

## High-resolution solid-state NMR studies of sulfate-promoted zirconia in relation to n-pentane isomerization

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### Abstract

Combined <sup>1</sup>H, <sup>15</sup>N and <sup>13</sup>C NMR studies have been performed to elucidate the role of proton donating (Brønsted) and electron accepting (Lewis) sites in isomerization and disproportionation of n-pentane catalyzed by sulfate-promoted zirconia. <sup>1</sup>H NMR MAS of proton sites in a series of sulfate-promoted zirconia as well as in ZrO<sub>2</sub> and Zr(SO<sub>4</sub>)<sub>2</sub> has revealed a variety of surface OH groups that differ in their chemical shifts. Their amounts as function of sample preparation procedure and evacuation temperature have been measured. Lewis acidic sites have been characterized by <sup>15</sup>N NMR of adsorbed N<sub>2</sub>. The results have shown that the most active zirconia catalysts have very strong Lewis acidic sites with a concentration of several μmol/g. Their amount has been found to decrease on increase of an evacuation temperature of samples up to 600°C. The numbers of Brønsted and Lewis sites have been correlated with the catalytic activity in reaction of n-pentane isomerization measured by in situ <sup>1</sup>H MAS NMR. Effects of catalyst treatment temperature and addition of CO and H<sub>2</sub>O have been studied. No correlation between the catalyst's activity in the reaction of n-pentane isomerization and the number and types of surface OH groups has been found. At the same time, the proportionality between the activity and the amount of the most strong Lewis sites detected by <sup>15</sup>N NMR of adsorbed N<sub>2</sub> has been revealed. The products of n-pentane conversion over sulfate-promoted zirconia have been identified by <sup>13</sup>C MAS NMR. The role of Lewis and Brønsted acidic sites in n-pentane isomerization and disproportionation is discussed.

*Keywords:* Acidity; Isomerization; NMR; n-Pentane; Sulfate-promoted oxide; Zirconia

### 1. Introduction

The high-resolution solid-state NMR characterizations of surface active sites and in situ studies of surface catalytic reactions over heterogeneous catalysts is a topic of basic interest since it provides information at the molecular level on the chemical nature and structure of catalyst active

centers and intermediate products of catalyzed chemical reactions [1].

Recently, superacidic catalysts based on sulfate-promoted zirconia have gained attention due to their ability to catalyze the heterolytic reactions of paraffins at relatively low temperature due to presence of strong acidic sites on their surface [2]. The exact chemical nature and structure of the superacidic sites of these catalysts still remain unclear. Moreover, it is an open question whether very strong Brønsted sites or strong Lewis sites or their combination are responsible for superacidic

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<sup>1</sup> This is one of the latest works of Prof. V.M. Mastikhin who died suddenly on February 8, 1995 at the age of 58.

properties. Indeed, it was suggested that the super-acid centers are Lewis sites associated with low coordinate Zr cations whose strength of acidity is enhanced by electron inductive effect of S=O bond [3]. On the other hand, many authors believe that strong Brønsted and Lewis sites are generated from adsorbed H<sub>2</sub>O molecules, with Brønsted sites easily interconverted to Lewis ones by evacuation in relatively mild conditions [4–8].

Recently, *ab initio* quantum chemistry analysis of several molecular structures including Zr atoms, sulfate groups and water molecules have been performed in respect to their Brønsted and Lewis acidities. It was concluded that the super-acidity is of Brønsted type and in presence of some residual water molecules the sulfate-promoted zirconia could be as acidic as liquid sulfuric acid [9]. The diffuse reflectance infrared spectroscopy investigation of zirconia modified with sulfate anions has showed that this modification enhances the strength of acidity of both Brønsted acid sites (terminal or bridging ZrOH groups) and Lewis sites (low coordinate Zr ions), however, the strength of the acid Brønsted centers appeared to be less compared with that for acid OH groups in zeolites. At the same time, new proton sites creating multicenter bonds with oxygen atoms of sulfate anions or with basic oxygen of ZrO<sub>2</sub> lattice and having the strength of acidity comparable to that of bridging OH groups in zeolites have been found [10,11].

The Raman and <sup>1</sup>H NMR MAS [12] revealed the formation of S=O groups of different distortion in sulfate-promoted zirconia as well as new OH groups with chemical shift exceeding by 2 ppm the corresponding values in nonsulfated ZrO<sub>2</sub>. The new OH groups have been claimed to exhibit an enhanced proton acid strength compared with OH groups of ZrO<sub>2</sub> and zeolites.

<sup>31</sup>P NMR MAS study of acidic sites in sulfate-promoted zirconia using trimethylphosphine as a probe has allowed us to determine the amounts of the Brønsted and Lewis sites on catalyst surface as function of their thermal treatment [13]. The comparison with the activity for the alkylation of

isobutane with 2-butene suggests that the strong acidic protons adjacent to Lewis sites on sulfate-promoted zirconia are responsible for catalysis. This supports the idea that the electrons are withdrawn from O–H bond by coordinatively unsaturated zirconium atoms, so that very acidic protons are formed [13].

The aim of this paper is to obtain information on whether very acidic proton sites or very strong Lewis centers are responsible for the high activity of sulfate-promoted zirconia in the isomerization of *n*-pentane, which is known to proceed on these catalysts at ambient temperature [14]. <sup>1</sup>H NMR MAS was used for characterization of proton sites, since this method allows one to make a quantitative determination of their types and, at least qualitatively, to draw a conclusion on their acid strength. <sup>15</sup>N NMR of adsorbed N<sub>2</sub>, which is suitable for detection of the strongest Lewis centers, was used for characterization of Lewis acidity. Catalysts of different preparation methods and evacuated at different temperatures were studied. These results were correlated with: i) the rates of *n*-pentane isomerization measured by *in situ* <sup>1</sup>H NMR MAS and ii) the <sup>13</sup>C NMR MAS data on reaction products to elucidate the role of surface sites of different types in catalytic reactions.

