Interaction of hydrogen and n-pentane with sulfated zirconia

E.A. Paukshtis, N.S. Kotsarenko and V.P. Shmachkova [*]

Boreskov Institute of Catalysis, Lavrentieva 5, Novosibirsk 630090, Russia
E-mail: vera@catalysis.nsk.su

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Interaction of hydrogen with sulfated zirconia catalysts was studied *in situ* at 473 K. Interaction of hydrogen with the sample evacuated at 673 K leads to the formation of new hydroxyl groups (wide bands near 3330 cm^{-1}) and water (1620 cm^{-1}). In the case of the sample evacuated at 873 K, SOH groups (3660 cm^{-1}) and zirconium hydrides (1555 cm^{-1}) form. Adsorption of n-pentane on sulfated zirconia catalysts in the range of 253–383 K was studied. It was shown that hydrides and protonated cyclopentadienes form at low temperatures. At higher temperatures, aromatic compounds are formed mainly. The reaction mechanism is discussed.

Keywords: sulfated zirconia, FTIR, skeletal isomerization, pentane, alkanes

1. Introduction

The cause for a unique catalytic activity of sulfated zirconia in skeletal isomerization of alkanes is still under discussion. Earlier reports referred to in [1–3] explained this property by the presence of superacid sites able to ionize bases with $pK_a < -14$. However, it was clearly demonstrated in [4–6] that superacid sites are absent in the catalyst.

Probably, catalytic activity is a specific property of sulfated zirconia and some other metal oxides, which are able to form metal hydrides during the reaction. While the hydride ion abstraction is one of possible ways for alkane activation, the ability of zirconium ions to form unstable surface hydrides is supposed to be the key step of the reaction. Therefore, it would be interesting to study the interaction between alkane or hydrogen and sulfated zirconia with infrared spectroscopy in order to detect zirconium hydrides and to determine their role in the reaction.

2. Experimental

Zirconium hydroxide was precipitated by ammonia from aqueous solution of $ZrO(NO_3)_2$ at pH 8–10 and vigorous stirring. The precipitate was washed and then dried at 383 K.

Sulfated zirconia was obtained by impregnation of zirconium hydroxide with an aqueous solution of sulfuric acid to incipient wetness. The samples were dried first at room temperature, then at 383 K, after which they were calcined in a flow of dry air at 673 or 873 K. The sample calcined at 673 K is amorphous. After calcination at 873 K, only the crystal zirconium oxide of tetragonal modification was found by XRD. SO_3 concentration in the samples and their specific surface area are 8% and 270 m^2/g, and 7% and 150 m^2/g, respectively.

Precalcined samples were placed in an IR cell and evacuated at 673 or 873 K for 60 min prior to adsorption. Hydrogen adsorption was carried out at 473 K for 10 min. Hydrogen was dried in a liquid nitrogen trap and adsorbed at 10 Torr pressure.

Prior to n-pentane adsorption, the samples were calcined in an IR cell at 873 K in oxygen at 20 Torr pressure for 60 min. The oxidation products were frozen out in a vacuum trap cooled to 173 K. Then the samples were cooled down to 523 K in oxygen and evacuated at this temperature for 60 min. n-pentane adsorption was carried out at 253, 293 and 383 K at pressure of 0.2, 2–5 and >10 Torr, respectively.

Spectra were recorded at the adsorption temperature with a Bruker IFS-113v spectrometer using thin (12–22 mg/cm^2) pellets of catalysts at 4 cm^{-1} resolution and 32–128 scans. Spectra were normalized by the pellet weight (A = absorbance × cm^2/g) and presented as differential spectra obtained by subtraction of the initial sample spectrum from the spectrum after adsorption.

3. Results and discussion

3.1. Hydrogen adsorption

The spectra recorded are shown in figure 1. As one can see, the hydrogen interacts with sulfated zirconia at 473 K. In the case of the sample evacuated at 673 K, such interaction is weak, and two new bands at 1620 (weak) and 3300 cm^{-1} (broad) indicate that small amount of water is formed (curve (1)). The results obtained show that hydrogen oxidation occurs when hydrogen interacts with sulfated zirconia. Probably, the oxygen from sulfate groups participates in this process.

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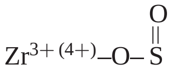
[*] To whom correspondence should be addressed.

