Effect of Reduction Temperature of a Pt/WO$_3$/ZrO$_2$ Catalyst on n-Heptane Isomerisation

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Abstract

The effect of reduction temperature of a Pt/WO$_3$/ZrO$_2$ catalyst (200–500 °C) on indicators of n-heptane isomerisation was studied. It was found that the maximum yield of the desired reaction products that are high-octane di- and trimethyl-substituted (DTMS) n-heptane isomers was reached (27–31 mass %) in the region of 250–300 °C. A rise in reduction temperature of the catalyst to 400–500 °C leads to an increase in the number of Lewis acid sites in 1.6–1.7 due to partial reduction of tungsten on the WO$_3$/ZrO$_2$ surface, which contributes to an increase in the catalyst activity; herewith, selectivity by the target products decreases due to enhancing side reactions of n-heptane cracking.

Key words: n-heptane, isomerisation, tungstate-containing zirconium dioxide, platinum

INTRODUCTION

The demands placed on commercial gasoline put into circulation in the Russian Federation are imposed by the technical regulations of the Customs Union [1]. To meet the requirements on the content of aromatic hydrocarbons in environmental class 5 gasoline, no more than 35 % should be contained in them (including benzene not more than 1 vol. %). Due to high contents of aromatic hydrocarbons (at a level of 60–80 mass %) in the major component in gas of Russian refineries – reformate, additional sources of high-octane non-aromatic components are required when compounding commercial gas. An example of such components is isomerisate composed mainly of isoalkanes with high octane ratings.

This work proposes isolation of an additional 65–100 °C fraction containing mainly heptanes of wide gasoline IBP-180 °C fraction and directing it to isomerization.

Systems based on tungstate-containing zirconia applied with platinum group metals are efficient systems as catalysts of n-heptane (models of raw materials) isomerisation [2–4].

Issues of the regularities of formation, the structure of acid sites in WO$_3$/ZrO$_2$ systems are discussed in [2, 5–10].

The finished catalyst is a composition of tungstate-containing ZrO$_2$ and applied to a metal component (usually Pt, Pd). To ensure the active operation of the catalyst its preliminary reduction with hydrogen prior to the reaction is required. Processes happening at WO$_3$/ZrO$_2$ systems reduction with hydrogen are given attention to in [11, 12]. Along with that, the effect of reduction conditions of metal component-applied WO$_3$/ZrO$_2$ on catalytic indicators of the n-heptane isomerisation reaction is not con-

sidered in the literature. In this regard, the work purpose is studying the effect of reduction temperature of a $Pt/WO_3/ZrO_2$ catalyst on this reaction.

EXPERIMENTAL

Catalyst preparation

Zirconium hydroxide was obtained by the precipitation method at addition of $ZrOCl_2 \cdot 8H_2O$ solution to an aqueous ammonia solution with constant (pH 9.5±0.5) and intense stirring. The resulting residue was aged in the mother liquor for 1 h, filtered of, washed with distilled wateruntil the absence of the qualitative reaction for Cl^- ions and dried at 100 °C for 5 h. Anion modification of zirconium hydroxide with an aqueous solution of ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}$ (Aldrich, >85 % mass WO_3), followed by moulding, drying at 120 °C for 3 h and air calcining at 950 °C for 2 h. Impregnation of WO_3/ZrO_2 with an aqueous solution of H_2PtCl_6 of a specified concentration gave $Pt/WO_3/ZrO_2$ to obtain the necessary content of platinum in the catalyst (1 mass %) followed by drying at 120 °C for 3 h. Samples were calcined in a current of air at 450 °C for 1 h. The resulting catalyst was designated as $Pt/xWZ(T)$, where x is mass % WO_3 in the catalyst, W is WO_3, Z is ZrO_2, T is the calcination temperature of WZ.

Isomerisation of n-heptane

Isomerisation of n-heptane was carried out in a flow setup with an isothermaltubular reactor with a fixed layer of catalyst (2 cm^3, 0.2–0.7 mm fraction). Prior to the reaction, the catalyst was reduced in a current of hydrogen at 200–500 °C for 3 h. The test conditions: $t = 140$–220 °C, $P = 1.5$ MPa, molar ratio of $H_2/CH = 3 : 1$, the feed space velocity of 1 h^{-1}.

Analysis of the reaction products was performed in the online mode using a Tsvet-800 gas chromatographer equipped with a flame ionization detector and a RESTEK CORP quartz capillary column with the Rtx-1 phase. n-Heptane conversion degree was used as a measure of activity of catalysts. Isomerisation selectivity was determined as a ratio of the yield of the amount of heptane isomers to the yield of all reaction products.

Thermoprogrammed reduction

Thermoprogrammed reduction (TPR) was performed using an AutoChem-2920 instrument (Micromeritics) with a thermal conductivity detector. Samples were reduced in a current of 10 vol. % H_2 with a heating rate of 10 °C/ min to 450 °C and spectra of hydrogen adsorption were registered.

