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Isomerization of *n*-alkanes on Pt/WO_3–SO_4/ZrO_2 systems

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Abstract

The role of the electronic state of Pt and acidic properties of anion-promoted support in *n*-alkane isomerization on Pt-containing sulfate- and tungstate-promoted zirconia (Pt/SZR and Pt/WZR) was studied. The addition of Pt with further oxidation and mild reduction is found to enhance the catalytic activity in *n*-hexane isomerization 10 times compared with metal-free system. The mechanism of the action of the pretreatment steps is proposed. Effect of the calcination temperature on the catalytic activity in *n*-alkane isomerization and physico-chemical properties of the catalysts is also evaluated. The catalytic activity of Pt promoted combined sulfated–tungstated zirconia (Pt/SWZR) catalysts in *n*-hexane and *n*-pentane isomerization decreases in the following order (the calcination temperature is shown in parentheses):

$$\mathrm{Pt/SZR}\,(625\,^{\circ}\mathrm{C}) > \mathrm{Pt/WSZR}\,(625\,^{\circ}\mathrm{C}) > \mathrm{Pt/WSZR}\,(800\,^{\circ}\mathrm{C}) \approx \mathrm{Pt/WZR}\,(800\,^{\circ}\mathrm{C})$$

The properties of WZR (800 °C) and SWZR (800 °C) are connected with the surface WO_4 groups. The presence of sulfate species in Pt/SZR (625 °C) and Pt/WSZR (625 °C) is responsible for the strong acidic properties of these catalysts. The performance of classical sulfated and tungstated catalysts is slightly improved by the combination of anions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *n*-Hexane isomerization; *n*-Pentane isomerization; Sulfated zirconia; Tungstated zirconia; Effect of Pt

1. Introduction

Recently, a special interest was devoted to sulfate- and tungstate-promoted metal oxides as the catalysts for *n*-paraffin isomerization [1–3]. It was found that modified SO_4^{2-}/ZrO_2 (SZR) catalysts exhibit high activity and selectivity in C_4–C_6 *n*-paraffin isomerization. However, these systems demonstrate some disadvantages. The low efficiency of hydrogen transfer leads to an increase in the rate of cracking, especially for long chain *n*-paraffins. Another negative side is a partial reduction of the sulfate species under reaction conditions and poisoning of the catalyst by the sulfur contaminants. New solid acid systems based on sulfur-free WO_x–ZrO_2 (WZR) were developed and proposed as perspective catalysts for paraffin isomerization [4,5]. These systems, although showing a medium strength of acid sites, are very active in *n*-paraffin isomerization and provide high isoparaffin yield and selectivity, especially for the long chain alkanes. The combination of both modifying additives may change the performance of catalysts and may result in an increase in the catalytic activity [6].

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The catalytic properties of the Pt-containing systems based on WZR and WO_3–SO_4^{2-}/ZrO_2 (SWZR) in *n*-pentane and *n*-hexane isomerization and their physico–chemical properties will be discussed in this paper. The concentration of WO_3 and SO_4^{2-}, the order of impregnation, the calcination temperature, and reduction conditions for binary systems were varied. The nature of the catalytic action of the systems will be rationalized on the basis of the experimental data.

2. Experimental

SWZR based catalysts were prepared by impregnation of $Zr(OH)_4$ ($S_{\text{sp.}} = 150\,\text{m}^2/\text{g}$, Magnesium Electron Co., grade XZO706/03) with a 1 N aqueous solution of H_2SO_4 and a hot aqueous solution of $(NH_4)_2WO_4$ (0.04 g of WO_4^{2-}/ml). The order of anion impregnation was varied. The concentration of WO_4^{2-} anions was 0–20 wt.%. The concentration of SO_4^{2-} anions was 0–5 wt.%. The catalysts were dried at 120 °C for 2 h and calcined in an air flow at 625 or 800 °C for 2 h (the calcination temperature is shown in parentheses for each sample). Platinum was supported on the catalysts from an aqueous solution of H_2PtCl_6 followed by drying at 120 °C for 6 h and calcination in an air flow at 450 °C for 2 h. To obtain the reduced form of platinum, the catalysts were treated in a hydrogen flow at 200 °C for 2 h.

Catalytic testing in *n*-pentane and *n*-hexane isomerization was performed in a flow system at 160–380 °C; LHSV $= 1$–$2\,\text{h}^{-1}$; $P = 0.1\,\text{MPa}$, molar hydrocarbon:H_2 ratio was 1:4. The performance of the catalysts was tested after 0.5 h time-on-stream at noted temperatures for each experiments.