## 2. Experimental

### 2.1. Materials

Two types of catalysts were prepared. The samples of the first type were prepared by impregnation of zirconia (chemically pure, surface area 75 m<sup>2</sup>/g, denoted below as ZrO<sub>2</sub>-1) with an aqueous solution of sulfuric acid to incipient wetness followed by calcination in air at 400°C (ZS-1-400) or 600°C (ZS-1-600). The samples of the second type were prepared by treatment of Zr(OH)<sub>4</sub> on a filter paper with 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution with subsequent drying and calcination either at 400°C (ZS-2-400) or 600°C (ZS-2-600).

For characterization of the proton sites, two samples of zirconia and Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O were

Table 1

Characteristics of the samples studied and total content of OH groups,  $C_{OH}$ , determined from  $^1H$  NMR for samples evacuated at different temperatures

Sample	Calcination temperature °C	SO <sub>3</sub> content wt. %	Specific surface area m <sup>2</sup> /g	$C_{OH}/10^{20} \text{ g}^{-1}$			Notes
				250°C	400°C	600°C	
ZrO <sub>2</sub> -1	500	–	75	1.7	–	–	monoclinic phase
ZrO <sub>2</sub> -2	420	–	180	1.4	–	–	monoclinic phase
ZrO <sub>2</sub> -3	700	–	2	0.3	–	–	tetragonal phase
Zr(SO <sub>4</sub> ) <sub>2</sub>	250	28.3	10	78	–	–	
ZS-1-400	400	2.8	70	1.6	0.5	–	prepared from ZrO <sub>2</sub> -1
ZS-1-600	600	1.9	81	1.4	0.5	–	prepared from ZrO <sub>2</sub> -1
ZS-2-400	400	5.5	171	2.2	1.2	–	prepared from Zr(OH) <sub>4</sub>
ZS-2-600	600	4.2	113	1.2	0.4	0.2	prepared from Zr(OH) <sub>4</sub>

also prepared. The characteristics of samples under study are presented in Table 1.

The catalytic activity in reaction of  $n\text{-C}_5\text{H}_{12}$  isomerization has been tested by ampoule method for a series of catalysts under study. Before reaction, the catalysts were evacuated ( $10^{-2}$  Torr, 300°C, 2 h). The reaction was carried out in thermostatted sealed ampoules at 30°C under intensive shaking. Reaction products were analyzed by gas–liquid (GL) chromatography with flame-ionization detector (3 m column with 5% Apiezon L on Chromosorb P AW-DMCX).

## 2.2. NMR spectroscopy

NMR spectra were measured on Bruker MSL-400 spectrometer (magnetic field 9.4 T, resonance frequencies 400.13, 100.6 and 40.5 MHz for  $^1H$ ,  $^{13}C$  and  $^{15}N$  nuclei, respectively) at room temperature. Magic angle spinning (MAS) was performed for sealed sample tubes in the quartz Andrew Beams rotor at a rotation frequency 3–3.2 kHz.

For measurements of  $^1H$  NMR MAS spectra a pulse width 5  $\mu\text{s}$  and recycle time 10 s were applied. Number of scans was 200. The chemical shifts were measured with respect to an external tetramethylsilane reference with an accuracy  $\pm 0.2$  ppm. Prior to the measurement of  $^1H$  NMR MAS spectra, the samples (typically ca. 0.4 g) were placed into the 7 mm o.d., 12 mm length glass sample tubes, evacuated (pressure ca.  $10^{-5}$

Torr) at temperatures of 250, 400 or 600°C during 12 h, then treated in O<sub>2</sub> at 300–400 Torr for 1 h at the evacuation temperature to remove organic deposits from the surface and finally evacuated at the same temperature for 2 h. The content of OH groups was determined by comparison of the integral of  $^1H$  NMR signal intensities with that from a standard silica sample containing  $5 \cdot 10^{19}$  protons.

The adsorption of fixed amount of  $n$ -pentane (300  $\mu\text{mol/g}$ ) on pretreated samples was performed before in situ  $^1H$  NMR MAS measurements of the rate of  $n$ -pentane isomerization at 20°C. After they were sealed the samples were kept in liquid nitrogen. Prior to kinetic experiments the sealed sample was quickly warmed up to room temperature (20°C), inserted into rotor and rotated. The period between warming up the sample and beginning of the experiment never exceeded 3 min. One hundred FIDs accumulated with 1 s delay were recorded in every 320 s.

The reaction products were identified with  $^{13}C$  NMR MAS using essentially the same samples, as in the case of  $^1H$  NMR experiments, after 24–48 h on beginning the reaction. Spectra were recorded with 5  $\mu\text{s}$  radio frequency pulses with repetition frequency 0.5 Hz. Total number of accumulations was from  $2 \cdot 10^4$  to  $5 \cdot 10^4$ . Broad band decoupling was employed. Chemical shifts were referenced to an external tetramethylsilane.  $n$ -Pentane with a natural abundance of  $^{13}C$  isotope was used.

