= CATALYSIS =

Pd/SAPO-41 Bifunctional Catalysts with Enhanced Pd Dispersion Prepared by Ultrasonic-Assisted Impregnation: High Selectivity for *n*-Hexadecane Hydroisomerization

Guozhi Jia^{*a*}, A. L. Maximov^{*b*}, Wei Wang^{*a*,*}, Xuefeng Bai^{*a*}, Xiaomeng Wei^{*a*}, Xiaofang Su^{*a*}, Tong Li^{*a*}, Chunmu Guo^{*a*}, and Wei Wu^{*a*,**}

 ^a National Center for International Research on Catalytic Technology, Key Laboratory of Functional Inorganic Material Chemistry (Ministry of Education), School of Chemistry and Material Sciences, Heilongjiang University, Harbin, Heilongjiang, 150080 China
^b Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia
*e-mail: wangw@hlju.edu.cn
*e-mail: wuwei@hlju.edu.cn

Received March 24, 2020; revised March 25, 2020; accepted March 25, 2020

Abstract—The preparation of bifunctional catalysts with high catalytic selectivity for the *n*-alkanes hydroisomerization still remains challenging for the production of bio-diesel. Herein, two series of Pd/SAPO-41 bifunctional catalysts are prepared by the ultrasonic-assisted impregnation (xPd/S41-U) with different treating time and conventional incipient wetness impregnation methods (0.30Pd/S41-I) on the SAPO-41 molecular sieve, respectively. The physico-chemical property of the synthesized SAPO-41 and prepared catalysts were studied by XRD, SEM, ICP, N₂ physical adsorption, H₂ chemisorption and Py-IR measurements. The catalytic performance for the *n*-hexadecane hydroisomerization over all catalysts is also studied. The characteristic results indicate that the xPd/S41-U catalysts show stronger Brønsted acidity compared with the 0.30Pd/S41-I catalyst. In addition, the Pd dispersion of the xPd/S41-U catalysts is almost two times higher than that of the 0.30Pd/S41-I catalyst, which leads more Pd cluster to enter into the micropores of the SAPO-41 molecular sieve. Furthermore, the 0.30Pd/S41-U catalyst with 0.30 wt % Pd loading shows promoted catalytic performance than that of the 0.30Pd/S41-I catalyst with the same Pd loading because of the stronger metal function and more favourable metal-acid balance caused by the larger C_{Pd}/C_{H+} ratio. Therefore, the ultrasonic-assisted impregnation prepared Pd/SAPO-41 catalysts are potential to be widely employed for the *n*-alkane hydroisomerization. Keywords: ultrasonic-assisted impregnation, Pd site, SAPO-41 molecular sieve, n-hexadecane hydroisomerization, bifunctional catalysts

DOI: 10.1134/S1070427220040047

INTRODUCTION

In recent years, the employment of clean renewable fuel has captured considerable attentions due to the increasing energy crisis and severe environmental problems [1, 2]. To achieve this purpose, the hydroisomerization of long chain *n*-alkane is an effective way to improve the quality of the second-generation bio-diesel, which is produced by the hydrodeoxygenation of bio-oil followed by the hydroisomerization of deoxygenated bio-oil [3–5]. In contrast to the traditional diesel with high contents of sulfur, nitrogen, alkenes, aromatic hydrocarbons and other impurities, the main composition of the secondgeneration bio-diesel is isomer alkanes. As a result, the serious air pollution caused by more generated PM2.5 from incomplete combustion of traditional diesel will be significantly suppressed [6, 7]. In addition, compared with the first-generation biodiesel, the second-generation bio-diesel shows more excellent blending property, promoted low-temperature fluidity and higher energy density [8, 9]. Furthermore, the second-generation biodiesel is directly obtained from renewable biomass like vegetable oil, animal oil and waste oil, which means the raw sources are plenty and renewable [10]. Therefore, it is necessary to develop the catalysts for hydroisomerization of long chain *n*-alkanes to improve the production of clean renewable bio-diesel.

To date, the bifunctional catalyst is the most widely used catalyst in the *n*-alkane hydroisomerization, which is composed of metal sites with (de)hydrogenation function and Brønsted acid sites with isomerization and cracking function [11]. During the hydroisomerization, the *n*-alkanes are firstly dehydrogenated to alkene intermediates on the metal sites. Then, the alkene intermediates are protonated, isomerized and deprotonated on the Brønsted acid sites. Finally, the formed isomerized alkene intermediates are hydrogenated to form iso-alkane products on the metal sites. It is worth noting that if the balance between the functions of two active sites is not ideal, the alkene intermediates would easily undergo further cracking, which would suppress the yield of desirable iso-alkane products [12, 13]. Generally, the Brønsted acid sites are provided by the molecular sieves. According to the reported works, the molecular sieves with one-dimensional micropore system are appropriate for the preparation of highly selective bifunctional catalysts, including ZSM-22, ZSM-23, SAPO-31 and SAPO-41 [14,15]. However, due to the higher Brønsted acidity, the selectivity to iso-alkane over zeolite-based catalysts is usually lower compared with SAPO-based catalysts because of the stronger cracking of iso-alkanes on the Brønsted acid sites [16, 17]. Based on the comparison of catalytic performance for the *n*-octane hydroisomerization over Zeolite and SAPO based bifunctional catalysts, Nghiem et al. found that the isooctane selectivity over Pt/SAPO-n catalysts were much higher than that over Pt/ZSM-n catalysts when the reaction temperature was 250°C [18]. Additionally, SAPO-41 has been proven to show ideal catalytic behaviours among all SAPO-n molecular sieves since the large pose size $(0.43 \times 0.73 \text{ nm})$ of SAPO-41 is beneficial for the formation and diffusion of desired iso-alkanes [19].