DRIFT spectra were recorded with a Nicolet Protégé 460 spectrometer equipped with a home-made diffuse-reflectance attachment. CD_3CN and C_2D_4 were used as test molecules for studying the strength and reactivity of acid sites. The electronic state of supported Pt was investigated by DRIFT spectroscopy using CO as a probe-molecule. After the spectra were recorded, the samples were evacuated with a stepwise temperature increase with registration of spectra at each temperature of evacuation.

3. Results and discussions

The catalytic systems for *n*-alkane isomerization prepared on the basis of sulfated and tungstated zirconia are the complex systems combining the acidic function of the modified oxide support and the dehydrogenation function of noble metals. Hence, the activity of catalysts depends on the interaction between the support and the metal and formation of a bifunctional system.

3.1. Role of platinum

To evaluate the role of platinum in *n*-alkane isomerization, the activity of 15WZR (where, 15 is the concentration of WO_4 species in wt.%) samples containing no platinum were tested in comparison with Pt-containing systems. The 15WZR (800 °C) system without platinum was inactive in *n*-hexane isomerization in a hydrogen flow (Fig. 1). The yield of isohexanes at 300 °C was only 6.1% at the selectivity of 50.8%. Modification of the 15WZR (800 °C) catalyst by Pt lead to a drastic increase in the isohexane yield up to 78.9% and the selectivity reached 98.6% at 260 °C. Similar results were obtained in the case of isomerization of *n*-pentane. Hence, the presence of Pt is the crucial step to achieve high activity in a hydrogen flow.

A further step is evaluation of the catalytic activity of the Pt/WZR catalyst as a function of the pretreatment conditions. The Pt/WZR catalyst treated in an air flow showed the highest activity in isomerization. The total isomers yield was as high as 77–78% and the yield of dibranched products was up to 23%. On the other hand, the activity of the system treated in an H_2 flow without oxidative treatment was significantly lower, especially in the formation of dibranched products. The total yield of isohexanes did not exceed 55%. The yield of dibranched products was three times lower as compared with the system treated in an air flow and was equal to 7.8%. The Pt/WZR catalyst activated in an air flow with further reduction showed intermediate activity. The total isohexanes yield was 75%; however, the yield of dibranched products was only 16.8–18.1%.

The analysis of the dependence of the catalytic activity of the Pt-promoted tungstated systems from the pretreatment conditions shows that the activity of

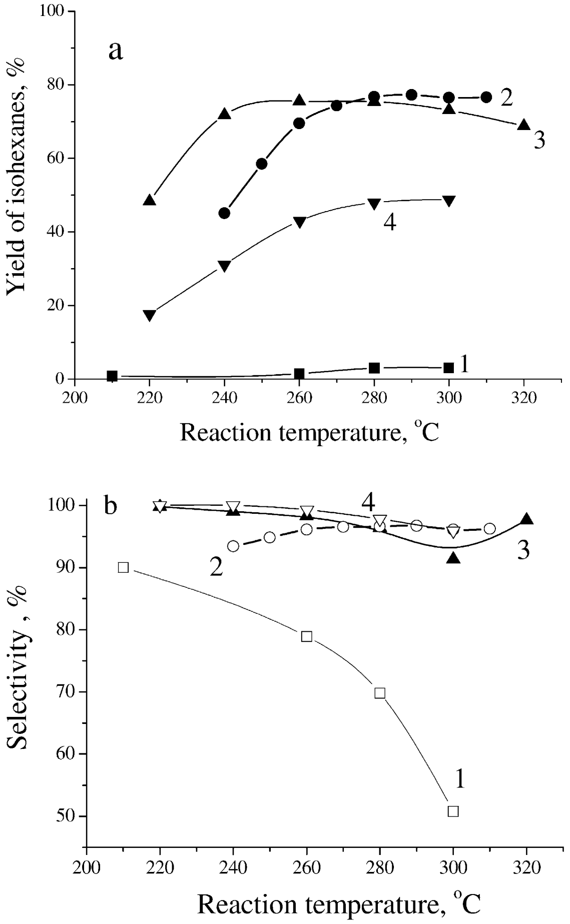

Fig. 1. The total yield of isohexanes (a) and selectivity (b) of (1) WZR and (2–4) Pt/WZR catalysts after oxidation at 450 °C (2), oxidation at 450 °C and further reduction at 200 °C (3), reduction at 200 °C (4).

catalysts could be connected with the electronic state and dispersion of Pt on the surface of the catalyst.

