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Hydroisomerization of n-heptane on the $Pt/H_3PW_{12}O_{40}/Zr$-MCM-41 catalysts

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ABSTRACT

Catalytic properties of the 1 wt.%Pt/25 wt.%$H_3PW_{12}O_{40}$/Zr-MCM-41-n (designated as Pt/HPW/WSZn, where n = Si/Zr = 25, 15, 8, 4, respectively) catalysts were evaluated in a microreactor system for the hydroisomerization of n-heptane at atmospheric condition. Catalytic results show that tungstophosphoric acid promoted mesoporous Pt/Zr-MCM-41 catalysts have potential important for the commercialization of n-heptane isomerization due to their high activity and unique selectivity to multibranched isoheptanes. It was found that 2-methylhexane was predominant in the monobranched isoheptanes and 2,3-dimethylpentane was the prevailing compound in the multibranched products. In the cracking products, only butane (isobutane and n-butane) and propane were formed. The formation of the multibranched isoheptanes had a close correlation with the mesopore diameters of the catalysts. The isomerization selectivity could be expressed by a parameter S_P, which is defined as a comprehensive function of Brönsted acid density, metal dispersion and geometry of the catalysts. The reaction mechanisms involving the formations of monobranched and multibranched isoheptanes as well as cracking products were discussed and postulated.

1. Introduction

The isomerization of n-alkanes to i-alkanes is one of the most important and economical catalytic processes in the petroleum refining industry. In this process, the straight chain alkanes are transformed into branched isomers boosting research octane number (RON) to improve the gasoline fuel quality. For example, the RON of n-heptane is 0, whilst, it raised up to 56, 92 and 120 for 3-methylhexane, 2,3-dimethylpentane and toluene, respectively.

Previous investigations have predominantly concentrated on the isomerization of n-pentane and n-hexane [1–7]; these processes were successfully commercialized in the last century. Unfortunately, the hydroisomerization of heavier hydrocarbons like n-heptane has not yet been commercialized [8–11]. The skeletal isomerization of n-heptane to isoheptane is rather difficult to be controlled and the cracking reactions through β-scission of C_7-carbenium ion intermediates on acidic sites, leading to low selectivity for di- and tri-branched isomers [12]. The cracking ability is more significantly exhibited for the hydrocarbons having long carbon chain, for example, reaction conditions that may selectively isomerize n-C_6 over zeolite catalysts would almost exclusively produce cracking products for n-C_8 [13]. This is one of the reasons why industrial isomerization is limited to C_4 and C_5/C_6 feedstock up to date. Investigation of heavier n-alkanes (including n-heptane) isomerization for the production of more amounts of reformate gasoline fuel is therefore very important and challenging.

It is well known that the hydroisomerization of C_5/C_6 is usually carried out on a bifunctional catalyst, consisting of a protonating acid and a metal function. According to the traditional mechanism, the noble metal catalyzes hydrogen transfer reactions (hydrogenation/dehydrogenation), while the isomerization and cracking of the hydrocarbon skeletons are performed on Brönsted acid sites. For a satisfactory catalyst, the metal and the acid functions must be well balanced. It was reported that the current industrial catalysts for C_5/C_6 isomerization like Pt/mordenite was not an ideal catalyst for n-heptane isomerization, because of strong diffusion limitations to di- and tri-branched isoheptane products due to the small dimension of 12 membered-ring pores in mordenite, around 0.65 nm in diameter, which results in significant cracking reactions and thus lowering the isomerization selectivity [14]. Chica and Corma studied the hydroisomerization of n-heptane by using 11 different zeolites-containing catalysts including USY, BETA, SAPO-5 and

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mordenite, etc. as support, and they claimed that none of these zeolites is adequate for producing a high-octane C_7 isomerate, because the i-C_7 products were predominantly composed of monomethyl compounds with very small amount of dimethylpentane and no trimethylbutane were formed [15].

Some authors concluded that the transport properties of the reactants in the catalysts channels are the most important parameter controlling the final catalyst selectivity [16]. In this decade, researchers and industrialists paid more attention to isomerization of n-heptane and novel solid acid catalysts with large pore diameter including mesoporous molecular sieves in order to develop new generation catalysts for the isomerization of heavier hydrocarbons [17,18]. The isomerization of heavier hydrocarbons currently encounters a technical neck-bottle in obtaining high molar ratio of multibranched to monobranched isomers in the products.

In a previous work, our group reported a tungstophosphoric acid promoted mesoporous Pt/Zr-MCM-41 catalysts showing high catalytic activity for n-heptane isomerization with unique selectivity to multibranched isoheptanes [19]. The molar ratio of multibranched to monobranched isoheptanes in the isomer products varies within a very narrow range between 0.8 and 1.2, which is several times greater than that reported in the literature at similar reaction conditions using zeolites supported catalysts. It may be regarded as an important advancement in the isomerization of heavier hydrocarbons. In the preparation of these catalysts, tetraethylorthosilicate (TEOS) was used as Si precursor. In order to reduce the synthetic cost, we tried to use cheap chemical, fumed silica, as Si precursor to replace TEOS, a series of Zr-modified MCM-41 mesoporous solids were also obtained. The cost of catalyst using fumed silica was reduced to half of that using TEOS. The results of synthesis and structural characterization of Zr-modified MCM-41 materials using fumed silica as Si source and the Pt loaded catalysts were reported [20].