In addition to the Brønsted acid sites, the modification of characteristics of metal sites is also very important for the enhancement of the catalytic performance. Because of the better catalytic stability and stronger hydrogenation function, noble metals (Pt and Pd) are usually employed as metal sites for bifunctional catalysts instead of non-noble metals (Ni) [20]. However, in order to keep the favourable metal-acid balance and high *iso*alkanes selectivity, the loading of noble metals are generally above 0.5 wt % [21]. This phenomenon leads to a high cost of the bifunctional catalysts and limits their further applications for the industrial production. Therefore, many strategies have been developed to promote the metal dispersion on the surface of molecular sieves and reduce the loading of noble metals, like depositing noble metal nanoparticle into the molecular sieves [22] or employing ion-exchange method [23]. But it is notably that the preparation of bifunctional catalysts through these methods may be complicated and expensive due to the hard encapsulation of noble metal nanoparticles and the waste of noble metal precursors. Accordingly, it is still essential to find simple methods for the preparation of bifunctional catalysts with high selectivity and low metal loading.

Over past years, the ultrasonic-assisted treatment is considered to be an effective method to reduce the metal loading of bifunctional catalysts owing to its low cost and simple measurement [24, 25]. During the ultrasonic treatment, the formation, growth and collapse of bubbles can lead to high temperature and pressure to accelerate the chemical reaction [26]. However, with the assistance of ultrasonic treatment, the strong reductant, the protective agents, the severe reaction conditions and long reaction time are still necessary to achieve highly dispersed noble metal catalysts [27]. Furthermore, the reported works about the preparation of bifunctional catalysts for *n*-alkane hydroisomerization by ultrasonicassisted treatment are very few. Therefore, the combination of the ultrasonic-assisted impregnation and hydrogenation reduction may be a simple and potential route to improve the metal dispersion, so that the metal loading of bifunctional catalysts can be evidently lowered.

In this study, two series of Pd/SAPO-41 bifunctional catalysts were prepared by ultrasonic-assisted impregnation and conventional incipient wetness impregnation methods, respectively. The effects of preparation methods on metal-acid balance and the *n*-hexadecane hydroisomerization over all catalysts were studied thoroughly.

EXPERIMENTAL

The Synthesis of SAPO-41 Molecular Sieve and Preparation of Pd/SAPO-41 Bifunctional Catalysts

For the synthesis of the SAPO-41 molecular sieve, the di-*n*-butylamine (DBA) (95.0%, Aldrich),

orthophosphoric acid (85.0%, Tianjin Guangfu, China), pseudoboehmite (74.1 wt % Al_2O_3 , Catapal B, Sasol) and silica sol (25.9 wt % SiO₂, Qingdao Yumin, China) were used as template, P, Al and Si sources, respectively. Pd(NO₃)₂ solution (5 wt %, Shanxi Kaida, China) was used as metal precursor solution to prepare Pd/SAPO-41 bifunctional catalysts.

The SAPO-41 molecular sieve was synthesized according to our previously works, while the composition of initial gel was of Al_2O_3 : SiO_2 : DBA : P_2O_5 : $H_2O =$ 1.0 : 0.6 : 3.0 : 1.0 : 55.0 [28]. The obtained sample was denoted as S41. For the Pd/SAPO-41 bifunctional catalysts prepared by ultrasonic-assisted impregnation method, 2 g SAPO-41 was impregnated of 50 mL $Pd(NO_3)_2$ solution (0.01 mol/L) with an ultrasonic bath at a frequency of 25 kHz and an input power of 300 W for 40, 80 and 120 min, respectively. Then, the obtained samples were washed by deionized water, dried overnight at 110°C, followed by the calcination in air at 600°C for 4 h and reduction at 400°C for 1 h with 40 mL/min hydrogen in a fixed-bed reactor. The prepared catalysts were denoted as xPd/S41-U, in which the x was the Pd loading (wt %) of the catalyst with different treating time. For comparison, the preparation of Pd/SAPO-41 bifunctional catalyst by the conventional incipient wetness impregnation method was carried out as follows: the 2 g SAPO-41 molecular sieve was impregnated with 0.12 g $Pd(NO_3)_2$ solution (0.01 mol/L) and 1.87 g deionized water to maintain the Pd loading was 0.30 wt % and the following steps were the same as those of xPd/S41-U catalysts. The prepared conventional Pd/SAPO-41 bifunctional catalyst was denoted as 0.30Pd/S41-I.