The electronic state of Pt in Pt/WZR systems treated at oxidative and reductive conditions was studied by DRIFT spectroscopy using CO as a probe molecule. The DRIFT spectra of CO adsorbed on Pt/WZR calcined in an air flow at 500 °C are shown in Fig. 2. The spectra indicate the presence of Pt^{4+} and Pt^{2+} ions in PtO_2 and PtO surface species (the bands at 2195 and 2148 cm^{-1}, respectively), and also $Pt^{\delta+}$ species (the band at 2100 cm^{-1}) formed during partial reduction of platinum [7]. Hence, after oxidative treatment the main part of Pt exists as surface oxide species. However, some part of Pt can be reduced to partial positively charged species $Pt^{\delta+}$ that can be active in *n*-alkane activation. It could be supposed that these species are well dispersed on the surface of catalyst.

The adsorption of CO on Pt/WZR oxidized and reduced at 250 °C provides evidence for the presence of metal Pt^0 particles (the bands at 2090 and 1885 cm^{-1}) as the main form of Pt on the surface. Partially reduced forms of Pt present in minor concentration (the shoulders at 2110 and 2160 cm^{-1}) were also observed. The presence of the reduced form of tungsten in surface compounds (the band at 2120 cm^{-1}) shows that Pt could catalyze the reduction of WO_3 species thus decreasing the temperature of reduction.

The adsorption of CO on Pt/WZR reduced in an H_2 flow without preliminary oxidative pretreatment leads to the appearance of the low-intense bands characteristic of the total reduced platinum (the band at 2090 cm^{-1}). The low intensity of the band could point to the low concentration of adsorption sites. The possible reasons are the formation of Pt particles with a low specific surface area due to formation of the surface tungstated–platinum species.

Thus, the comparison of the catalytic activity of Pt/WZR systems with data of spectroscopic study shows that the oxidized system containing a maximum concentration of $Pt^{\delta+}$ species is most active in the isomerization of *n*-hexane. The oxidation step prevents the interaction of Pt with tungstated species resulting in the formation of tungstated–platinum species and, hence, catalyst deactivation. On the other hand, the $Pt^{\delta+}$ species may play role of centers of the formation of well-dispersed small metal particles under reaction conditions and provide the high activity in dehydrogenation and hydrogen transfer.

The reduction of the preliminary oxidized system at high temperatures leads to the formation of larger metal particles. It slightly increases the catalytic activity of reduced catalyst compared with oxidized system at low temperatures; however, it also decreases the maximal activity of reduced system at optimal temperatures.

3.2. Role of the support nature

The main factors affecting the properties of the support are the concentration and composition of additives and temperature of calcination.

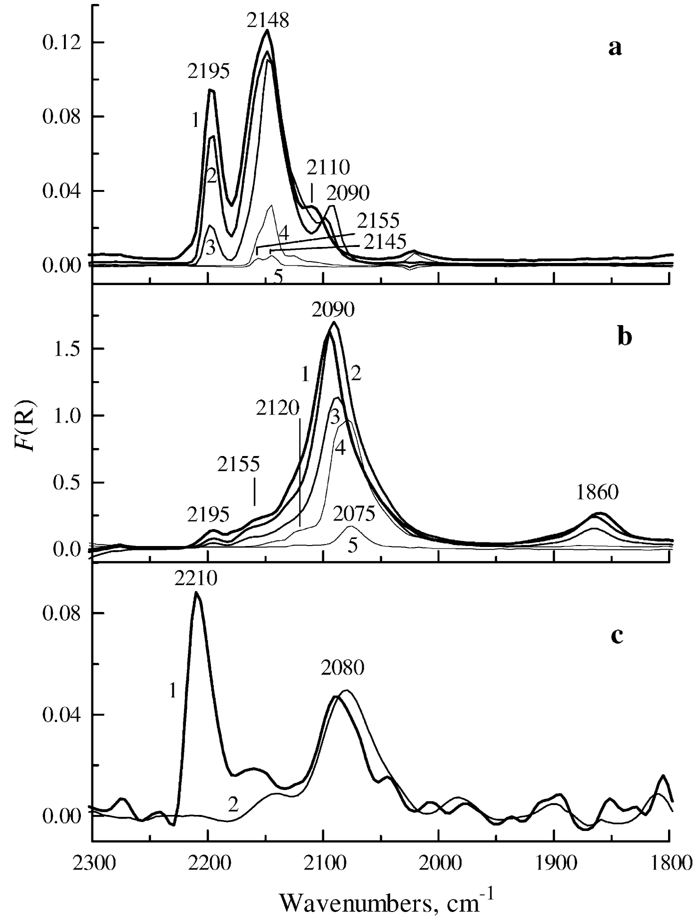

Fig. 2. DRIFT spectra of CO adsorbed on Pt/WZR (a) after oxidation at 450 °C, (b) oxidation at 450 °C with further reduction at 200 °C and (c) reduction at 200 °C. Spectra recorded (1) after adsorption and after evacuation at (2) 20, (3) 100, (4) 200 and (5) 300 °C.

