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Article *in* Procedia Engineering · December 2015

DOI: 10.1016/j.proeng.2015.07.291

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Procedia Engineering 113 (2015) 62 – 67

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International Conference on Oil and Gas Engineering, OGE-2015

$Pt/WO_3/ZrO_2$ catalysts for n-Heptane isomerization

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Abstract

Researches of catalysts $Pt/WO_3/ZrO_2$ (Pt content is 1 wt.%) at varying WO_3 concentrations (10-35% wt.) are carried out in the isomerization reaction of n-heptane, under the following conditions: temperature range is 140-220ºC, pressure is 1.5 MPa, the ratio H_2/n-heptane is 3 (mol.), heptane volume velocity is 1h-1. X-ray analysis, N_2 adsorption-desorption, infrared spectroscopy, temperature-programmed desorption of ammonia are used to characterize the physical and chemical properties of the prepared catalysts, atomic emission spectrometry with inductively coupled plasma is for WO_3 analysis. Maximum catalysts activity and selectivity in the isomerization reaction of n-heptane is obtained at the reaction temperature of 170°C on the catalyst with a content of 25% wt WO_3.: conversion of n-heptane is 84%, the selectivity to the heptane isomers sum is 71.9 %, dimethyl and trimethyl heptane isomers yield is 22.8% wt.

Peer-review under responsibility of the Omsk State Technical University

Keywords: n-heptane isomerization; $Pt/WO_3/ZrO_2$; high octane number component; gasoline; catalyst

1. Introduction

Modern environmentally friendly motor fuels have specified requirements for reducing the aromatic hydrocarbons proportion that are harmful to the environment. In turn, the decrease in the aromatic hydrocarbons content in gasoline will lead to the loss of octane number, which can be compensated by non-aromatic high octane components – branched n-alkanes. In the oil refining industry the processes of pentane-hexane fraction isomerization on various catalysts are successfully implemented [1-4].

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1877-7058
Peer-review under responsibility of the Omsk State Technical University
doi:10.1016/j.proeng.2015.07.291

An additional source of high octane isomerate can be a fraction 75-105 of wide gasoline fraction consisting mainly of n-heptane and a small amount of isomers that are traditionally included in the reforming raw material and is mostly toluene-forming fraction. Currently, there is no process of heptane fraction isomerization in the industry, however, its implementation will allow to meet long-term environmental requirements for commercial gasoline. The study and search for efficient catalysts of n-heptane isomerization in the last years has caused wide interest [5-8]. The authors [9-11] have shown high catalysts selectivity of WO_3/ZrO_2 in the n-heptane isomerization. In 1987 M. Hino and K. Arata [12] first reported the catalytic activity of these systems in the butane and pentane isomerization reaction.

In the present study we investigated the effect of the WO_3 content in catalysts $Pt/WO_3/ZrO_2$ on the composition phase, texture characteristics, and acidic properties and catalyst indicator of the n-heptane isomerization reaction.

2. Experimental

2.1. Catalysts preparation

Zirconium hydroxide was prepared by subsidence with adding a solution of Zr(SO4)2 in ammonia water solution at constant pH=9.5±0.5 and rapid mixing. The residuum was in the kept mother liquor for 1 hour, then the residuum was filtered, washed with distilled water until there is reaction to SO42--ions with BaCl2 solution and then dried at 100 °C for 5 hours. WO3/ZrO2 was obtained by anionic modifying of zirconium hydroxide with a solution of ammonium metatungstate (Aldrich,> 85% wt WO3), with subsequent forming, drying at 120 °C for 3 hours and heat treatment in air at 800 °C for 2 hours. Pt/WO3/ZrO2 was prepared by WO3/ZrO2 infiltration with H2PtCl6 solution in an amount of the Pt content in the catalyst 1% wt. with the following by drying at 120°C for 3 hours and heat treatment in a dry air flow at 450 °C for 1 hour. The resulting catalyst was designated as /xWZ, where x is % wt. WO3 in the catalyst (10-35% wt.).