The  $^{15}\text{N}$  NMR spectra of adsorbed  $\text{N}_2$  were obtained at room temperature employing a pulse width  $12\ \mu\text{s}$  and a recycle delay 2 s. The chemical shifts were measured with reference to an external liquid nitromethane. The number of scans was from  $10^3$  to  $10^4$ . Prior to  $^{15}\text{N}$  NMR measurements, the catalysts (2–3 g) were placed into glass tubes (10 mm o.d., 35 mm length) and treated as described above. The adsorption of a fixed amount (5–400  $\mu\text{mol/g}$ ) of  $\text{N}_2$  enriched to 90% with  $^{15}\text{N}$  isotope was performed at 77 K, then the sample tubes were sealed off. The convention of a positive shift for a downfield resonance with respect to the reference signal was used.

### 3. Results

#### 3.1. $^1\text{H}$ NMR MAS

The  $^1\text{H}$  NMR MAS spectra of three zirconium oxides and  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  are presented in Fig. 1. The contents of proton sites are collected in Table 1.

Zirconium oxide is known to exist in three crystal modifications. The low temperature monoclinic baddeleyite, transforms to tetragonal ruffite at temperatures above  $700^\circ\text{C}$ , the latter undergoes the phase transition to cubic arcelite above  $1900^\circ\text{C}$  [15].

The spectra of two monoclinic zirconia samples of different preparations exhibit two poorly resolved peaks around 3–6 ppm (Fig. 1, spectra 1, 2), that tentatively could be attributed to the bridged and terminal Zr–OH groups, in accord with results of previous infrared studies [16,17]. The largest content of OH groups and the largest chemical shift has been found for  $\text{ZrO}_2$ -1 (Fig. 1, spectrum 1). The number of surface OH groups is close to those obtained from the adsorbed trimethylphosphine studies [15]. The difference in chemical shifts of two  $\text{ZrO}_2$  samples ( $\text{ZrO}_2$ -1 and  $\text{ZrO}_2$ -2) could be due to either different percentage of different crystallographic planes in these samples or different contributions of hydrogen

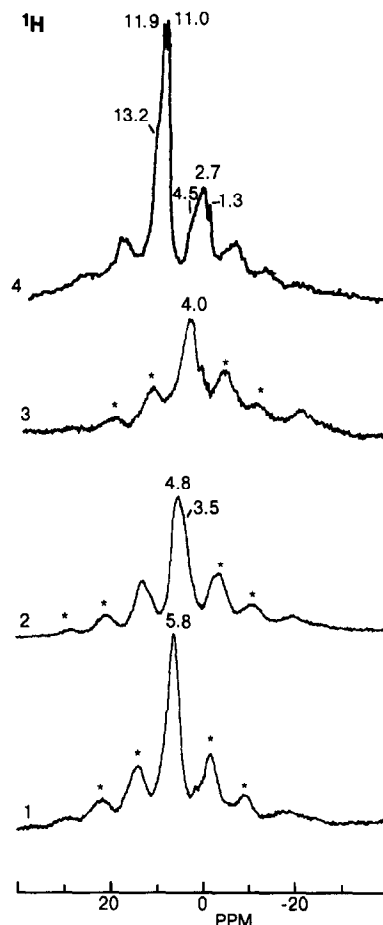


Fig. 1.  $^1\text{H}$  NMR MAS spectra of three different  $\text{ZrO}_2$  samples and  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ : 1 –  $\text{ZrO}_2$ -1 starting material for preparation of sulfate-promoted zirconia; 2 –  $\text{ZrO}_2$ -2, monoclinic modification; 3 –  $\text{ZrO}_2$ -3, tetragonal modification; 4 –  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  calcined at  $250^\circ\text{C}$ , 6 h. Before NMR measurements all samples were evacuated at  $250^\circ\text{C}$ , 14 h,  $10^{-5}$  Torr.

bonds to chemical shift. The spectrum of tetragonal  $\text{ZrO}_2$ -3 sample (Figs. 1-3) demonstrates a peak at 4.0 ppm with a shoulder from an unresolved line at ca. 1.5 ppm.

The  $^1\text{H}$  NMR MAS spectrum of  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  sample after calcination at  $250^\circ\text{C}$  shows along with peaks at 4.5 and 2.7 ppm which are close to those for ZrOH groups in zirconium oxides, also intensive narrow lines at ca. 11 ppm with a shoulder at ca. 13 ppm from S–OH groups. The large chemical shift of the latter is characteristic for a strong hydrogen bonding and/or a high strength of acidity of S–OH protons in this sample.

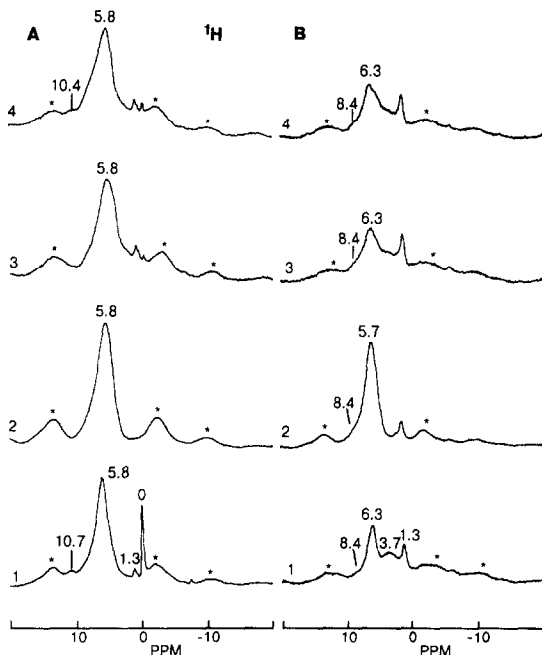


Fig. 2.  $^1\text{H}$  NMR MAS spectra of sulfate-promoted zirconia, treated at: A  $-250^\circ\text{C}$ , B  $-400^\circ\text{C}$ ; 1 –ZS-2-600; 2 –ZS-2-400; 3 –ZS-1-600; 4 –ZS-1-400.