Characterization of SAPO-41 Molecular Sieve and Pd/S41 Bifunctional Catalysts

The Powder X-ray diffraction (XRD) patterns of the synthesized SAPO-41 molecular sieve was measured using a Bruker D8 Advance X-ray diffractometer with the standard CuK_{α} ($\lambda = 1.5406$ Å, 40 kV, 40 mA) over the range of angles 5–55°. The crystal phase and diffraction peaks of the SAPO-41 were identified by the JCPDS database. The scanning electronic microscopy (SEM) images of SAPO-41 molecular sieves were obtained on S-4800 (Hitachi, Japan) at 30 kV. The metal loading of

xPd/S41-U catalysts were also detected by inductively plasma optical coupled emission spectrometry (ICP-OES, PerkinElmer, Optima 5300DV). The N₂ adsorption-desorption measurements of SAPO-41 and all catalysts were performed on an Autosorb-iQ₂ instruments (Quantachrome). Prior to the tests, all samples need to be degassed at 350°C in a vacuum of 1.0×10^{-3} Pa for 12 h. After that, the characterization was carried out at liquid nitrogen temperature $(-196^{\circ}C)$. The specific surface areas and pore volumes of samples were determined using the method of Brunauer-Emmett–Teller (BET) and the *t*-plot, respectively. The metal dispersion of all catalysts was characterized by using a Micromeritics AutoChem II 2920 chemisorption analyser instrument. During the process, approximately 200 mg samples were loaded into a tube and pretreated under hydrogen at 400°C for 1 h. Then, the sample was treated under argon at 450°C for 2 h, cooled to room temperature and then adsorbed by a 10% H₂-Ar mixture until saturation. The pyridine-adsorbed IR (Py-IR) of the samples was measured on a Perkin Elmer Spectrum Frontier transform infrared spectrometer (PE-100). At first, all samples (diameter: 10mm, weight: about 20 mg) were dehydrated at 350°C for 2 h under vacuum (1.33 \times 10⁻³ Pa), followed by the pure pyridine was adsorbed at 90°C for 0.5 h. The pyridine was desorbed at 150°C, 250°C, 350°C orderly after that. The Brønsted acid sites was calculated based on area of the band centered at ~1540 cm⁻¹ [29].

Catalytic Performance Tests

The hydroisomerization of *n*-hexadecane was carried out in a fixed-bed reactor with 1.0 g catalyst (20–40 mesh) over all catalysts. Before the test, the catalyst was placed into the reaction tube and treated under a flow of H₂ at 400°C for 1 h. Furthermore, the tests were conducted at weight hourly space velocity (WHSV) of 3.70 h⁻¹, H₂ pressure of 2.0 MPa, H₂/*n*-hexadecane molar ratio of 8.72 and reaction temperature at the range of 280–370°C. The reaction products were analyzed by using the Agilent 6820 gas chromatograph, which was equipped with a flame ionization detector (FID) and a HP-1 capillary column (60 m × 0.25 mm × 1.00 µm). The conversion of *n*-hexadecane (%) and the yield of *iso*-hexadecane (%) are calculated by the following formula:

Conversion of *n*-hexadecane = $\frac{\text{the amount of } n\text{-hexadecane consumed}}{\text{the amount of } n\text{-hexadecane in feed}} \times 100\%$,

Selectivity to *iso*-hexadecane = $\frac{\text{the amount of$ *iso* $-hexadecane formed}}{\text{amount of$ *n* $-hexadecane consumed}} \times 100\%$

Yield of *iso*-hexadecane = $\frac{\text{the amount of$ *iso* $-hexadecane formed}}{\text{the amount of$ *n* $-hexadecane in feed}} \times 100\%$,

RESULTS AND DISCUSSION

Characteristics of SAPO-41 Molecular Sieve and All Pd/SAPO-41 Bifunctional Catalysts

Figure 1a shows the XRD pattern of the SAPO-41 molecular sieve synthesized by using DBA as template. It can be found that the sharp characteristic diffraction peaks existing at 6.8°, 9.7°, 13.7°, 18.3°, 16.3° and 20.5-25.7°, which are ascribed to the AFO topology of SAPO-41. The strong intensity of these peaks suggests that the synthesized SAPO-41 molecular sieve is highly crystalline. Simultaneously, no additional peaks are observed, indicating that the synthesized SAPO-41 molecular sieve is free from impure phase. The SEM image of SAPO-41 in Fig. 1b presents the typical morphology of the AFO topology, which are columnarshaped aggregates with 2.5 µm of diameter and 5.0 µm of length [28]. Moreover, the SEM image confirms the absence of amorphous species and demonstrates the high crystallinity of the synthesized SAPO-41, which is consistent with the results of XRD pattern.