In the case of the sample evacuated at 873 K, spectrum (2) shows a narrow band at 3660 cm^{-1} and a band at 1555 cm^{-1}. One can also see a shoulder near 1620 cm^{-1} that may indicate the formation of water through hydrogen oxidation similar to the case of the sample evacuated at a lower temperature. The band at 1555 cm^{-1} can be assigned to zirconium hydride. Similar bands were described in [7]; a band near 1565 cm^{-1} was reported to appear reversibly upon hydrogen adsorption at room temperature on zirconia precalcined at 973 K. This band was assigned to the dissociation of a hydrogen molecule on a pair of Zr^{3+} ions followed by the formation of two Zr^{4+}–H species. It was shown earlier [7–10] that the Zr–H band position can vary depending on the nature of compound: from 1565 ($\mathrm{ZrO_2}$) to 1660 cm^{-1} ($\mathrm{Zr(BH_4)/SiO_2}$). In contrast to [7], in our case zirconium hydride does not decompose upon evacuation (curve (3)). This fact shows that zirconium hydrides on the surface of zirconia and sulfated zirconia are of a different nature. Probably, the interaction of hydrogen with sulfated zirconia proceeds via dissociation of H_2 on a



$$\mathrm{Zr^{3+(4+)}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{S}}$$

pair followed by the formation of zirconium hydride and a S–OH group, which can be observed as a band at 3660 cm^{-1}. This process can be presented as a heterolytic dissociation of the H_2 molecule followed by localization of H^+ on basic oxygen and H^- on acidic zirconium atoms.

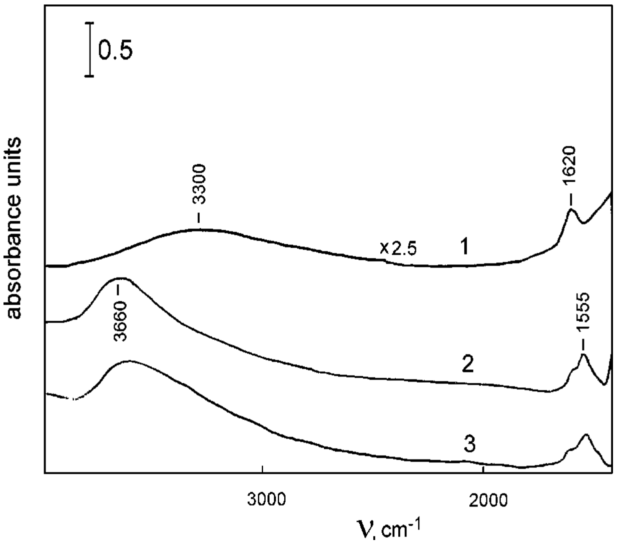


Figure 1. Differential IR spectra after hydrogen adsorption on sulfated zirconia at 473 K. Pretreated sample evacuated at 673 (1) and 873 K (2), (3) after evacuation of (2) at 473 K.

3.2. *n*-pentane adsorption

The spectra obtained upon pentane adsorption at room temperature are shown in figure 2. One can see that the OH-group bands at 3652 and 3743 cm^{-1} decrease and a new broad band at 3560 cm^{-1} forms (figure 2). Shifting of the OH-group bands to the low-frequency region indicates the formation of a H bond between OH groups and adsorbed pentane [11]. The band at 3560 cm^{-1} does not change with time (spectrum (6), figure 2) and vanishes upon evacuation. Note that a part of OH groups does not restore after evacuation, which can be seen from the negative peaks at 3652 and 3743 cm^{-1} in the differential spectrum (spectrum (7), figure 2).

It is important to note that the S=O stretching band at 1416 cm^{-1} decreases and no additional bands appear in the range of 1300–1410 cm^{-1}. This fact allows us to conclude that the observed band at 1416 cm^{-1} does not correspond to the perturbation caused by base absorption [12]. A new band at 1580–1590 cm^{-1} appears and increases slightly