The dependence of catalytic activity on the concentration of WO_4^{2-} ions in the samples in *n*-pentane isomerization is shown in Fig. 3. The maximum activity is achieved for the sample containing 15–20 wt.% of WO_4^{2-} ions. However, the selectivity to isopentane formation is slightly lower for the catalyst containing 20% of WO_4^{2-} ions. A decrease in the concentration of WO_4^{2-} ions to 10 wt.% leads to the diminution of the isopentane yield and selectivity.

The role of the temperature of the calcination of the oxide support is even more important. The Pt/WZR (625 °C) catalyst exhibits the low activity (Fig. 4). The isopentane yield was 21.8% and the selectivity was 49.7%. Rising reaction temperature leads to an increase in the isopentane yield; however, the rate of cracking enhances, too. A growth of the calcination temperature up to 800 °C causes a three-fold increase in the isopentane yield as compared to the catalyst calcined at 625 °C. The isopentane yield at 280 °C reached 63.3% and the selectivity was 93.8%. The catalyst shows the high stability.

In order to decrease the isomerization temperature and, hence, to shift the system toward more thermodynamically favorable conditions, the tungsten–zirconia sample was modified by addition of SO_4^{2-} anions at the step of preparation. The addition of 5.0 wt.% of SO_4^{2-} anions improves the catalytic activity of the system calcined at 625 °C in *n*-pentane and *n*-hexane

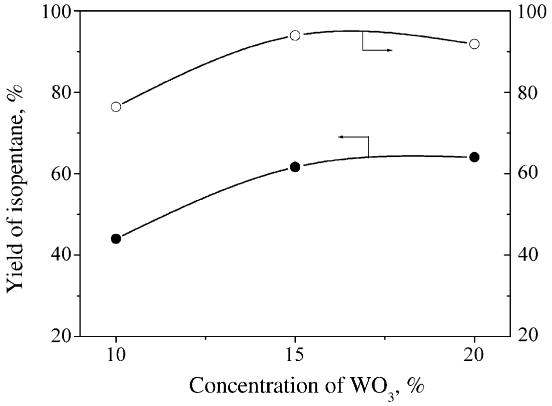

Fig. 3. The influence of the concentration of WO_4^{2-} anions on the performance of Pt/WZR catalysts in *n*-pentane isomerization.

isomerization (Fig. 5). The isopentane yield reached 66.1% and the selectivity was boosted to 93.2%. The temperature corresponding to the maximum isopentane yield and selectivity decreased from 280–300 to 200 °C. However, an increase in the reaction temperature lead to the deterioration of the catalytic activity due to catalyst deactivation.

A growth of the calcination temperature to 800 °C changed the properties of WO_3- and SO_4^{2-}-promoted systems. The activity of Pt/SWZR (800 °C) is close to the activity of sulfur-free samples. The temperature corresponding to the maximum isopentane yield increased to 260–280 °C. The reasons behind the changes in the catalytic activity for the different acid catalysts will be discussed later.

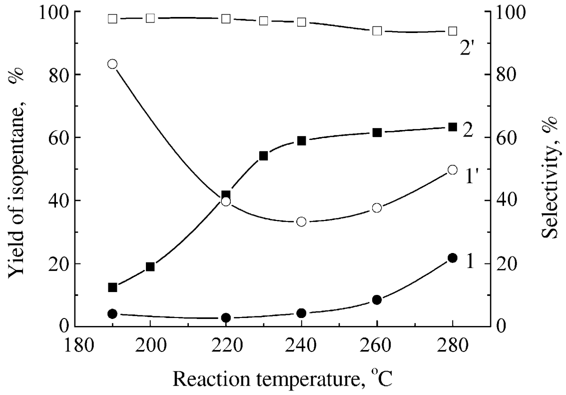

Fig. 4. The yield of isopentanes (1, 2) and selectivity (1′, 2′) of Pt/WZR catalysts calcined at 625 °C (1, 1′) and 800 °C (2, 2′).