The Pd loading of xPd/S41-U catalysts is investigated by ICP measurement and the results are shown in Table 1. The ICP results reveal that as the time of the ultrasonicassisted impregnation increases from 40 to 80 min, the Pd loading of xPd/S41-U changes from 0.10 wt % to 0.27 wt %. But when the treating time becomes 120 min, the Pd loading of 0.30Pd/S41-U catalyst is 0.30 wt %, which increases slightly compared with the 0.27Pd/S41-U catalyst. This phenomenon suggests that the growth of Pd deposition amount is not linear as the treating time changes longer. The textural properties of the SAPO-41 molecular sieve and all Pd/SAPO-41 bifunctional catalysts are determined by N₂ physical adsorption measurements. The N2 adsorption-desorption isotherms of all samples are shown in Fig. 2 and the calculated textural properties are listed in Table 1. The isotherm of SAPO-41 exhibits a sharp increase at the relative pressure (P/P_0) of 10-6. In addition, a hysteresis loop is found at high P/P_0 for all samples, which are assigned to the intergranular mesopores formed by the crystal aggregation. For all Pd/SAPO-41 catalysts, the isotherms are similar to that of the SAPO-41 but the textural properties change evidently. Compared with the SAPO-41 molecular sieve, the micropore surface area (S_{micro}) and the micropore volumes (V_{micro}) of the xPd/S41-U catalysts are both lower due to the partial micropores blockages of SAPO-41 molecular sieve after the deposition of Pd nanoparticles [30]. In addition, as the Pd loading of xPd/S41-U catalysts increases, the S_{micro} and V_{micro} both decrease continuously, indicating more micropore blockages because of the higher Pd deposition amount. Furthermore, it is notably that



Fig. 1. (a) XRD pattern and (b) SEM image of the SAPO-41 molecular sieve.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 93 No. 4 2020

GUOZHI JIA et al.

Samples		Su	rface area, m	² /g	Pore volume, cm ³ /g			
	Pa loading", wt %	$S_{\rm BET}{}^{\rm b}$	S _{micro} ^c	S _{ext}	$V_{\rm total}{}^{\rm d}$	V _{micro}	V _{meso} e	
S41	_	251	228	23	0.132	0.081	0.051	
0.10Pd/S41-U	0.10	219	190	29	0.147	0.073	0.074	
0.27Pd/S41-U	0.27	204	165	39	0.161	0.065	0.096	
0.30Pd/S41-U	0.30	199	158	41	0.156	0.062	0.094	
0.30Pd/S41-I	0.30	194	164	30	0.097	0.065	0.032	

Table 1. The ICP results and textural properties of the SAPO-41 molecular sieve and all Pd/SAPO-41 catalysts

^a Determined by ICP; ^b determined by BET method; ^c determined by *t*-plot method; ^d determined at $P/P_0 = 0.995$; ^c $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

Table 2. The Py-IR and H₂ chemisorption results of the SAPO-41 molecular sieve and all Pd/SAPO-41 catalysts

Sampla		Brønsted ac	idity ^a , μmol/g	D b %	C _{Pd} ^c ,	C /C d	
Sample	total weak medium strong		strong	$D_{\rm Pd}^{\circ}, 70$	µmol/g	$C_{Pd'}C_{H^{+-}}$	
S41	89.4	9.9	23.3	56.2	_	_	_
0.10Pd/S41-U	45.3	7.0	9.2	29.1	51.2	4.8	0.11
0.27Pd/S41-U	41.0	5.2	8.1	27.7	53.5	13.6	0.33
0.30Pd/S41-U	39.9	9.3	10.5	20.1	61.1	17.2	0.43
0.30Pd/S41-I	43.2	7.5	10.8	24.9	27.3	7.7	0.18

^a Determined by Py-IR method. ^b Calculated by H_2 chemisorption method. ^c Calculated from the loading and dispersion of Pd. ^d The amount ratio of exposed Pd atoms (C_{Pd}) to total Brønsted acid density

the 0.30Pd/S41-U catalyst reveals smaller micropore surface and pore volume than those of 0.30Pd/S41-I catalyst with the same Pd loading. This result may be originated from the entrance of more Pd cluster into the microporous channels caused by the increase of



Fig. 2. N_2 adsorption-desorption isotherms of the SAPO-41 molecular sieve and all Pd/SAPO-41 catalysts.

Pd dispersion, which is further confirmed by the H_2 chemisorption measurement.

In order to investigate the Pd dispersion of all Pd/ SAPO-41 catalysts, the H₂ chemisorption measurement is carried out and the results are listed in Table 2. It can be found that the Pd dispersion of xPd/S41-U catalysts is significantly higher compared with the 0.30Pd/S41-I catalyst. Especially for the 0.30Pd/S41-U catalyst, the 61.1% of the Pd dispersion is two times higher than that of the 0.30Pd/S41-I catalyst (27.3%). This result demonstrates that the ultrasonic-assisted impregnation method is very effective to increase the Pd dispersion of the bifunctional catalysts. This is because the high temperature and pressure generated by the ultrasonic treatment can evidently improve the diffusion of Pd²⁺ ions, which is beneficial for the entrance of more Pd²⁺ ions into the microporous channels or highly disperse outside of the SAPO-41 molecular sieve [27]. Based on the Pd dispersion, the exposed Pd atoms (C_{Pd} value) are calculated and the results are listed in Table 2. Among all catalysts, the 0.10Pd/S41-U catalyst reveals the smallest C_{Pd} value because of the lowest Pd loading. Moreover, the C_{Pd} values of the 0.27Pd/S41-U and 0.30Pd/S41-U



Fig. 3. Py-IR spectra of all Pd/SAPO-41 catalysts at (a) 150°C, (b) 250°C and (c) 350°C.

catalysts are both larger compared with 0.30Pd/S41-I catalyst due to the higher Pd dispersion, suggesting that more accessible Pd active sites are formed on these two catalysts.