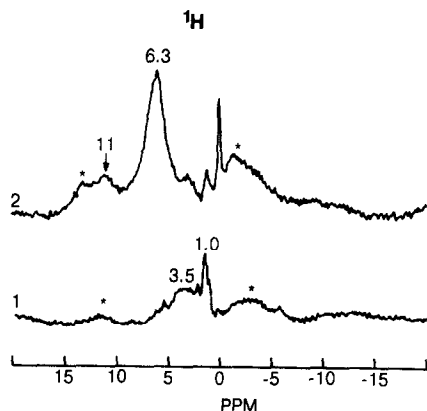


Fig. 3.  $^1\text{H}$  NMR MAS spectra of ZS-2-600 catalyst, evacuated at  $600^\circ\text{C}$  (1); the same sample after adsorption of  $2 \cdot 10^{19}$   $\text{H}_2\text{O}$  molecules per gram of catalyst (2).

Spectra of sulfate-promoted zirconia after evacuation at 250 and  $400^\circ\text{C}$  are presented in Fig. 2. The main peak in these spectra is centered near 6 ppm, in accordance with the data of ref. [12]. At the same time, in the spectra of some samples a shoulder at ca. 8.4 ppm could be seen. A line of small intensity at ca. 10.7 ppm, i.e. with a shift, close to that in  $\text{Zr}(\text{SO}_4)_2$ , has been found in the spectra of samples ZS-1-400 and ZS-2-600 evacuated at  $250^\circ\text{C}$  (Fig. 2A-1, 4). Evacuation at

$400^\circ\text{C}$  completely removes this line from the spectra. A peak at ca. 3.7 ppm from monoclinic  $\text{ZrO}_2$  could be seen in the spectra of samples ZS-2-600 (Fig. 2B-1), ZS-1-600 (Fig. 2B-3) and ZS-1-400 (Fig. 2B-4) evacuated at  $400^\circ\text{C}$ . The evacuation of ZS-2-600 sample at  $600^\circ\text{C}$  results in the disappearance of signal at ca. 6 ppm, a line of small intensity at ca. 3 ppm could be seen in the spectrum (Fig. 3-1). Adsorption of  $2 \cdot 10^{19}$   $\text{H}_2\text{O}$  molecules/g restores the peak at ca. 6 ppm and a peak of small intensity at ca. 11 ppm (Fig. 3-2). Narrow peaks at ca. 1 ppm and 0 ppm in the spectra are due to traces of mobile water (in the closed pores) that were not removed from the sample during evacuation.

### 3.2. Testing of Lewis acidic centers by $^{15}\text{N}$ NMR of adsorbed $^{15}\text{N}_2$

Molecular nitrogen has low basicity (proton affinity,  $\text{PA} = 113$  kcal/mol, ref. [18]) and therefore could be used for testing of the most strong Lewis acidic sites [19,20]. Chemical shift of  $\text{N}_2$  physically adsorbed on silica is  $-75.3$  ppm [19]. The interaction of  $\text{N}_2$  with electron accepting sites would change the chemical shift of  $^{15}\text{N}$  NMR line

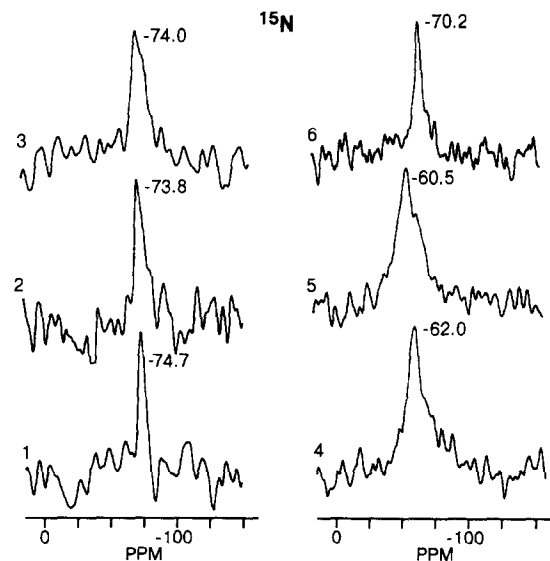


Fig. 4.  $^{15}\text{N}$  NMR spectra of  $\text{N}_2$  adsorbed on sulfate-promoted zirconia ( $5\text{--}10 \mu\text{mol/g}$ ): 1 –ZS-2-400, 2 –ZS-1-400, 3 –ZS-1-600 evacuated at  $400^\circ\text{C}$ ; 4 –ZS-2-600 evacuated at  $250^\circ\text{C}$ ; 5 –ZS-2-600 evacuated at  $400^\circ\text{C}$ ; 6 –ZS-2-600 evacuated at  $600^\circ\text{C}$ .