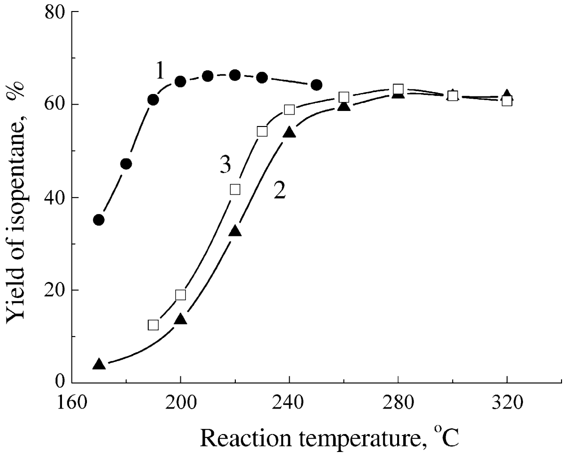

Fig. 5. The performance of Pt/SWZR catalysts in *n*-pentane isomerization: (1) Pt/SWZR (625 °C), (2) Pt/SWZR (800 °C) and (3) Pt/WZR (800 °C).

Similar results were obtained for *n*-hexane isomerization. The sulfated system shows the high activity at low temperatures (Fig. 6a). The maximum isohexanes yield was close to 70% at 200 °C. Further increase in the temperatures leads to a decrease in the catalytic activity due to deactivation and a decrease in the selectivity due to enhance in the rate of cracking. The pure tungstated system is active at significantly higher temperatures. The maximum isohexanes yield was obtained at 260 °C. However, the total yield of isomers and stability of the catalysts is also higher compared with sulfated catalyst (yield of *iso*-C_6 was 78%).

We can observe the close yield of methylpentanes for both systems (∼55%); however, the yield of dimethylbutanes (DMB) is higher for Pt/WZR system (Fig. 6b and c). The yield of DMB grows from 13% for Pt/SZR to 25% for Pt/WZR. We can suppose that the reason of the difference in the yield of DMB is the different lifetime of intermediates on the catalyst surface.

The performance of Pt/SWZR (800 °C) is very close to that of Pt/WZR (800 °C). More interesting data were obtained for Pt/SWZR (625 °C). *n*-Hexane isomerization on the Pt/SWZR (625 °C) catalyst proceeds in intermediate temperature region. The maximum activity was obtained at 230–240 °C. The total yield of isomers was ∼80 °C higher than that for both monoanion promoted system. The yield of DMB in 20–21% was close to maximal obtained on Pt/WZR (800 °C)

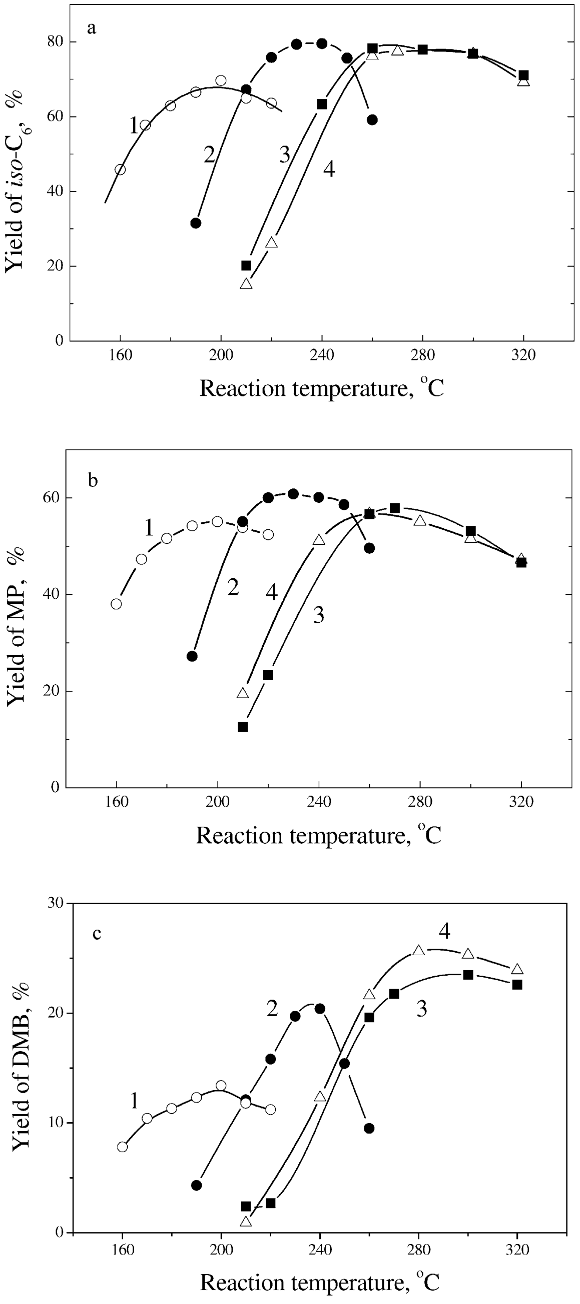

Fig. 6. The total yield of isohexanes (a), yield of 2- and 3-methylpentanes (b) and 2,2- and 2,3-dimethylbutanes on the Pt/SWZR catalysts: (1) Pt/SZR (625 °C), (2) Pt/SWZR (625 °C), (3) Pt/SWZR (800 °C) and (4) Pt/WZR (800 °C).