2.2. Catalysts characterization

X-ray diffraction analysis (XRD) was performed on the powder X-ray diffractometer D8 Advance (Bruker) in the Cu-kα radiation (wavelength is 0.15406 nm) using a position-sensitive linear detector Lynxeye at a voltage of 40 kV and a filament current of 40 mA, the scan area is 2θ:5-80º. The interpretation of the obtained XRD samples was performed using the database of powder diffraction ICDD PDF-2, year 2006. Quantitative analysis of crystalline phases was carried out acording to the Rietveld method in the program TOPAS 4.2 (Bruker).

Textural properties of the samples were measured by N2 adsorption-desorption at the Sopromatic 1900 apparatus. Determination of the samples specific surface was performed according to the BET method based on measurement of the nitrogen adsorption equilibrium at 77 K.

Acid catalysts study by FTIR-spectroscopy was carried out using the CO molecules probe on the Fourier spectrometer Shimadzu 8300. Samples were compressed into tablets with density (20-35)×10-3 g/sm2 for spectra recording. Catalysts were vacuumized at 450 °C for 1 h, then the CO adsorption was carried out at pressures 0.013-1.33 kPa and spectra were recorded at 77 K.

Thermoprogrammed desorption (TPD) of ammonia was carried out on the AutoChem-2920 (Micromeritics) with a thermal conductivity detector. The samples were heated in a flow of O2 10% vol. in helium up to 700 °C and kept at that temperature for 1h, then cooled in flowing helium at 100 °C and the ammonia adsorption was carried out for 1 hour, using a NH3 mixture of 10% vol. in helium. Weakly bound ammonia was removed by blowing-off with helium at a temperature of 100 °C for 1 hour. Ammonia TPD was conducted in the temperature range of 100-700ºC with heating rate 10 ° C/min.

Quantitative analysis of the catalysts was carried out by atomic emission spectrometry with inductively coupled plasma (ICP-AES) on the Varian 710-ES (Agilent Technologies). Samples decomposition was carried out in a microwave system Multiwave 3000 (AntonPaar).

2.3. Catalytic tests

The n-heptane isomerization was conducted at flow unit with an isothermal tubular reactor with fixed bed catalyst (2 sm^3, 0.2-0.7 mm fraction) at a pressure of 1.5 MPa and a temperature range of 140-240ºC. Before the reaction, the catalyst was reduced in a hydrogen flow at 300 °C for 3 hours, then the reactor was cooled to reaction temperature and n-heptane was fed with volume velocity of 1h-1) in a H2/n-heptane ratio =3 (mol.).

Analysis of the reaction products was carried out in the online mode using a gas chromatograph (Tsvet-800) equipped with a flame ionization detector and capillary column PONA/PIONA (J&W Scientific). The measure of catalyst activity was the n-heptane conversion . Isomerization selectivity was defined as the ratio of the heptane isomers sum yield to all isomerization products.

3. Results and discussion

3.1. Effect of WO_3 concentration on textural characteristics and phase composition

The prepared samples nomenclature, texture characteristics and phase composition are presented in Table. 1. As can be seen from the data presented in Table. 1, the WO3 10% wt addition to ZrO_2. leads to an increase in surface area from 44 to 85 m2/g; with further increase in the WO_3 concentration the specific surface area gradually decreases, and is 56 m2/g for Pt/35WZ sample. WO_3 concentration influences the phase composition as follows: WO_3 adding to the catalyst from 10 to 25% wt. gradually stabilizes ZrO_2 tetragonal phase, a further increase in the WO_3 concentration leads to its reduction and the simultaneous increase in the proportion of the WO_3 crystalline phase.

Table 1. Nomenclature, textural properties and XRD data for Pt/xWZ catalysts.