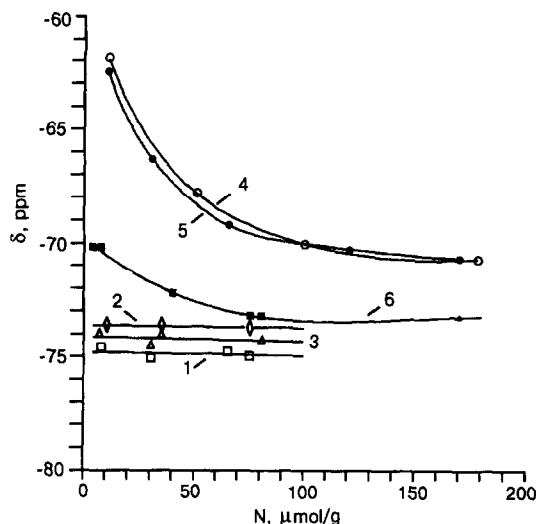


Fig. 5. The dependence of  $^{15}\text{N}$  NMR chemical shifts of adsorbed  $\text{N}_2$  upon  $\text{N}_2$  loading ( $\mu\text{mol/g}$ ): 1 –ZS-2-400, 2 –ZS-1-400, 3 –ZS-1-600 evacuated at  $400^\circ\text{C}$ ; 4 –ZS-2-600, evacuated at  $250^\circ\text{C}$ ; 5 –ZS-2-600 evacuated at  $400^\circ\text{C}$ ; 6 –ZS-2-600 evacuated at  $600^\circ\text{C}$ .

due to the donation of the electron density from p-orbitals of nitrogen to vacant orbitals of Lewis sites and broaden the line due to interaction of adsorbed nitrogen molecule with neighboring nuclei. Fig. 4 illustrates the  $^{15}\text{N}$  NMR spectra of  $\text{N}_2$  adsorbed on catalysts under study at lowest loadings. It can be seen from these data that effect of adsorption is different for various catalysts. For some catalysts (ZS-1-400, ZS-1-600, ZS-2-400) the position of the line of adsorbed  $\text{N}_2$  is very close to that for physically sorbed  $\text{N}_2$ . This suggests the weak interaction of  $\text{N}_2$  with surface sites. Chemical shifts exceeding 10 ppm were found for ZS-2-600 catalyst indicating presence of strong adsorption sites in this case. The chemical shifts for some catalysts (ZS-1-400, ZS-1-600, ZS-2-400) do not depend upon  $\text{N}_2$  loading,  $N$ , (Fig. 5),

while for ZS-2-600 the chemical shift demonstrates dependence on  $\text{N}_2$  loading (Fig. 5). The first case corresponds to the formation of 'weak' adsorption complexes ( $K\delta_c n_L \ll 1$ ) [21], where  $K$  is the complex formation constant for equilibrium reaction



$n_L$  – number of surface Lewis acidic sites  $\text{L}$ ,  $\delta_c$  – chemical shift of adsorption complexes  $\text{N}_2 \cdot \text{L}$ . The second case takes place for 'strong' complexes when  $K\delta_c n_L \gg 1$  [18], thus indicating presence of stronger adsorption sites on catalyst surface.

$^{15}\text{N}$  NMR chemical shifts,  $\delta$ , of  $\text{N}_2$  adsorbed on ZS-2-600 catalyst treated at 250, 400 and  $600^\circ\text{C}$  versus  $\text{N}_2$  loading  $N$  were used for determination of the complex formation constant  $K$  and of  $\delta_c n_L$  values with the use of equation

$$\delta = KN\delta_c / (1 + K\delta_c n_L) \quad (2)$$

where  $K$  and  $\delta_c$  values relate to the strength of adsorption complex, and therefore to the strength of acidity of Lewis sites, interacting with  $\text{N}_2$ . Linearization of the  $\delta$  vs.  $N$  curves in the  $\delta$  vs.  $\delta N$  coordinates provides the  $K$  and  $\delta_c n_L$  values, which are collected in Table 2.

Since the  $K$  values are very close to each other for samples evacuated at different temperatures, one might expect for them also the close or the same  $\delta_c$  values. Therefore as an approximation,  $\delta_c n_L$  value could be considered as proportional to the number of Lewis sites  $n_L$ . The results presented in Table 2 show that the samples treated at 250 and  $400^\circ\text{C}$  have about the same  $\delta_c n_L$  values. The treatment at  $600^\circ\text{C}$  decreases this quantity by about three times. Assuming  $\delta_c$  to be in a range of

Table 2

The complex formation constant  $K$  and  $\delta_c n_L$  values measured from  $^{15}\text{N}$  NMR spectra of adsorbed  $\text{N}_2$  for ZS-2-600 catalyst, and its catalytic activity in the isomerization of n-pentane measured by in situ  $^1\text{H}$  NMR

Treatment conditions	$K/10^4 \text{ g} \cdot \text{mol}^{-1}$	$\delta_c n_L / 10^{-4} \text{ ppm} \cdot \text{mol} \cdot \text{g}^{-1}$	Activity/ $10^{-6} \text{ mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$
$250^\circ\text{C}$	$2.8 \pm 0.3$	$5.3 \pm 0.9$	$8.3 \pm 0.2$
$400^\circ\text{C}$	$3.0 \pm 0.1$	$5.3 \pm 0.3$	$8.2 \pm 0.2$
$600^\circ\text{C}$	$2.6 \pm 0.3$	$1.7 \pm 0.3$	$5.0 \pm 0.2$
$600^\circ\text{C} + 2 \cdot 10^{19} \text{ H}_2\text{O/g}$	–	–	$2.7 \pm 0.2$
$600^\circ\text{C} + 10^{19} \text{ CO/g}$	–	–	0

Table 3

Reaction products of the isomerization of  $n\text{-C}_5\text{H}_{12}$  at  $30^\circ\text{C}$ , 3 h (catalyst:pentane = 1:2 by weight) on catalysts pretreated at  $300^\circ\text{C}$  (determined by GLC)