($\sim$25%). The system works stable up to temperatures of sulfate species reduction (250 °C [8]). The selectivity to isohexanes for all tungstated systems was significantly high.

In order to understand the specificity of catalytic properties of Pt/SWZR catalysts calcined at 625 or 800 °C, the physicochemical properties of the $SO_4{}^{2-}$ and $WO_4{}^{2-}$-promoted supports were studied by DRIFT spectroscopy using C_2D_4 and CD_3CN as molecular probes.

DRIFT spectra of SZR (625 °C), SWZR (625 °C), SWZR (800 °C) and WZR (800 °C) are shown in Fig. 7. In the spectrum of SZR (625 °C), the bands of SO_4 groups vibrations at 2760, 2040 and 1400 cm^{-1} corresponding to $\nu_{0\rightarrow 2,\mathrm{S{=}O}}$, $\nu_{0\rightarrow 2,\mathrm{S{-}O}}$, and $\nu_{0\rightarrow 1,\mathrm{S{=}O}}$, respectively, are observed. In the region of the stretching vibrations of OH groups, the bands at 3630 cm^{-1} and the broad band at 2900–3200 cm^{-1} assigned to three-fold bridging OH groups and OH groups forming multicentered bonds with oxygen in the oxide framework and SO_4 group are found [9]. The addition of $WO_4{}^{2-}$ in the case of the sample pretreated at low temperatures (SWZR (625 °C)) somewhat decreases the intensity of the bands attributed to OH and SO vibrations. The bands corresponding to WO_4 species were not observed. In the common, the spectrum of SWZR (625 °C) is close to the spectrum of SZR (625 °C).

The calcination at 800 °C (SWZR (800 °C) leads to a dramatic decrease in the intensity of the bands of OH groups and disappearance of the bands corresponding to the vibrations of S=O and S–O bonds. The new bands at 2020 cm^{-1} assigned to $\nu_{0\rightarrow 2,\mathrm{W{=}O}}$ in the WO_4 group are found. This spectrum is close to the spectrum of WO_3/ZrO_2 (800 °C).

Adsorption of CD_3CN was used as a test for Brønsted and Lewis acid sites (BAS and LAS). For all the samples, weak perturbation of isolated OH groups after adsorption of CD_3CN is observed. The nature of the most acidic BAS, i.e. protons forming multicentered bonds does not allow the observation of perturbed OH groups of this type because of considerable line broadening after CD_3CN adsorption.

In the spectra of SZR (625 °C), the band at 2305 cm^{-1} is found in the region of the C≡N bond stretching vibrations (Fig. 8). This band could be assigned to CD_3CN adsorbed on surface sites formed by SO_4 groups [10]. In the spectra of WZR (800 °C), the

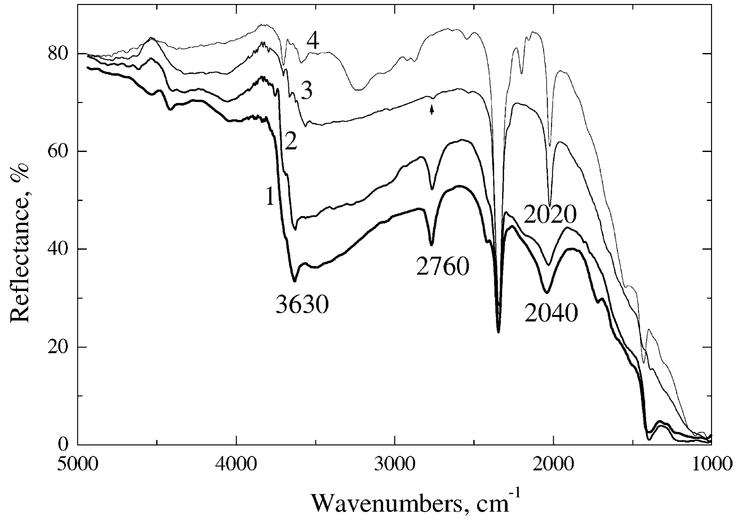

Fig. 7. DRIFT spectra of SZR (625 °C) (1), SWZR (625 °C) (2), SWZR (800 °C) (3) and WZR (800 °C) (4).

bands at 2314 and 2290 cm^{-1} that could be attributed to CD_3CN adsorbed on two types of sites formed by the surface WO_4 groups are observed. The properties of SWZR depend on the temperature of calcination. After calcination at 625 °C, the spectrum of CD_3CN is close to that of SZR (625 °C) with adsorbed acetonitryle: a single band is revealed at 2305 cm^{-1}; however, the band is narrower compared with SZR sample. It could be indicative of a decrease in the concentration of BAS formed the shoulder at low frequencies due to partial dilution by WO_x species. The spectra of SWZR (800 °C) after adsorption of the molecular probe resemble the spectra of CD_3CN adsorbed on WZR (800 °C).