The present work follows the first part published in Refs. [19,20]. The catalytic behaviours of a series of 1 wt.%Pt/25 wt.% $H_3PW_{12}O_{40}$/Zr-MCM-41-n catalysts prepared using fumed silica as Si precursor for the hydroisomerization of n-heptane under atmospheric condition were studied. The catalytic activity and selectivity of these catalysts were comparatively examined in order to correlate the catalyst properties with the surface acidity, metal dispersion and pore geometry. The product distributions were also analyzed in detail to elucidate the possible isomerization mechanisms and the cracking pathways.

2. Experimental

2.1. Synthesis of Zr-MCM-41 and catalysts

The Zr-based mesoporous molecular sieves were prepared by using cationic surfactant cetyltrimethylammonium chloride as synthetic template, zirconium-n-propoxide (70% in propanol) as zirconium precursor and fumed silica as Si source. The detail synthesis information of the support can be seen in the first part of the work [20]. The obtained solids Zr-MC-41-n prepared are sometimes referred to as WSZn (n = Si/Zr = 25, 15, 8 and 4).

The 1 wt.%Pt/25 wt.%$H_3PW_{12}O_{40}$/WSZn catalysts were prepared by a two-step impregnation method. Firstly, the Zr-MCM-41 samples were impregnated with 20 ml of a methanol solution containing a given amount of $H_3PW_{12}O_{40}$ (designated as HPW hereafter). The solvent was entirely removed at 40 °C in a vacuum evaporator and the 25 wt.%HPW/Zr-MCM-41 solids were then impregnated with 20 ml of a water solution containing H_2PtCl_6. A 1 wt.% Pt dried sample was obtained after the solvent was evaporated at 80 °C in an evaporator under vacuum condition. It was noted that the *Kiggen* structure of the pure or dispersed heteropolyacid $H_3PW_{12}O_{40}$ would be decomposed at around 600 °C [21,22]. To avoid any possible decomposition or structural degradation, the 1 wt.%Pt/25 wt.%$H_3PW_{12}O_{40}$/Zr-MCM-41-n catalysts were set to calcination at 300 °C in air for 2 h. The 1 wt.%Pt/25 wt.%$H_3PW_{12}O_{40}$/Zr-MCM-41-n catalysts were designated as Pt/HPW/WSZn.

2.2. Hydrogen chemisorption isotherms

The metal dispersion of the Pt/HPW/WSZn catalysts was measured in a TPD/TPR 2900 analyzer (Micromeritics). 0.2 g of solid sample was placed in a U-type quartz tube and was thermally treated at 300 °C for 1 h under a 99.9% He stream at a rate of 40 ml/min to purge off the adsorbed species. The sample was reduced with hydrogen at that temperature for 2 h. Once again, 99.9% He current was introduced to remove any adsorbed molecular hydrogen on the sample during the reduction. Afterwards, the temperature of the sample was cooled down to 25 °C under the He stream, followed by introduction of a mixture of 10% H_2–90% Ar for hydrogen adsorption. The volume of adsorbed hydrogen was measured to calculate the Pt metal dispersion and particle size by suggesting that a hydrogen atom was chemisorbed by one Pt metal atom under the experimental condition.

2.3. Measurement of N_2 adsorption–desorption isotherms

The specific surface area, pore volume and pore size distribution of the samples were measured with a Digisorb 2600 equipment by low temperature N_2 adsorption–desorption isotherms. Before the measurement, the sample was evacuated at 350 °C. The surface area was computed from these isotherms by using the multi-point Brunauer–Emmett–Teller (BET) method based on the adsorption data in the partial pressure P/P_0 range from 0.01 to 0.2. The value of 0.1620 nm^2 was taken for the cross-section of the physically adsorbed N_2 molecule. The mesopore volume was determined from the N_2 adsorbed at a $P/P_0 = 0.4$. The pore diameter and pore volume were determined by using the (BJH) method. In all cases, correlation coefficients above 0.99 were obtained.

2.4. Surface acidity measurement

To evaluate and analyze the strength and type of the acid sites, pyridine adsorption on the samples was performed on a 170-SX Fourier-transform infrared (FTIR) spectrometer in the temperature range between 25 and 400 °C. Before pyridine adsorption, the samples were heated to 400 °C in a vacuum, and then cooled to room temperature. Afterwards, the solid wafer was exposed to pyridine, by breaking, inside the spectrometer cell, a capillary-containing 50 μl of liquid pyridine. The IR spectra were recorded at various conditions by increasing the cell temperature from 25 to 400 °C. The number of Brönsted and Lewis acid sites was calculated according to the integral area of the bands at 1540 and 1450 cm^{-1}, respectively.

2.5. Catalytic evaluation for n-heptane hydroisomerizaton

The catalytic reactions for n-heptane isomerization were carried out in a down-flow fixed-bed U-shape reactor (i.d. = 1 cm, 20 cm in length) in the presence of hydrogen at atmospheric conditions. 0.2 g catalyst was loaded and the H_2/n-heptane molar ratio was 12. The liquid n-heptane was placed in a glass saturator with a water bath to control the temperature. Hydrogen (99.9%) passed through it at a flow rate of 40 ml/min and brought the n-heptane feed into the reactor with a partial pressure of 0.077 atm. The reaction temperature was varied from 200 to 320 °C with a programmed temperature