catal. Rev.-Sci. Eng. 38 (1996) 329.
[2] G.D. Yadav, J.J. Nair, Micropor. Mesopor. Mater. 33 (1999) 1.
[3] M. Hino, S. Kobayashi, K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
[4] M. Hino, K. Arata, React. Kinet. Catal. Lett. 19 (1982) 101.
[5] A.G. Stepanov, M.V. Luzgin, A.V. Krasnoslobodtsev, V.P. Shmachkova, N.S. Kotsarenko, Angew. Chem., Int. Ed. 39 (2000) 3658.
[6] M.V. Luzgin, A.G. Stepanov, V.P. Shmachkova, N.S. Kotsarenko, Mendeleev Commun. (2001) 23.
[7] M.V. Luzgin, A.G. Stepanov, V.P. Shmachkova, S.N. Kotsarenko, J. Catal. 203 (2001) 273.
[8] S. Delavarenne, M. Simon, M. Fauconet, J. Sommer, J. Am. Chem. Soc. 111 (1989) 383.
[9] S. Delavarenne, M. Simon, M. Fauconet, J. Sommer, J. Chem. Soc., Chem. Commun. (1989) 1049.
[10] H. Pines, V.N. Ipatieff, J. Am. Chem. Soc. 69 (1947) 1337.
[11] M.V. Luzgin, A.G. Stepanov, A. Sassi, J. Sommer, Chem. Eur. J. 6 (2000) 2368.
[12] T.-K. Cheung, F.C. Lange, B.C. Gates, J. Catal. 159 (1996) 99.
[13] M.-T. Tran, N.S. Gnep, G. Szabo, M. Guisnet, Appl. Catal. A 171 (1998) 207.
[14] D. Farcasiu, A. Ghenciu, J.Q. Li, J. Catal. 158 (1996) 116.
[15] A. Ghenciu, D. Farcasiu, Catal. Lett. 44 (1997) 29.
[16] V.M. Mastikhin, A.V. Nosov, S.V. Filimonova, V.V. Terskikh, N.S. Kotsarenko, V.P. Shmachkova, V.I. Kim, J. Mol. Catal. A 101 (1995) 81.
[17] R.K. Harris, Nuclear Magnetic Resonance Spectroscopy. A Physicochemical View, Pitman, London, 1983.
[18] E. Breitmaier, W. Voelter, ^{13}C NMR Spectroscopy, Methods and Applications in Organic Chemistry, VCH, Weinheim, 1978.
[19] G.E. Hawkes, K. Herwig, J.D. Roberts, J. Org. Chem. 39 (1974) 1017.
[20] A. Ejchart, Org. Magn. Reson. 15 (1981) 22.
[21] O. Farooq, M. Marcelli, G.S.K. Prakash, G.A. Olah, J. Am. Chem. Soc. 110 (1988) 864.
[22] T.H. Clingenpeel, T.E. Wessel, A.I. Biaglow, J. Am. Chem. Soc. 119 (1997) 5469.
[23] C.R. Vera, J.C. Yori, J.M. Parera, Appl. Catal. A 167 (1998) 75.
[24] J.C. Yori, J.C. Luy, J.M. Parera, Catal. Today 5 (1989) 493.
[25] M. Bensitel, O. Saur, J.C. Lavalley, B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.
[26] L.J. Bellamy, The Infra-Red Spectra of Complex Molecules, Chapman & Hall, London, 1975.
[27] G.A.M. Hussein, N. Sheppard, M.I. Zaki, R.B. Fahim, J. Chem. Soc., Faraday Trans. 85 (1989) 1723.
[28] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, third ed., Academic Press, New York, 1990.
[29] J.-P. Lange, A. Gutsze, J. Allgeier, H.G. Karge, Appl. Catal. 45 (1988) 345.
[30] E.A. Paukshtis, N.S. Kotsarenko, V.P. Shmachkova, Catal. Lett. 69 (2000) 189.
[31] P.E. Eberly Jr., J. Phys. Chem. 71 (1967) 1717.
[32] D. Spielbauer, G.A.H. Mekhemer, E. Bosch, H. Knozinger, Catal. Lett. 36 (1996) 59.
[33] A.G. Stepanov, M.V. Luzgin, S.S. Arzumanov, H. Ernst, D. Freude, J. Catal. 211 (2002) 165.
[34] C. Morterra, G. Gerrato, S. Di Ciero, M. Signoretto, F. Pinna, G. Strukul, J. Catal. 165 (1997) 172.
[35] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971.
[36] The Infrared Spectra Handbook of Inorganic Compounds, Sadtler Heyden, New York, 1984.
[37] J. Sommer, J. Bukala, Acc. Chem. Res. 26 (1993) 370.