Catalyst	BET surface area (m^2 g^{-1})	Pore size (nm)	Pore volume, (cm^3 g^{-1})	W nm^{-2} (calculated)	Percentage of phase	
					ZrO_2 tetragonal	WO_3 monoclinic
ZrO_2	44	-	-	0	8	not determined
Pt/10WZ	85	10.7	0.228	3	66	not determined
Pt/15WZ	75	11.9	0.224	5	73	not determined
Pt/20WZ	70	17.9	0.314	7	79	not determined
Pt/25WZ	67	16.1	0.269	10	94	6
Pt/30WZ	59	18.0	0.266	13	89	11
Pt/35WZ	56	19.5	0.274	16	68	32

3.2. Effect of WO_3 concentration on the acidic properties

Effect of WO_3 concentration on the acidic properties of the catalysts was examined by IR spectroscopy of adsorbed CO (Table 2).

Table2. FTIR-spectroscopy of absorbed CO data for Pt/xWZ catalysts.

Catalyst	BAS (μmol g-1), (wavenumber (cm-1))	LAS (μmol g-1), (wavenumber (cm-1))
ZrO_2	not determined	196 (2180-2190)
Pt/10WZ	14 (2162)	96 (2191)
Pt/15WZ	96 (2165)	102 (2193)
Pt/25WZ	not transparent	

Pt/35WZ	not transparent

Table 2 shows that ZrO_2 without anion-modifying agent is characterized as Lewis acidic sites (LAS). WO_3 addition in the catalyst leads to the formation of Bronsted acidic sites (BAS) and with WO_3 increasing from 10 to 15% wt. their amount increases considerably (from 14 to 96 mmol/g). Catalysts containing $WO_3 \geq 25\%$ wt. appeared to be nontransparent to infrared radiation. In this connection, the catalyst acidity was additionally studied by ammonia TPD method (Fig. 1).

TPD curves of the samples can be divided into 2 groups: with a maximum at approx. 245 °C with WO_3 content of 10 to 35% wt. (Fig. 1b) and with approx. 260 °C with WO_3 content of 15 to 25% wt. (Fig. 1c). All Pt/xWZ samples are characterized with the arm on the area of 187 °C, which corresponds to the first peak of unmodified ZrO_2. As shown below, the samples of the first group are less active in the n-heptane isomerization reaction, and the second group they are active. Thus, the higher the WO_3 concentration, the narrower the TPD curve peak of catalyst in comparison to the peak of unmodified ZrO_2 (according to infrared spectrometry they have Lewis acidic sites) and the catalyst with a minimum WO_3 content of 10 wt% (Fig. 1a). This dependence, coupled with the infrared spectrometry data, may indirectly indicate a change in the quality of acid sites: reducing the number of LCC with increasing WO_3 concentrations in the catalysts.

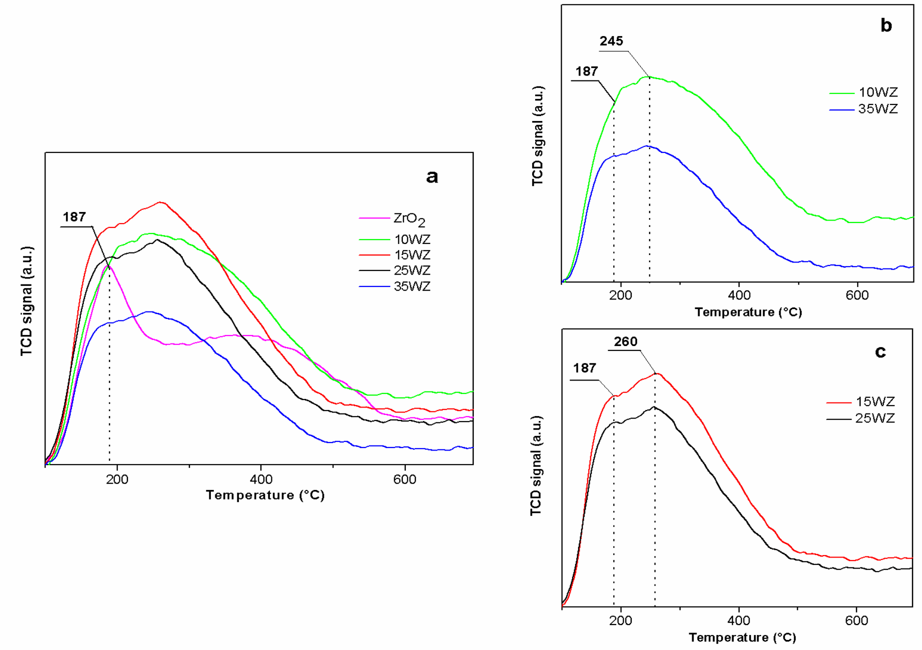


Fig. 1. NH_3-TPD curves of *x*WZ for all catalysts (a), the first group with maxima of 245°C (b) and the second group with maxima of 260°C (c).