IR spectroscopy

Acid properties of catalysts were studied by the IR spectroscopic method of adsorbed pyridine molecules using a Shimadzu 8300 Fourier spectrometer. To register spectra samples were pressed in tablets without a binder of a density of $(20-35) \cdot 10^{-3}$ g/cm^2. A tablet was placed into a cuvette that enables to conduct pre-treatment of samples at elevated temperatures and carry out pyridine adsorption. All catalysts tablets were pre-vacuumed at 300–500 °C for 1.5 h. Pyridine adsorption was carried out at 150 °C for 15 min, then physadsorbed pyridine was pumped out for 1 h at the same temperature.
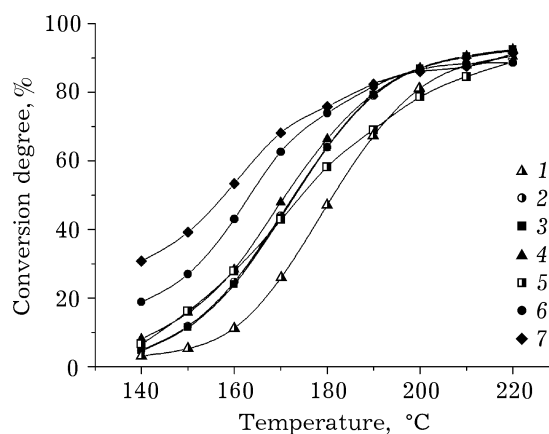

Fig. 1. Temperature dependence of n-heptane conversion degree for a Pt/25WZ(950) catalyst reduced at temperatures (°C): 200 (*1*), 250 (*2*), 300 (*3*), 350 (*4*), 400 (*5*), 450 (*6*), 500 (*7*).

RESULTS AND DISCUSSION

In works [4, 13, 14], a study on the effect of the composition and preparation conditions of a platinum-containing catalyst based on WO$_3$/ZrO$_2$ was carried out by usfor the n-heptane isomerisation reaction. It was found that the maximum yield of the target reaction products that are high-octane di- and trimethyl-substituted (DTMS) n-heptane isomers was reached in case of a catalyst with WO$_3$ content of 25 mass %, 1 mass % P and calcination temperature of a WO$_3$/ZrO$_2$ carrier of 950 °C.

In this regard, this catalyst (Pt/25WZ(950)) was selected as a basic sample to study the effect of reduction temperature on the n-heptane isomerisation reaction. Reduction temperature was varied in a range of 200−500 °C. Catalytic test results are given in Figs. 1−3.

It can be seen (see Fig. 1) that a decrease in reduction temperature of the catalyst from 200 to 500 °C leads to an increase in the catalyst activity, which is testified by a shift of conversion graphs to the side of lower temperatures.

Depending on the selectivity by isomers, catalysts can be divided into two groups (see Fig. 2): with reduction temperatures in a region of 200−350 °C and those of 400−500 °C. The selectivity at a conversion of 80−85 % for catalysts of the first group is found at a level of 85−95 %, the yield of DTMS isomers is maximum and amounts to 27−31 mass % (see Fig. 3).

Fig. 3. Yield of di- and trimethyl-substituted (DTMS) isomers of heptane vs reduction temperature of Pt/25WZ(950).

A noticeable decrease in catalytic selectivity is observed at an increase of reduction temperature to 400−500 °C: selectivity is 65−75 % at the same conversion degree (80−85 %). The yield of DTMS reduces by 7−10 mass % and amounts to 20−21 mass %.

Figure 4 presents TPR spectra for 25WZ(950) sample without platinum and after applying Pt. Hydrogen adsorption above 300 °C for WO$_3$/ZrO$_2$ on TPR curves refers to partial reduction of tungsten atoms WO$_3 \rightarrow$ WO$_{2.9}$ [11, 12].

For a platinum-containing sample, TPR profile is characterized by the availability of two reduction regions: the first one − before TPV (250 °C), where platinum reduction [12, 15, 16]
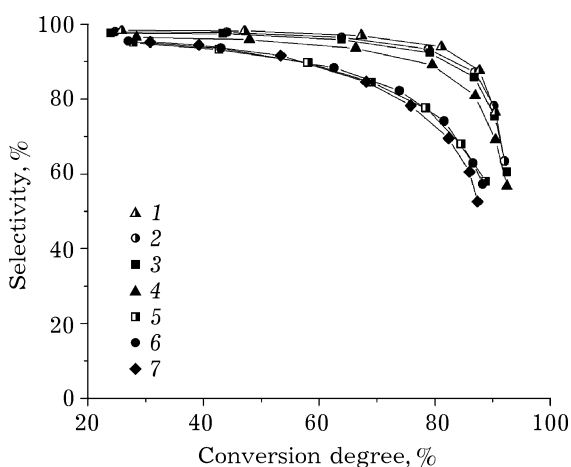