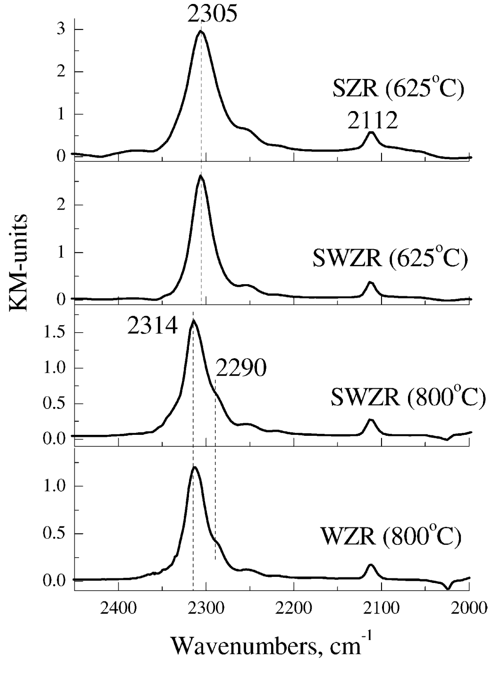

Fig. 8. DRIFT spectra in the region of CN bond vibrations of CD_3CN adsorbed on SZR (625 °C), SWZR (625 °C), SWZR (800 °C) and WZR (800 °C) catalysts.

The reactivity of acid sites was tested in oligomerization of C_2D_4 at room temperature (Fig. 9). The oligomerization of C_2D_4 on the surface sites is accompanied by the H–D exchange reaction that allows testing the nature of acid sites responsible for the reaction. It should be noted that unmodified ZrO_2 does not show any activity in oligomerization and H–D exchange at temperatures below 200 °C.

After adsorption of C_2D_4 on WZR (800 °C) at 20 °C, the bands at 2195 and 2090 cm^{-1} corresponding to stretching antisymmetric and symmetric vibrations of CD_2 groups in the linear oligomer chain appeared. Simultaneously, the intensity of the bands at 2885 and 2600–2400 cm^{-1} assigned to the vibrations of the CH bond in CDH groups and OD groups, respectively, increased. These data show that the WZR (800 °C) catalyst contains the acid sites active

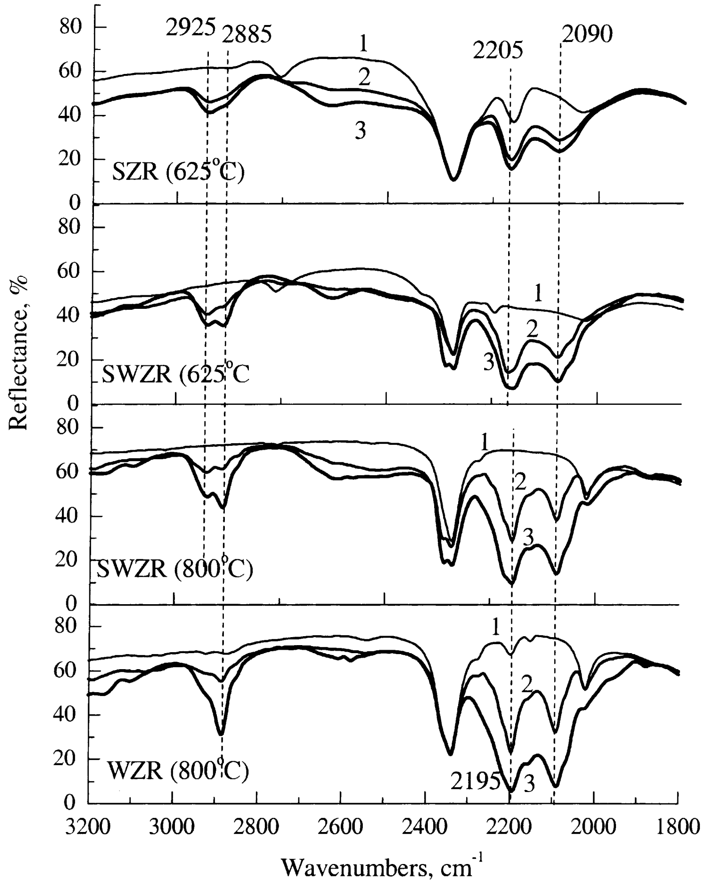

Fig. 9. DRIFT spectra of C_2D_4 adsorbed on SZR (625 °C), SWZR (625 °C), SWZR (800 °C) and WZR (800 °C) catalysts; spectra recorded (1) before and after (2) 10 min and (3) 2 h.