3.3. *Effect of WO_3 concentration on the catalytic indicators*

Indicators of the n-heptane isomerization reaction on Pt/xWZ catalysts are shown in Table 3. As seen from Table 3, in all samples there is a high n-heptane conversion at 80-85% at a reaction selectivity of 70-75% the stable catalysate yield of 80-85%. Fig. 2 shows the change in catalyst activity and yield of the desired reaction products – dimethyl and trimethyl heptane isomers (DTMSes) depending on the WO3. content. From the data it follows that the optimal WO3 concentration in the catalysts in the test range is 15-25% wtt. These samples show maximum activity in the n-heptane isomerization reaction and the maximum yield of the desired products (DTMSes) at the level of 22-23% wy.

Table 3. Catalytic results and products distribution for n-Heptane isomerization over Pt/xWZ (the best results for each catalyst are shown).

Catalyst	Pt/10WZ	Pt/15WZ	Pt/20WZ	Pt/25WZ	Pt/30WZ	Pt/35WZ
Reaction temperature (ºC)	220	180	170	170	180	200
Conversion (%)	79.0	81.1	81.2	84.0	85.8	82.9
Selectivity (%)	69.1	74.3	73.8	71.9	70.5	71.1
Yield (wt.%)						
Catalyzate [a]	79.8	83.7	83.7	82.8	79.8	80.7
DTMSes [b]	18.5	21.7	21.9	22.8	22.7	21.9
MMSes [c]	36.1	38.6	38.1	37.6	37.8	37.1
Cracking products [d]	20.2	16.3	16.3	17.3	20.2	19.3

[a] Sum of hydrocarbons with C atom higher than 4

[b] Dimethyl and trimethyl substituted isomers – sum of 2,2-Dimethylpentane, 2,3-Dimethylpentane, 2,4-Dimethylpentane, 3,3-Dimethylpentane and 2,2,3-Trimethylbutane

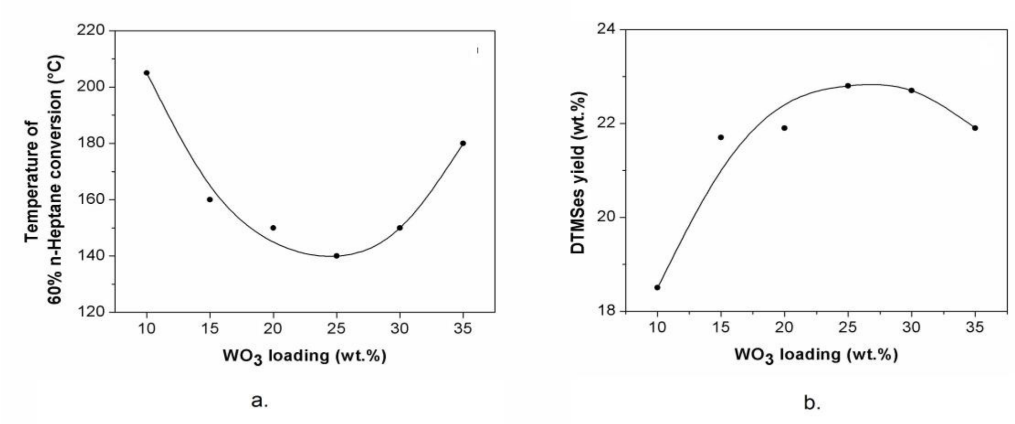
[c] Monomethyl substituted isomers – sum of 2-Methylhexane, 3-Methylhexane and 3-Ethylpentane