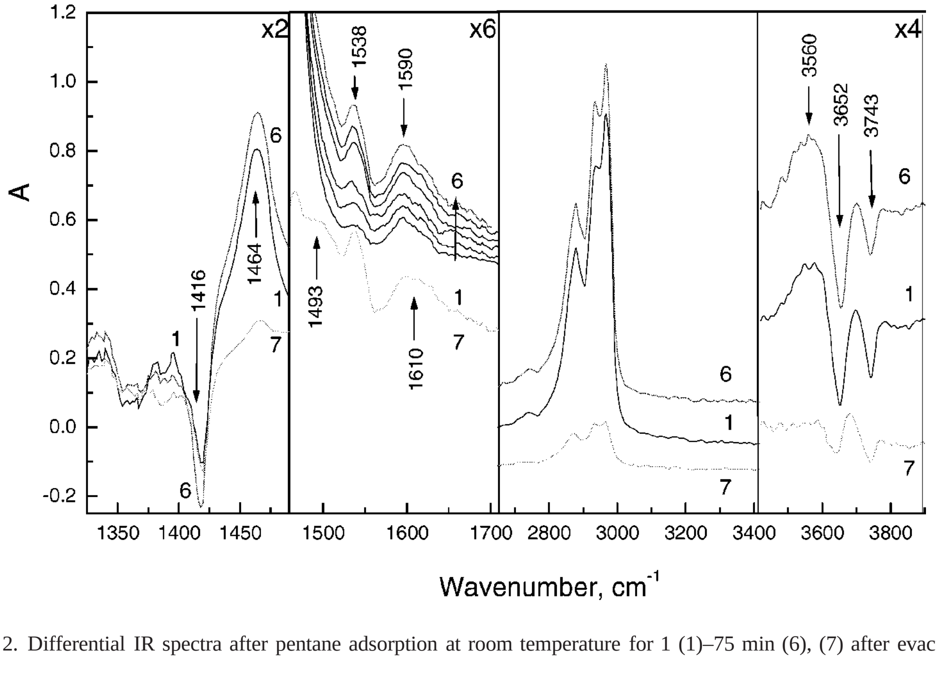


Figure 2. Differential IR spectra after pentane adsorption at room temperature for 1 (1)–75 min (6), (7) after evacuation.

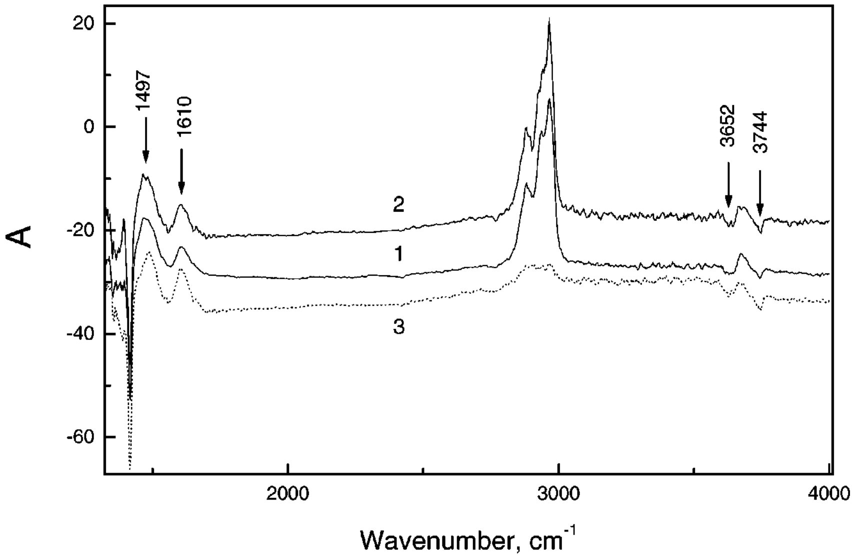


Figure 3. Differential IR spectra after pentane adsorption at 383 K for 1 (1) and 15 min (2), (3) after evacuation.