Sample	Reaction products, mol. %		
	iso- $\text{C}_5\text{H}_{12}$	$n\text{-C}_5\text{H}_{12}$	iso- $\text{C}_4$ , iso- $\text{C}_6$
ZrO <sub>2</sub> -1	0	100	–
ZS-1-400	24.4	75.0	0.6
ZS-1-600	9.4	90.1	0.5
ZS-2-400	0	100	–
ZS-2-600	46.6	52.8	0.6
ZS-2-600 + 760 Torr CO	0	100	–

– 50 to – 100 ppm, which seems to be reasonable for adsorbed  $\text{N}_2$ , it gives  $n_L \approx (0.3\text{--}3) \cdot 10^{19}$  molecules/g or  $(0.3\text{--}3) \cdot 10^{-1}$  molecules/nm<sup>2</sup>. These values are considerably smaller than an amount of sulfate anions on catalyst's surface (ca. 4 anions/nm<sup>2</sup> for catalyst ZS-2-600) and a value, measured by adsorption of trimethylphosphine [13].

Thus, the number of the most strong sites that could be detected by <sup>15</sup>N NMR of adsorbed  $\text{N}_2$  represent only a small part of the total amount of sulfated Zr atoms on catalysts surface. The numbers of such sites are very close in catalysts treated at 250 and 400°C, but decrease with increase of the evacuation temperature to 600°C.

### 3.3. Catalytic activity

The results of the catalytic activity testing (Table 3) showed that the most active catalyst appeared to be ZS-2-600. Catalysts ZS-1-400 and ZS-1-600 showed considerably smaller yields of iso-pentane. No activity has been detected for ZrO<sub>2</sub> and ZS-2-400 samples. The treatment of catalyst ZS-2-600 with CO (equilibrium pressure 760 Torr) stopped the reaction. Results showed that the main reaction product was iso-pentane, small traces of iso-butane were also detected. The measurements of reaction yield at 20, 30 and 40°C gave the activation energy of isomerization 95.2 kJ/mol, in accord with the data of ref. [21,22].

### 3.4. <sup>1</sup>H NMR MAS reaction kinetics

<sup>1</sup>H NMR MAS in situ reaction kinetics has been measured for the catalyst ZS-2-600 evacuated at 250, 400 and 600°C. In addition, the effect of preadsorption of CO and H<sub>2</sub>O on the catalysts evacuated at 600°C has been studied.

<sup>1</sup>H NMR chemical shifts for  $n$ -pentane are 0.89 ppm ( $\text{CH}_3$ ) and 1.30 ppm ( $\text{CH}_2$ ) with the relative integral intensities of the corresponding lines 6:6 (Fig. 6-1). The chemical shifts of iso-pentane are 0.86 ppm ( $\text{CH}_3$ ); 1.25 ppm ( $\text{CH}_2$ ) and 1.45 ppm ( $\text{CH}$ ) with relative intensities 9:2:1 (Fig. 6-2). <sup>1</sup>H NMR MAS spectrum of adsorbed  $n\text{-C}_5\text{H}_{12}$  shows two lines: one from methyl groups of  $n$ -pentane with  $\delta = 0.9$  ppm and the other from  $\text{CH}_2$  protons of  $n\text{-C}_5\text{H}_{12}$  at 1.3 ppm (Fig. 6-3). Conversion of  $n$ -pentane to iso-pentane would result in increase of signal intensity from  $\text{CH}_3$  protons by a factor 1.5 (line at  $\delta = 0.9$  ppm) and in two-fold decrease of a line from  $\text{CH}_2$  and  $\text{CH}$  protons ( $\delta = 1.3$  ppm). Thus the change of the intensities of peaks at 0.9 and 1.3 ppm could be used for the

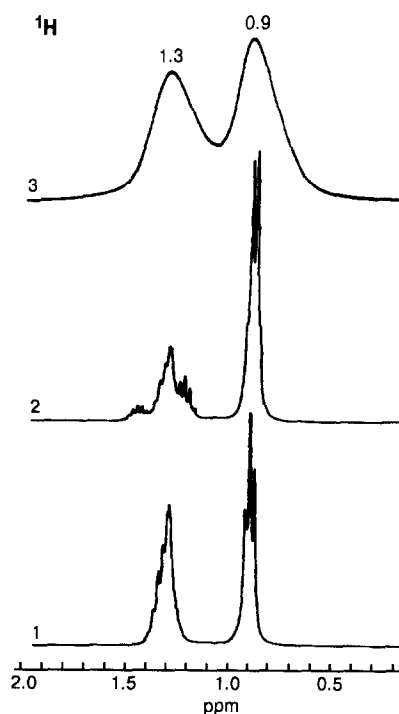


Fig. 6. <sup>1</sup>H NMR MAS spectra: 1 –liquid  $n\text{-C}_5\text{H}_{12}$ ; 2 –liquid  $n\text{-C}_5\text{H}_{12}$  + iso- $\text{C}_5\text{H}_{12}$  (volume ratio 3:7); 3 – $n\text{-C}_5\text{H}_{12}$  adsorbed on ZS-2-600.