[d] Sum of hydrocarbons with C atom less than 5

4. Conclusion

In the paper we have shown high activity and selectivity of the Pt/WO_3/ZrO_2 catalysts in the n-heptane isomerization reaction. The study of the catalysts acidity with the WO3 concentration in the range of 10-35% wt. demonstrated that WO_3 concentration increasing from 10 to 25% wt. leads to the increase of the amount of Bronsted acid sites involved in the n-heptane isomerization reaction. Further increasing of the WO_3 concentration to 35% wt. reduces the overall acidity, which causes catalyst activity loss.

The best reaction results have been achieved at 170 °C with a catalyst containing WO_3 o25% wt.: conversion is 84%, the selectivity is 71.9%, stability catalyzate yield is 82.8% wt. and the yield of the desired reaction products – dimethyl and trimethyl heptane isomers (DTMSes) is 22.8% wt. According to the XRF, this catalyst is characterized by the maximum number of ZrO_2 active tetragonal phase.



a. b.

Fig. 2. Activity (a) and DTMSes yield (b) dependence from WO_3 loading.

Acknowledgements

The Authors are grateful for research assistance to Omsk Research Collaboration Centre of Siberian Branch of Russian Academy of Sciences.

References

[1] J.M. Hidalgo, M. Zbuzek, R. Černý, P. Jíša, Current uses and trends in catalytic isomerization, alkylation and etherification processes to improve gasoline quality, Cent. Eur. J. Chem. 12 (2013) 1–13.

[2] P.J. Kuchar, J.C. Bricker, M.E. Reno, R.S. Haizman, Paraffin isomerization innovations, Fuel Process. Technol. 35 (1993) 183–200.

[3] A. Chica, A. Corma, Hydroisomerization of Pentane, Hexane, and Heptane for Improving the Octane Number of Gasoline, J. Catal. 187 (1999) 167–176.

[4] H. Weyda, E. Köhler, Modern refining concepts-an update on naphtha-isomerization to modern gasoline manufacture, Catal. Today. 81 (2003) 51–55.

[5] P. Liu, M.-Y. Wu, J. Wang, W.-H. Zhang, Y.-X. Li, Hydroisomerization of n-heptane over MoP/Hβ catalyst doped with metal additive, Fuel Process. Technol. 131 (2015) 311–316.

[6] Z. Chai, E. Lü, H. Zhang, J. Ren, Effect of ethanol on the isomerization of n-heptane over Pt/SAPO-11 and Pt/ZSM-22 catalysts, J. Fuel Chem. Technol. 42 (2014) 207–211.

[7] P.N. Kuznetsov, A.V. Kazbanova, L.I. Kuznetsova, V.I. Kovalchuk, Y.L. Mikhlin, Bulk and surface characterization and isomerization activity of Pt/WO42−/ZrO2 catalysts of different preparations, React. Kinet. Mech. Catal. 113 (2014) 69–84.

[8] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Large Scale Hydroisomerization Reactions of n-Heptane on Partially Reduced MoO3/TiO2, Appl. Catal. A Gen. 361 (2009) 81–85.

[9] M.A. Arribas, F. Márquez, A. Martínez, Activity, Selectivity, and Sulfur Resistance of Pt/WOx–ZrO2 and Pt/Beta Catalysts for the Simultaneous Hydroisomerization of n-Heptane and Hydrogenation of Benzene, J. Catal. 190 (2000) 309–319.

[10] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, Structural and Catalytic Characterization of Solid Acids Based on Zirconia Modified by Tungsten Oxide, J. Catal. 181 (1999) 57–72.

[11] W. Hua, J. Sommer, Alumina-doped Pt/WOx/ZrO2 catalysts for n-heptane isomerization, Appl. Catal. A Gen. 232 (2002) 129–135.

[12] M. Hino, K. Arata, Synthesis of solid superacid of tungsten oxide supported on zirconia and its catalytic action for reactions of butane and pentane, J. Chem. Soc. Chem. Commun. (1987) 1259.