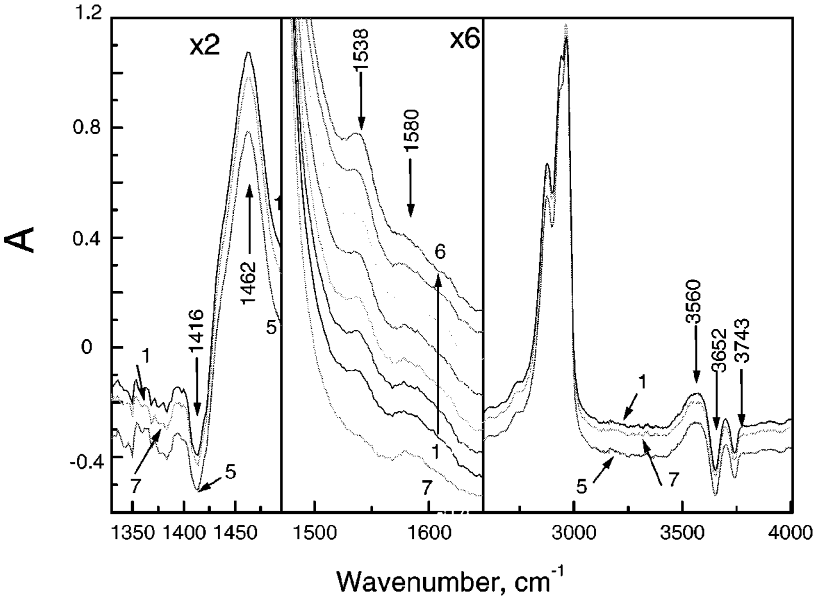


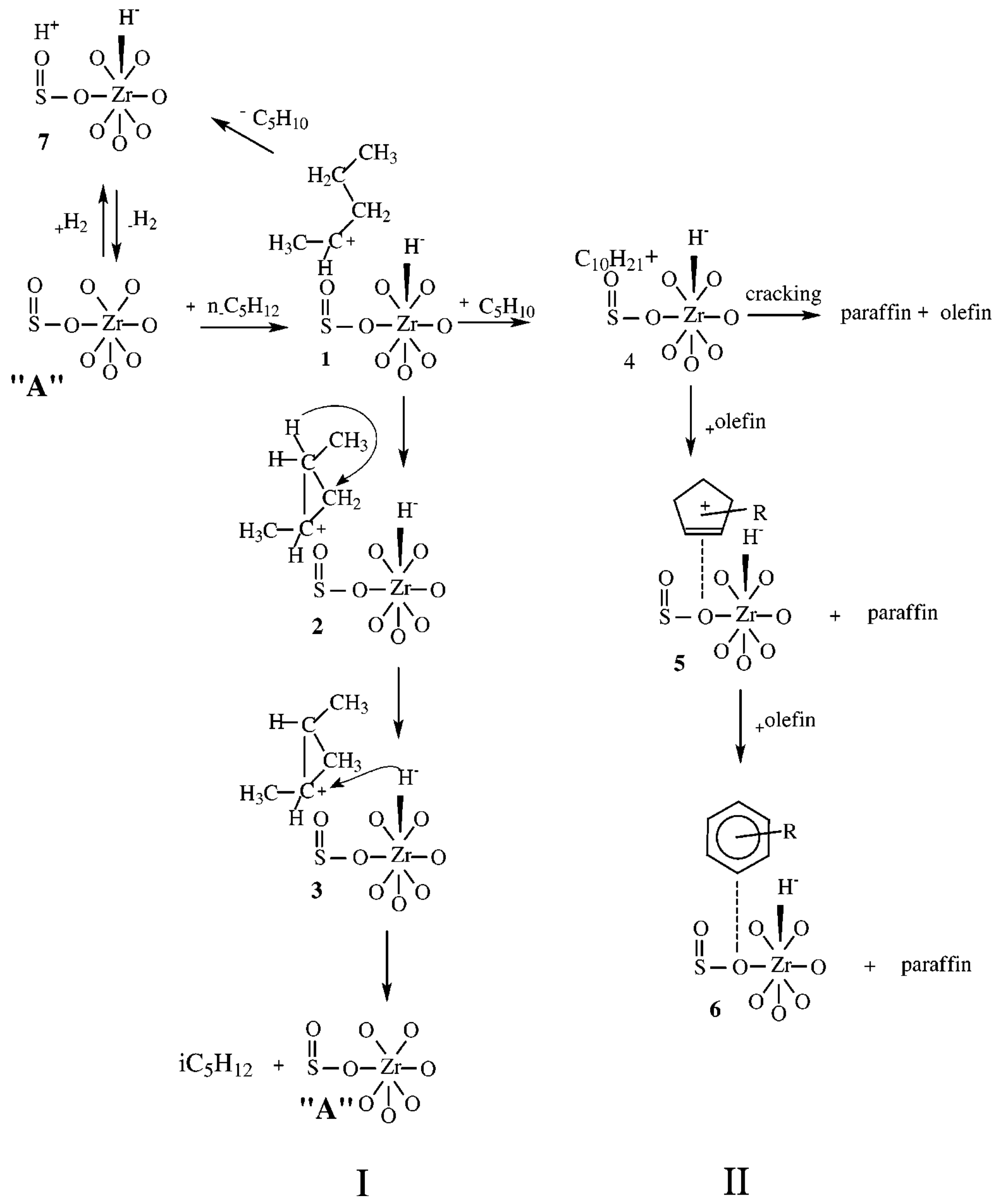
Figure 4. Differential IR spectra after pentane adsorption at 253 K for 1 (1)–60 (5) and 75 min (6), (7) after evacuation.

with time. Later, the second band appears at 1538 cm^{-1}. The spectra show an increase in the bands at 1538 and 1580–1590 cm^{-1} with time (figure 2). The intensity of the band at 1538 cm^{-1} grows faster with time than that of the band at 1580–1590 cm^{-1}. It means that the complex characterized by the band at 1580–1590 cm^{-1} forms before the complex with the band at 1538 cm^{-1}.