Beyond the characteristics of Pd sites, the Brønsted acid density is also very important for the improvement of the catalytic performances over the bifunctional catalysts. To study the Brønsted acidity with different strength, the Py-IR measurements are conducted for the SAOP-41 molecular sieve and all catalysts, and the results are shown in Fig. 3 and Table 2. In the Py-IR spectra of all samples, the band located at ~1543 and \sim 1445 cm⁻¹ are assigned to the adsorption of pyridine on the Brønsted and Lewis acid sites respectively, while the band at ~1490 cm⁻¹ is assigned to the adsorption on two acid sites. Accordingly, the ~1543 cm⁻¹ band area of Py-IR spectrum recorded at 150 and 350°C are attributed the total and strong Brønsted acid density, respectively. Then, the weak and medium Brønsted acid density can also be calculated based on the area

difference of Py-IR spectra recorded at different temperature. From Table 2, the total Brønsted acid density of all Pd/SAPO-41 catalysts is lower compared with the SAPO-41 molecular sieve owing to the deposition of Pd nanoparticles. Simultaneously, the total Brønsted acid density of the xPd/S41-U catalysts decrease gradually as the Pd loading increases, which may be originated from the larger coverage of Brønsted acid sites located outside of the SAPO-41 molecular sieve and more micropore blockages caused by the entrance of highly dispersed Pd cluster[11]. In addition, compared with the 0.30Pd/S41-I catalyst, although the total Brønsted acid density of the 0.30Pd/S41-U catalyst is lower due to the higher Pd dispersion, the adsorption band of pyridine on Brønsted acid sites of the 0.30Pd/ S41-U catalyst (1544-1546 cm⁻¹) is higher. This phenomenon indicates that the Brønsted acid strength of 0.30Pd/S41-U catalyst is greater. Furthermore, by combining the results of H₂ chemisorption and Py-IR spectra, the ratio of exposed Pd atoms to total Brønsted

Items	0.10Pd/S41-U	0.27Pd/S41-U	0.30Pd/S41-U	0.30Pd/S41-I
<i>n</i> -Hexadecane conversion, %	88.4	89.7	90.0	91.5
iso-Hexadecane selectivity, %	65.5	80.1	95.8	91.7
iso-Hexadecane yield, %	57.9	71.8	86.2	83.9
Mono-branched iso-hexadecane distribution, %				
2-MeC ₁₅	7.6	7.8	9.9	7.6
3-MeC ₁₅	8.6	8.8	12.2	9.0
4-MeC ₁₅	8.3	8.5	12.0	8.8
5-MeC ₁₅	8.1	8.5	12.6	9.2
6-MeC ₁₅	7.5	7.8	10.5	9.0
7,8-MeC ₁₅	15.6	16.0	6.0	15.6
Total MeC ₁₅	55.7	57.4	63.2	59.2
Total multi-branched iso-hexadecane distribution, $\%$	44.3	42.6	36.8	40.8
I/C ratios	1.9	4.0	22.8	11.0

Table 3. The catalytic test results over all Pd/SAPO-41 catalysts at about 90% of *n*-hexadecane conversion

acid density (C_{Pd}/C_{H+}) is calculated, which is commonly employed to characterize the balance between metal function and acid function of the prepared bifunctional catalysts [31]. As shown in Table 2, the C_{Pd}/C_{H+} ratio of the 0.30Pd/S41-U (0.43) catalysts are 2.4 times of the 0.30Pd/S41-I catalyst (0.18), suggesting that the 0.30Pd/ S41-U catalysts prepared via the ultrasonic-assisted impregnation method reveals a stronger metal function.

Catalytic Behaviours over All Pd/SAPO-41 Bifunctional Catalysts for the n-Hexadecane Hydroisomerization

It is well known that the Brønsted acidity, metal function and metal-acid balance have direct influences on the catalytic behaviours of *n*-alkane hydroisomerization over bifunctional catalysts. Therefore, to further investigate the positive effects of ultrasonic-assisted impregnation method on the catalytic performances of prepared *x*Pd/S41-U catalysts compared with the 0.30Pd/S41-I catalyst prepared by the conventional incipient wetness impregnation method, the *n*-hexadecane hydroisomerization is tested over all Pd/SAPO-41 catalysts.