Fig. 2. Selectivity depending on n-heptane conversion degree for a Pt/25WZ(950) catalyst reduced at temperatures (°C): 200 (1), 250 (2), 300 (3), 350 (4), 400 (5), 450 (6), 500 (7).
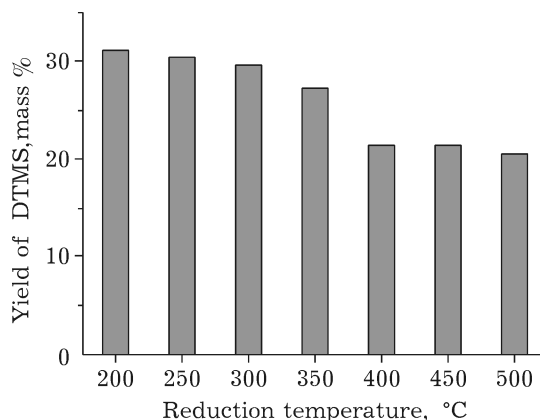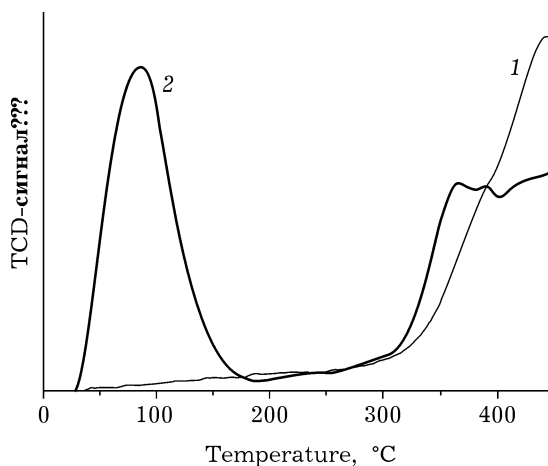

Fig. 4. Thermoprogrammed reduction of WO$_3$/ZrO$_2$ samples: 1 − 25WZ(950), 2 − Pt/25WZ(950).

TABLE 1

Acid properties of a $Pt/WO_3/ZrO_2$ catalyst according to IRS of adsorbed pyridine

Temperature reduction of Pt/WZ, °C	LAS-1		LAS-2		BAS	
	μmol/g	v, cm^{-1}	μmol/g	v, cm^{-1}	μmol/g	v, cm^{-1}
300	21	1445	3	1453	48	1538
500	33	1446	5	1452	36	1538

happens; the second region characterizes tungsten reduction processes and corresponds to temperatures above 300 °C [11, 12].It is assumed that the maximum reduction temperature in the first region at 85 °C refers to reduction of Pt^{4+} to Pt^{2+} [15, 17]. Reduction region above 300 °C characterizing tungsten reduction processes undergoes a quantitative change, which can testify the interaction of platinum atoms with surface tungsten atoms.

It is assumed [11, 12] that reduction in WO_3/ZrO_2 systems occurs step-wise following the scheme: $WO_3 \rightarrow WO_{2.9} \rightarrow WO_2 \rightarrow W$. The first stage proceeds at 300−500 °C, the second one − in a temperature region of 550−700 °C and reduction of tungsten dioxide to metallic tungsten happens at 750−850 °C.

The effect of reduction temperature of a $Pt/WO_3/ZrO_2$ catalyst on its acid properties was studied by IR spectroscopic techniques using pyridine molecules as a probe (Table 1). Infrared spectroscopic data (see Table 1) indicate that Brønstein (absorption band of 1538 cm^{-1}) and two types of Lewis acid sites (absorption bands at 1445−1446 and 1452−1453 cm^{-1}).

The total number of acid sites almost does not change with an increase in reduction temperature from 300 to 500 °C and amount to 72−74 μmol/g, herewith, a decrease in the number of BAS in 1.3 times (from 48 to 36 μmol/g) and an increase in the of both weak LAS and stronger ones in 1.6−1.7 times is observed.

It can be concluded from TPR (see Fig. 4) and IR (see Table 1) data that reduction of a platinum-containing tungstate-zirconium catalyst at temperatures above 300 °C is accompanied by the formation of additional LAS because of partial reduction of W atoms on the surface of a $Pt/WO_3/ZrO_2$ catalyst.

CONCLUSION

It was found that an increase in reduction temperature of a $Pt/WO_3/ZrO_2$ catalyst up to 500 °C led to a decrease in the number of Brønstein acid sites and an increase in the number of Lewis acid sites resulting in an increase in catalytic activities and selectivity by isomeric products decreases due to developing side cracking reactions of heptanes.

The best indicators in the n-heptane isomerisation reaction are reached in the presence of a $Pt/WO/ZrO_2$ catalyst reduced at 250−300 °C. Platinum reduction processes are terminated in this temperature region.

Acknowledgement

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