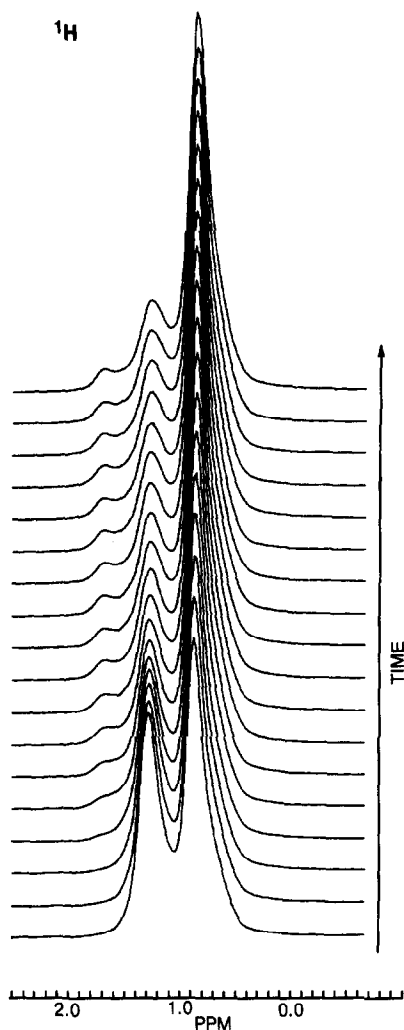


Fig. 7.  $^1\text{H}$  NMR MAS spectra illustrating kinetics of n-pentane conversion over ZS-2-600 catalyst, evacuated at  $250^\circ\text{C}$ . The time between recording spectra is 320 s.

measurement of activity provided that other reactions do not contribute substantially to spectra.

The example of  $^1\text{H}$  NMR MAS reaction kinetics is illustrated in Fig. 7. It follows from these spectra that indeed the redistribution of the  $\text{CH}_3$  and  $\text{CH}_2$  peaks intensities occurs in the course of reaction. At the same time a relatively weak peak at  $\delta = 1.65$  ppm develops in the spectra due to formation of disproportionation products. The latter have been identified by  $^{13}\text{C}$  NMR MAS (Fig. 8). The main product was found to be iso-butane (peaks at 24.2 and 23.8 ppm) in agreement with the data of ref. [14]. Other peaks in Fig. 8 were attributed to n-

pentane (13.2, 22.6 and 34.4 ppm), iso-pentane (11.7, 21.9, 30.3 and 32.0 ppm) and most probably to two isomers of dimethylbutane (2,2-dimethylbutane and 2,3-dimethylbutane).

The isomerization activity (A) of catalyst was characterized as the number of moles of n-pentane transformed into iso-pentane in 21 min after the beginning of the reaction (when the contribution from the disproportionation reactions is still small, as judged from the small intensity of the  $^1\text{H}$  NMR peak at 1.65 ppm) per gram of catalyst ( $20^\circ\text{C}$ ):

$$A = (n_o - n) / n_o t \quad (3)$$

where  $n_o$  and  $n$  are amounts of n-pentane before reaction and after 21 min ( $t$ , 21 min =  $4 \times 320$  s) respectively; while  $(n_o - n) = x$  is amount of i-pentane produced. Denoting the intensities of the  $\text{CH}_2$   $^1\text{H}$  NMR peak (at 1.3 ppm) before reaction and after time ( $t$ ) as  $I_o(\text{CH}_2)$  and  $I(\text{CH}_2)$ , respectively, one can obtain

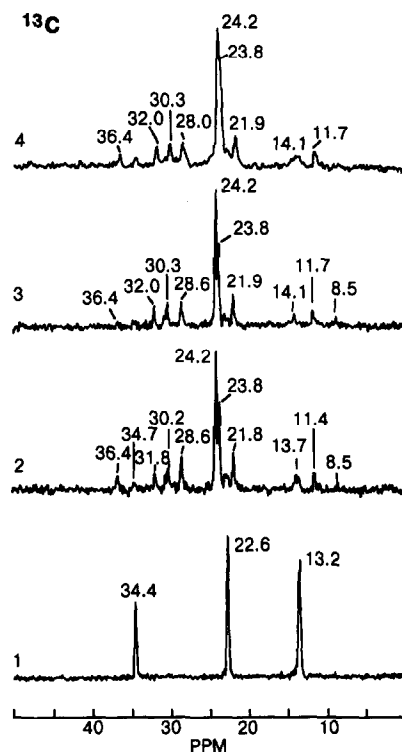


Fig. 8.  $^{13}\text{C}$  NMR MAS spectra of the products of n-pentane conversion at  $20^\circ\text{C}$  over sulfate-promoted zirconia: 1 – ZS-2-600, evacuated at  $600^\circ\text{C}$ , addition of  $10^{19}$  CO molecules/g; 2 – ZS-2-600, evacuated at  $250^\circ\text{C}$ ; 3 – ZS-2-600, evacuated at  $400^\circ\text{C}$ ; 4 – ZS-2-600, evacuated at  $600^\circ\text{C}$ , addition of  $2 \cdot 10^{19}$   $\text{H}_2\text{O}$  molecules/g.