in the low-temperature oligomerization of ethylene. The low intensity of the bands of CH and OD groups after 10 min of the reaction indicates that BAS are not responsible for the initial steps of the reaction.

Adsorption of C_2D_4 on SZR (625 °C) leads to an increase in the intensity of the bands at 2205 and 2090 cm^{-1}. The position and shape of the bands are indicative of the superposition of two bands assigned to the vibrations of CD_2 and CD_3 groups. The bands at 2925 and 2885 cm^{-1} could be attributed to the vibrations of the CH bond in CD_2H and CDH groups. The estimation of the intensity of the bands corresponding to exchanged groups shows that BAS play the main role in oligomerization of C_2D_4 on SZR (625 °C).

Analysis of the spectra of C_2D_4 adsorbed on SWZR (625 °C) shows that the process follows by the scheme that is close to oligomerization on SZR (625 °C). However, the higher intensity of the bands attributed to CHD groups (the band at 2885 cm^{-1}) testifies that the tungstate species also participate in surface reactions on SWZR (625 °C). An increase in the temperature of calcination to 800 °C turns the oligomerization process to the route analogous to the conversion of C_2D_4 on WZR (800 °C).

Thus, we can conclude that the calcination of SWZR at 800 °C forms the surface almost similar to WZR (800 °C) and we observe the similar catalytic properties for both Pt-promoted systems. The properties of WZR (800 °C) and SWZR (800 °C) are connected with the surface WO_4 groups. In this case, we should expect a decrease in the Brønsted acidity as compared with sulfate-containing samples, on the one hand and an increase in the stability under reaction condition, on the other.

Calcination of SWZR at 625 °C remains a part of sulfate species and the acidity is higher compared with WZR (800 °C). However, sulfate species is “diluted” by $W(OH)_x$ species, thus the acidity of surface layer is decreased compared with SZR (625 °C). As a result, we observe a high temperature shift compared with Pt/SZR and increase in the activity compared with Pt/WZR. The high density of acid sites in SZR is favorable for proceeding of bimolecular interaction between alkanes or carbenium ions adsorbed on adjacent sites leading to the formation of side products of disproportionation. A decrease in the concentration and higher dispersion of BAS in SWZR (625 °C) system prevents the proceeding of side processes and the selectivity improves. It leads to the additional stabilization of adsorbed species and favors secondary reaction of isomerization leading to the formation of dibranched isomers on Pt/SWZR system.

4. Conclusions

Thus, the role of key factors influencing on the catalytic activity of SWZR based catalysts promoted with Pt was studied. The electronic state of Pt and acidic properties of anion-promoted support are found to be the most important.

The addition of Pt with further oxidation and mild reduction allows one to enhance the catalytic activity in *n*-hexane isomerization 10 times compared with metal-free system. The oxidation step prevents the strong interaction of Pt with tungstated species result in the formation of tungstated–platinum species and, hence, catalyst deactivation. Mild reduction under reaction conditions leads to the formation of well-dispersed small metal particles and provides the maximum activity in dehydrogenation and hydrogen transfer.

The catalytic activity of Pt/SWZR catalysts in *n*-hexane and *n*-pentane isomerization decreases in the following order:

$$\mathrm{Pt/SZR}\,(625\,^{\circ}\mathrm{C}) > \mathrm{Pt/WSZR}\,(625\,^{\circ}\mathrm{C}) > \mathrm{Pt/WSZR}\,(800\,^{\circ}\mathrm{C}) \approx \mathrm{Pt/WZR}\,(800\,^{\circ}\mathrm{C})$$

The yield of dibranched isomers increases in the same order. The properties of WZR (800 °C) and SWZR (800 °C) are connected with the surface WO_4 groups. The presence of sulfate species in Pt/SZR (625 °C) and Pt/WSZR (625 °C) is responsible for the strong acidic properties of these catalysts. A lower concentration and higher dispersion of BAS in SWZR (625 °C) system due to partial dilution by $W(OH)_x$ species prevents the proceeding of side processes and improves the selectivity and yield of dibranched products compared with Pt/SZR (625 °C) system.

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