The catalytic performances for the *n*-hexadecane hydroisomerization over xPd/S41-U catalysts are presented in Fig. 4 and Table 3. From Fig. 4a, it can be found that the *n*-hexadecane conversion over all catalysts increases as the reaction temperature changes from 280 to 370°C. At the same reaction temperature, the conversion of *n*-hexadecane over all catalysts decreases

in the order of 0.30 Pd/S41-U > 0.27 Pd/S41-U > 0.10 Pd/S41-U, which is consistent with the order of C_{Pd}/C_{H^+} ratios. This result indicates that the metal-acid balance may demonstrate stronger influences to the conversion of *n*-hexadecane compared with the total Brønsted acid density when the metal density is low and the (de)hydrogenation is a speed control step. In addition, as shown in Figs. 4b, 4c, the order of the iso-hexadecane selectivity and yield over all catalysts at *n*-hexadecane conversion of about 90% is the same as that of the n-hexadecane conversion. Especially for the 0.30Pd/S41-U catalyst, the *iso*-hexadecane selectivity is 95.8% at the *n*-hexadecane conversion of 90.0%, which is relatively high among reported catalysts with much higher noble metal loading (listed in Tables 3 and 4). This result suggests that the larger C_{Pd}/C_{H^+} ratio is also beneficial for the improvement of metal-acid balance and the promotion of *iso*-hexadecane yield. During the hydroisomerization process (illustrated in Fig. 4d), the n-alkane molecular is firstly dehydrogenated on the Pd sites to become the nalkene intermediates. Then, the *n*-alkene intermediates transformed to the iso-alkene intermediates on the Brønsted acid sites followed by the hydrogenation on the Pd sites to form the desired *iso*-alkane products. Therefore, in order to achieve the ideal catalytic performance, the metal function of bifunctional catalysts should exceed the Brønsted acid function. This is because an insufficient amount or a weak hydrogenation function of metal sites can lead to stronger cracking reactions of isomers on the Brønsted acid sites [32]. For the 0.10Pd/S41-U



Fig. 4. The catalytic performance of *n*-hexadecane hydroisomerization over xPd/S41-U catalysts. (a) The *n*-hexadecane conversion versus the reaction temperature; (b) the *iso*-hexadecane selectivity versus the *n*-hexadecane conversion; (c) the *iso*-hexadecane yield versus the *n*-hexadecane conversion and (d) the illustration of *n*-hexadecane hydroisomerization over xPd/S41-U bifunctional catalysts.

catalyst with the smallest C_{Pd}/C_{H+} ratio, the metal function is too weak to keep the favourable balance with the Brønsted acid function, so that the isomer alkene intermediates interact with more Brønsted acid sites to undergo further cracking before the hydrogenation on the Pd metal sites. As a result, the yield of *iso*-hexadecane over the 0.10Pd/S41-U catalyst (57.9%) is the lowest among all catalysts. On the contrary, for the 0.30Pd/ S41-U catalyst with the highest C_{Pd}/C_{H+} ratio, the isomer alkene intermediates are faster hydrogenated to become *iso*-hexadecanes on Pd sites instead of further cracking owing to the more favourable metal-acid bal-

Table 4	.Т	he rel	levant	: work	done	for t	the per	formance of	f <i>n</i> -alkanes	hy	droi	somerization	over	bifun	ctional	catal	ysts.

Catalyst	n-Alkanes	Reaction temperature, °C	<i>n</i> -Alkanes conversion, %	<i>iso</i> -Alkanes selectivity, %	Reference
0.3Pd/SAPO-11	<i>n</i> -C ₁₀	360	90.8	89.8	[15]
0.8Pd/SAPO-41	<i>n</i> -C ₁₆	340	94.0	94.6	[18]
0.5Pt/SAPO-11	<i>n</i> -C ₁₂	340	93.5	75.8	[33]
0.5Pd/SAPO-11	<i>n</i> -C ₁₀	350	85.8	89.4	[34]
0.5Pd/SAPO-31	<i>n</i> -C ₁₀	380	80.0	90.6	[35]
1.0Pt/SAPO-11	<i>n</i> -C ₁₂	300	92.1	83.2	[36]
0.30Pd/S41-U	<i>n</i> -C ₁₆	320	90.0	95.8	This work

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 93 No. 4 2020

ance, which leads to the highest iso-hexadecane yield among all catalysts. This conclusion is also proved by the the distribution of mono- and multi-branched isohexadecane products over all Pd/SAPO-41 catalysts. As listed in the Table 3, the distribution of mono-branched iso-hexadecane products over 0.30Pd/S41-U catalyst is the highest among all catalysts, while the ratio of isohexadecane products to cracking products (I/C ratios) is the lowest. This result indicates that the further isomerization and cracking of alkene intermediates over the 0.30Pd/S41-U catalyst is suppressed due to the highest C_{Pd}/C_{H^+} ratio and strongest metal function. Additionally, the comparison of the catalytic performances over 0.30Pd/S41-U and 0.30Pd/S41-I catalysts is also shown in Table 3. It can be found that the *n*-hexadecane conversion, the maximum iso-hexadecane yield, the monobranched iso-hexadecane distribution and the I/C ratio of the 0.30Pd/S41-U catalyst are all higher than those of the 0.30Pd/S41-I catalyst. This result confirms that the higher C_{Pd}/C_{H+} ratio of the 0.30Pd/S41-U catalyst leads to the promoted catalytic performance compared with the catalysts prepared by the conventional incipient wetness impregnation method.