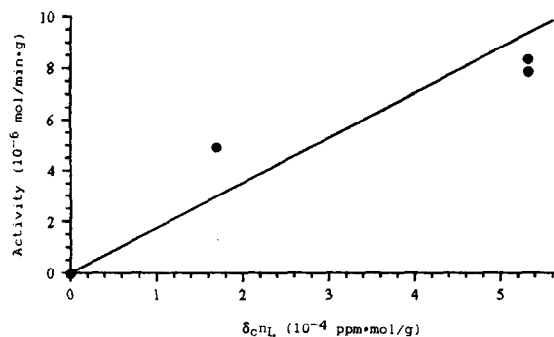


Fig. 9. Relation between the value of  $\delta_c n_L$  and the isomerization activity measured by  $^1\text{H}$  NMR at  $20^\circ\text{C}$ .

$$I_o(\text{CH}_2) = 6kn_o \quad (4)$$

$$I(\text{CH}_2) = 6k(n_o - x) + 3kx = k(6n_o - 3x) \quad (5)$$

where  $k$  is the coefficient of proportionality between intensity of the  $\text{CH}_2$  peak and a number of corresponding protons. Therefore, the activity can be represented as:

$$A = 2n_o(1 - I(\text{CH}_2)/I_o(\text{CH}_2))/t \quad (6)$$

The  $^1\text{H}$  NMR in situ measured activities of ZS-2-600 catalyst (evacuated at  $250$ ,  $400$ ,  $600^\circ\text{C}$  as well as pretreated with  $\text{CO}$  or  $\text{H}_2\text{O}$ ) in reaction of  $n$ -pentane isomerization at  $20^\circ\text{C}$ , are summarized in Table 2.

These data show that the activities for samples evacuated at  $250$  and  $400^\circ\text{C}$  are close to each other but they decrease after catalyst evacuation at  $600^\circ\text{C}$ . The addition of  $2 \cdot 10^{19}$   $\text{H}_2\text{O}$  molecules/g to the sample, evacuated at  $600^\circ\text{C}$ , decreases the activity by more than 2 times, while the addition of  $10^{19}$   $\text{CO}$  molecules/g reduces the activity to zero. The relationship between the activity and  $\delta_c n_L$  values, obtained from  $^{15}\text{N}$  NMR of adsorbed  $\text{N}_2$  is presented in Fig. 9.

#### 4. Discussion

The results presented above show that combined  $^1\text{H}$ ,  $^{15}\text{N}$ ,  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR in situ kinetics studies together with catalytic data provide an important information on the types of the

Brønsted and Lewis sites present on the surface of sulfate-promoted zirconia and on their relation to the  $n$ -pentane conversion.

In particular, it seems possible to determine which types of surface sites, Brønsted or Lewis, play a key role in  $n$ -pentane isomerization. Occurrence in these systems of very acidic  $\text{S-OH}$  groups ( $^1\text{H}$  NMR MAS lines at ca. 11 and 8 ppm) provides a temptation to attribute the superacidic properties to formation of extremely acidic Brønsted sites. Results presented here show that the high catalytic activity of sulfated zirconia in paraffin isomerization cannot be only due to the formation of acidic  $\text{S-OH}$  groups.

Indeed, the evolution of presumably most of the acidic OH groups (signal at ca. 11 ppm) with twofold decrease of the total OH group content (Table 1) after evacuation at  $400^\circ\text{C}$  does not change the rate of isomerization. Moreover, addition of water to the catalyst treated at  $600^\circ\text{C}$  decreases activity by about two times against the expected increase if OH groups were active in the catalysis.

It seems that the small amount of the most strong Lewis sites detected in this work by  $^{15}\text{N}$  NMR of adsorbed  $\text{N}_2$  is responsible for the  $n$ -pentane isomerization. This follows from the proportionality of the catalyst activity in the isomerization reaction and the  $\delta_c n_L$  value, proportional to the number of such sites, as follows from Fig. 9. This conclusion is supported also by the stopping of the reaction upon addition of  $\text{CO}$ . The latter is expected to adsorb on the electron accepting sites but does not influence Brønsted sites, at least at ambient temperature.

This conclusion is in good agreement with some literature data that the active centers in sulfate-promoted zirconia are Lewis sites associated with coordinatively unsaturated metal cations whose strength of acidity is strongly enhanced by electron induction effect of  $\text{S=O}$  bond in surface sulfur complex [3].

Comparison of the number of Lewis sites measured by  $^{31}\text{P}$  NMR of adsorbed trimethylphosphine [13] with the data presented here shows that the surface Lewis sites in the catalysts under study are

not homogeneous, and have a distribution of their strength of acidity. The amount of the strongest sites estimated from  $^{15}\text{N}$  NMR is several  $\mu\text{mol/g}$  (ca.  $10^{-2}/\text{nm}^2$ ), i.e. considerably smaller than their amount measured by  $^{31}\text{P}$  [13]. This means that the coordinatively unsaturated zirconium sulfate complexes of specific structure are the strongest electron acceptor sites active in paraffin isomerization. Its detailed structure needs quantum chemistry consideration.

Formation of reaction products (iso-pentane, iso-butane and dimethylbutanes) is in a good agreement with the presently accepted schemes of the conversion of paraffins over heterogeneous acid catalysts [22–24]. Two mechanisms are considered. The first one assumes the formation of primary carbenium ions of pentane  $\text{C}_5^+$  stabilized by chemisorption on the catalyst surface with their subsequent isomerization into iso-pentane. The second mechanism assumes that isomerization of n-pentane proceeds via a bimolecular way, i.e. initially alkene  $\text{C}_5^-$  is formed from n-pentane, followed by interaction of  $\text{C}_5^+$  with  $\text{C}_5^-$  and formation of a  $\text{C}_{10}^+$  ion. The isomerization and  $\beta$ -fission of  $\text{C}_{10}^+$  oligomers leads to iso-pentane products. The  $^{13}\text{C}$  NMR MAS observation that disproportionation of n-pentane into  $\text{C}_4$  (iso-butane) and  $\text{C}_6$  (dimethylbutanes) accompanies isomerization also suggests that the reaction can proceed via a  $\text{C}_{10}$  intermediate [25,26].

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