The presence of aromatic compounds is evidenced by two bands at 1493 and 1610 cm^{-1} appearing in the spectra, the first of them emerging after pentane evacuation (figure 2, curve (7)) [13]. The band at 1538 cm^{-1} is typical of protonated methyl-substituted cyclopentadienes. This band was observed upon adsorption of alkenes on HZSM-5 zeolite at 373 K [14,15]. Moreover, such structures can be easily detected upon interaction of alkanes with sulfuric acid [16–19]. Such structures are known to be intermediates in the formation of higher unsaturated hydrocarbons and aromatic compounds [20]. As for the band at 1580–1590 cm^{-1}, its location, typical of zirconium hydrides in various complexes, allowed us to assign it to Zr–H groups.

After adsorption carried out at 383 K, H complexes are absent, although the OH stretching bands at 3652 and 3744 cm^{-1} decrease (figure 3). The bands at 1538 and 1590 cm^{-1} do not appear at this adsorption temperature. Two intensive bands at 1497 and 1610 cm^{-1} appear in the low-frequency region (aromatic compounds). The bands described above remain unchanged upon evacuation (spectrum (3)).

Low-temperature adsorption experiments show some features (figure 4). High concentration of H complexes



Scheme 1.

is observed, and almost all hydroxyl groups are occupied at a pentane pressure of 0.2 Torr. The band at 1580–1590 cm^{-1} appears just after adsorption, and its intensity does not change with time, while the 1416 cm^{-1} band vanishes and the band at 1538 cm^{-1} increases slowly.

These facts allow us to assume the presence of several processes proceeding with different rates. The fastest one is able to proceed at low temperature; it results in a decrease of S=O groups concentration and in the formation of Zr–H groups. This result is close to that upon hydrogen adsorption.

The second process takes place at medium temperature, leading to the formation of protonated cyclopentadienes.

At a higher temperature (383 K in our case), the formation of aromatic compounds occurs. Such reaction is typical of alkenes adsorbed on zeolites at temperatures about 473 K [21–25]. One can suppose that the formation of aromatic compounds occurs along with decomposition of cyclopentadienyl derivatives. The data presented in [21] clearly show that protonated cyclopentadienes form from alkenes together with saturated hydrocarbons leading to aromatics at elevated temperature.

In general, the processes developed by sulfated zirconia upon pentane adsorption are presented in scheme 1. The surface zirconium hydride formation is an important step of the reaction. It can proceed under mild conditions. Probably, in addition to ZrH, the reaction leads also to carbenium ion formation (complex **1**). Complex **1** can transform in different ways.

Complex **1** can lead to isopentane in the gas-phase reaction products (root I), since the sequence of transformations in complexes **1**–**2**–**3** results in skeletal isomerization which is typical of free carbenium ions. Complexes **1**–**3** are unstable intermediates. According to the concept of alkyl carbenium ion existence as transition state, these intermediates could not be detected by spectral methods. Only the reaction products can confirm their formation. In particular, the ^{13}C NMR study showed quick label shifts in the n-pentane molecule. The distribution of topomeres indicated the formation of cyclic structures [26]. Processes of dimerization are possible when complex **1** interacts with alkenes (pentane is shown as an example). The dimer (complex **4**) formed is not likely to desorb into the gas phase. The formation of paraffins and olefins is most probable for the cracking, the formation of iso-molecules being possible. The formed olefin molecules participate in the oligomerization reaction and hydrogen transfer process attended by cyclization (root II). It is quite easy to predict that the lighter fragments (n-butane or isobutane) are more probable to be transferred to the gas phase. Transformation of the dimer (complex **4**) into the cyclic cation is more probable in the case. The oligomerization process leads to catalyst deactivation.

Complex **7** can be easily turned to the original site "**A**" through hydrogen molecule abstraction. As follows from spectrum (2) in figure 1, this process is reversible. In the literature, there are no data on hydrogen presence in the reaction products. Special studies are needed to elucidate the possibility of this process.

Thus, it can be concluded that the zirconium hydride formation is the key step of skeletal isomerization of n-pentane. Hydrogen redistribution processes suppress the reaction and inhibit the "**A**" sites. The formation of alkenes should be suppressed for effective proceeding of the reaction.

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