CONCLUSIONS

In this work, the ultrasonic-assisted impregnation method is employed to prepare a series of xPd/S41-U catalysts with high Pd dispersion. By simply changing the treating time from 40 to 120 min, the Pd loading on the SAPO-41 molecular sieve increases from 0.10 wt % to 0.30 wt %. Compared with the 0.30Pd/S41-I catalyst prepared by the conventional incipient wetness impregnation method, the 0.30Pd/S41-U catalyst with the same Pd loading demonstrates evidently higher Pd dispersion and C_{Me}/C_{H+} ratio. In addition, the catalytic performance over the 0.30Pd/S41-U catalyst is excellent due to the enhanced metal function and more favourable metal-acid balance. Therefore, the ultrasonic-assisted impregnation method is a simple and effective method to prepare highly selective bifunctional catalysts with low noble metal loading for the *n*-alkane hydroisomerization and other (de)hydrogenation reaction in petroleum refining and petrochemical industrial production.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (No.21676074, No.21706053), Intergovernmental International Science and Technology Innovation Cooperation Key Project (2018YFE0108800), National Ministry of Education "Silk Road 1+1" Research Cooperation Project, the Transformation for Science and Technology Achievements in University of Department of Education of Heilongjiang Province (TSTAU-C2018015) and Heilongjiang University graduate student innovation research project funding (YJSCX2019-175HLJU).

CONFLICT OF INTEREST

Co-author A.L. Maksimov claims to be the editor-in-chief of the Journal of Applied Chemistry; the remaining co-authors have no conflict of interest.

REFERENCES

- Avinash, A. and Murugesan, A., *Fuel*, 2018, vol. 216, pp. 322–329. https://doi.org/10.1016/j.fuel.2017.12.029
- Uvarkina, D.D., Piryutko, L.V., Danilova, I.G., Budukva, S.V., Klimov, O.V., Kharitonov, A.S., and Noskov, A.S., *Russ. J. Appl. Chem.*, 2015, vol. 88, no. 11, pp. 1827–1838. https://doi.org/10.1134/S10704272150110142
- Jeon, Y., Chi, W.S., Hwang, J., Kim, D.H., Kim, J.H., and Shul, Y.G., *Appl Catal B-Environ.*, 2019, vol. 242, pp. 51–59. https://doi.org/10.1016/j.jiec.2019.07.029
- Gaile, A.A., Saifidinov, B.M., Kolesov, V.V., and Koldobskaya, L.L., *Russ. J. Appl. Chem.*, 2010, vol. 83, no. 3, pp. 464–472. https://doi.org/10.1134/S1070427210030171
- Li, P., Sakuragi, K., and Makino, H., *Fuel Process. Technol.*, 2019, vol. 193, pp. 295–303. https://doi.org/10.1016/j.fuproc.2019.05.009
- Liu, X., Deng, B., Fu, J., Xu, Z., Liu, J., Li, M., Li, Q., Ma, Z., and Feng, R., *Chem. Eng. J.*, 2019, vol. 355, pp. 170–180. https://doi.org/10.3390/app9183721
- Pimerzin, A.A., Savinov, A.A., Ishutenko, D.I., Verevkin, S.P., and Pimerzin, A.A., *Russ. J. Appl. Chem.*, 2019, vol. 92, no. 12, pp. 1772–1779. https://doi.org/10.1134/S1070427219120198
- Mantovani, M., Mandelli, D., Gonçalves, M., and Carvalho, W.A., *Chem. Eng. J.*, 2018, vol. 348, pp. 860– 869. https://doi.org/10.1016/j.cej.2018.05.059
- Singh, D., Sharma, D., Soni, S.L., Sharma, S., and Kumari, D., *Fuel*, 2019, vol. 253, pp. 60–71. https://doi.org/10.1016/j.fuel.2019.04.174
- 10. Santamaria, L., Lopez, G., Arregi, A., Amutio, M.,

Artetxe, M., Bilbao, J., and Olazar, M., *Appl. Catal. B-Environ.*, 2019, vol. 242, pp. 109–120. https://doi.org/10.1016/j.apcatb.2018.09.081

- Wang, W., Liu, C., and Wu, W., Catal. Sci. Technol., 2019, vol. 9, pp. 4162–4187. https://doi.org/10.1039/C9CY00499H
- 12. Guisnet, M., *Catal. Today*, 2013, vol. 218, pp. 123–134. https://doi.org/10.1016/j.cattod.2013.04.028
- Pastvova, J., Kaucky, D., Moravkova, J., Rathousky, J., Sklenak, S., Vorokhta, M., Brabec, L., Pilar, R., Jakubec, I., Tabor, E., Klein, P., and Sazama, P., ACS Catal., 2017, vol. 7, no. 9, pp. 5781–5795. https://doi.org/10.1021/acscatal.7b01696
- Smit, B., and Maesen, T.L., *Nature*, 2008, vol. 451, pp. 671–678. https://doi.org/10.1038/nature06552
- Song, X., Bai, X., Wu, W., Kikhtyanin, O.V., Zhao, A., Xiao, L., Su, X., Zhang, J., and Wei, X., *Mol. Catal.*, 2017, vol. 433, pp. 84–90. https://doi.org/10.1016/j.mcat.2016.12.017
- Yue, T., Liu, W., Li, L., Zhao, X., Zhu, K., Zhou, X., and Yang, W., *J. Catal.*, 2018, vol. 364, pp. 308–327. https://doi.org/10.1016/j.jcat.2018.06.003
- Park, K.C., and Ihm, S.K., *Appl. Catal. A-Gen.*, 2000, vol. 203, pp. 201–209. https://doi.org/10.1016/S0926-860X(00)00490-7
- Nghiem, V.T., Sapaly, G., Mériaudeau, P., and Naccache, C., *Top. Catal.*, 2000, vol. 14, pp. 131–138. https://doi.org/10.1023/A:1009071403372
- Mériaudeau, P., Tuan, V.A., Sapaly, G., Nghiem, V.T., and Naccache, C., *Catal. Today*, 1999, vol. 49, pp. 285–292. https://doi.org/10.1016/S0920-5861(98)00435-0
- 20. Kim, M.Y., Lee, K., and Choi, M., J. Catal., 2014, vol. 319, pp. 232–238. https://doi.org/10.1016/j.jcat.2014.09.001
- Parmar, S., Pant, K.K., John, M., Kumar, K., Pai, S.M., and Newalkar, B.L., *J. Mol. Catal. A-Chem.*, 2015, vol. 404, pp. 47–56. https://doi.org/10.1016/j.molcata.2015.04.012
- Liu, Y., Li, Z., Yu, Q., Chen, Y., Chai, Z., Zhao, G., Liu, S., Cheong, W.C., Pan, Y., Zhang, Q., Gu, L., Zheng, L., Wang, Y., Lu, Y., Wang, D., Chen, C., Peng, Q., Liu, Y., Liu, L., Chen, J., and Li, Y., *J. Am. Chem. Soc.*, 2019, vol. 141, pp. 9305–9311. https://doi.org/10.1021/jacs.9b02936

- Samad, J.E., Blanchard, J., Sayag, C., Louis, C., and Regalbuto, J.R., *J. Catal.*, 2016, vol. 342, pp. 203–212. https://doi.org/10.1016/j.jcat.2016.08.004
- Nemamcha, A., Rehspringer, J.L., and Khatmi, D., J. Phys. Chem. B., 2006, vol. 110, pp. 383–387. https://doi.org/10.1021/jp0535801
- Su, X., Vinu, A., Aldeyab, S.S., and Zhong, L., *Catal. Lett.*, 2015, vol. 145, pp. 1388–1395. https://doi.org/10.1007/s10562-015-1537-0
- Li, J., and Bai, X., J. Mater. Sci., 2016, vol. 51, pp. 9108– 9122. https://doi.org/10.1007/s10853-016-0164-5
- Li, J., Bai, X., and Lv, H., Ultrason. Sonochem., 2020, vol. 60, pp. 104746. https://doi.org/10.1016/j.ultsonch.2019.104746
- Wei, X., Kikhtyanin, O.V., Parmon, V.N., Wu, W., Bai, X., Zhang, J., Xiao, L., Su, X., Zhang, Y., *J. Porous Mater.*, 2017, vol. 25, pp. 235–247. https://doi.org/10.1007/s10934-017-0437-7
- Schmidt, F., Hoffmann, C., Giordanino, F., Bordiga, S., Simon, P., Carrillo-Cabrera, W., and Kaskel, S., *J. Catal.*, 2013, vol. 307, pp. 238–245. https://doi.org/10.1016/j.jcat.2013.07.020
- Zhang, Y., Wang, W., Jiang, X., Su, X., Kikhtyanin, O.V., and Wu, W., *Catal. Sci. Technol.*, 2018, vol. 8, pp. 817– 828. https://doi.org/10.1039/C7CY02106B.
- Alvarez, F., Ribeiro, F.R., Perot, G., Thomazeau, C., and Guisnet, M., *J. Catal.*, 1996, vol. 162, pp. 179–189. https://doi.org/10.1006/jcat.1996.0275
- 32. Kim, J., Han, S.W., Kim, J.C., and Ryoo, R., ACS Catal., 2018, vol. 8, no.11, pp. 10545–10554. https://doi.org/10.1021/acscatal.8b03301
- Ge, L., Yu, G., Chen, X., Li, W., Xue, W., Qiu, M., and Sun, Y., *New J. Chem.*, 2020, vol. 44, no. 7, pp. 2996– 3003. https://doi.org/10.1039/C9NJ06215G
- 34. Yang, L., Wang, W., Song, X., Bai, X., Feng, Z., Liu, T., and Wu, W., *Fuel Process. Technol.*, 2019, vol. 190, pp. 13–20. https://doi.org/10.1016/j.fuproc.2019.02.027
- 35. Yang, J., Kikhtyanin, O.V., Wu, W., Zhou, Y., Toktarev, A.V., Echevsky, G.V., and Zhang, R., *Micropor. Mesopor. Mat.*, 2012, vol. 150, pp. 14–24. https://doi.org/10.1016/j.micromeso.2011.09.020
- 36. Kim, M.Y., Lee, K., and Choi, M., J. Catal., 2014, vol. 319, pp. 232–238. https://doi.org/10.1016/j.jcat.2014.09.001