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Melting-assisted solvent-free synthesis of SAPO-11 for improving the hydroisomerization performance of *n*-dodecane

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ABSTRACT

A novel melting-assisted solvent-free route using solid oxalic acid was proposed for the post-treatment of SAPO-11 zeolite, followed by loading with 0.5 wt% Pt by the incipient wetness impregnation method. Subsequently, the performance of the obtained bifunctional catalysts toward the hydroisomerization of *n*-dodecane was examined. The prepared samples were characterized by XRD, SEM, BET, XRF, Py-IR, and solid-state NMR. From the results, it was found that the high crystallinity and uniform morphology were retained after the post-treatment and that more (002) crystal faces were exposed, which was beneficial since more acid sites were provided. More importantly, the total Brønsted acid sites and the ratio (R_a) of the micropore area to the total surface area were optimized by this method. Thus, the catalytic performance was enhanced significantly, and the prepared Pt-SAPO-11-10% catalyst had the highest *i*-dodecane yield of 80.1% compared to 55.3% of Pt-SAPO-11. Expectedly, this facile and cost-effective method is promising for the hydroisomerization of normal paraffin in the production of lubricant base oils.

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1. Introduction

The hydroisomerization of normal long-chain paraffin is an efficient process applied in lubricant base oil production, and it can effectively improve the low-temperature physicochemical properties of lubricating oil [1–6]. Various types of catalysts have been developed to catalyze this reaction [7–12]. Among them, bifunctional catalysts prepared by loading noble metals such as Pt with a one-dimensional pore molecular sieve, such as SAPO-11 (AEL), ZSM-22 (TON), and ZSM-23 (MTT), have

made a great contribution [13–16]. In particular, SAPO-11 with the AEL topology, which has a one-dimensional ten-membered ring channel structure, has been considered as a potential material for the hydroisomerization of normal paraffin due to its suitable pore structure and moderate acidity [13]. The action of bifunctional catalysts toward hydroisomerization involves two major parts: the hydro-/dehydrogenation reaction of alkane molecules occurring at the metal center, and the alkane skeleton isomerization reaction occurring at an acidic site of a molecular sieve. The acidic property plays a very important role in

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guaranteeing the isomerization conversion of normal paraffin, and the micropore structure properties mainly control the isomer selectivity of the reaction [17,18].

According to the pore mouth and key-lock mechanism, the Brönsted acid sites located near the outer layer of the molecular sieve crystal were determined to contribute greatly to the isomerization of the *n*-paraffin carbon skeleton [19,20]. When the supported metal content of the catalyst is sufficient to catalyze the hydro-/dehydrogenation reaction, optimizing the physicochemical properties of the molecular sieve is the key to improving the hydroisomerization performance [17,20]. In recent years, post-treatment methods with an acid or base as the etchant have been widely used to modify the physicochemical properties of molecular sieves [21–28]. Perez-Ramirez et al. [21] found that the external surface was enhanced after treatment with an alkali solution, which increased the conversion of the reaction. Reportedly, hydrochloric acid and citric acid treatments of SAPO-11 could enhance the methylation of naphthalene, owing mainly to the number of secondary mesopores [29]. In our previous work, we reported that the hydroisomerization performance could be enhanced by alkaline post-treatment of the ZSM-22 zeolite [30]. However, the current post-treatment method mainly involves aqueous acid or alkali solutions, which produce a large amount of wastewater. Moreover, the use of etching solutions leads to a low yield of molecular sieves. In 2012, a novel solvent-free route for synthesizing zeolites was reported, which provided a new idea for zeolite synthesis [31]. However, the development of solvent-free based post-treatment for preparing zeolite catalysts remains a great challenge. Recently, our group proposed a post-processing route to synthesize SAPO-34 with butterfly patterned hierarchical pores through a melting-assisted post-synthesis route that could improve the MTO performance [32].

Herein, we propose a new melting-assisted post-synthesis route to treat a molecular sieve (SAPO-11). It involves solid oxalic acid as the etching agent. The absence of water greatly reduces environmental pollution and improves the yield of SAPO-11. This is the first time a green post-processing route has been developed to tailor the pores and acid sites of SAPO-11. In this work, SAPO-11 with a one-dimensional pore structure of the AEL topology was used as the carrier of bifunctional catalyst. The parent SAPO-11 was treated with 5%, 10%, and 15% solid oxalic acid. Thereafter, the prepared samples were characterized by XRD, SEM, BET, Py-IR, NMR, etc. Afterward, the noble metal, Pt (0.5 wt%), providing the hydro-/dehydrogenation site was loaded on the bifunctional catalysts [25,33]. Finally, *n*-dodecane was chosen as a model feed to investigate the hydroisomerization performance of the prepared catalysts under different experimental conditions.

2. Experimental

2.1. Synthesis of parent SAPO-11 and post-treatment of SAPO-11

The conventional hydrothermal method was used to pre-

pare the SAPO-11 raw powder. Tetraethyl orthosilicate, pseudo-boehmite, and orthophosphoric acid were used as the Si source, Al source, and P source, respectively. *n*-Butanol was used as a co-solvent and di-*n*-propylamine was used as a template. The synthesis steps are as follows: first, 6.79 g of pseudo-boehmite was slowly added to the phosphoric acid solution (9.01 g of phosphoric acid dissolved in 21.16 g of H₂O) and stirred for 4 h; subsequently, 1.63 g of tetraethyl silicate was dissolved in 6.37 g of *n*-butanol, added dropwise, and stirred for 1 h. Next, 5.54 g of di-*n*-propylamine was slowly added and stirred for 1 h; finally, the gel obtained with the general composition of 1 Al₂O₃: 1 P₂O₅: 0.2 SiO₂: 1.4 DPA: 2.3 *n*-butanol: 35 H₂O was transferred to a stainless steel reaction vessel with a polytetrafluoroethylene liner and reacted in an oven at 210 °C for 24 h. The reaction product was washed with deionized water to neutrality, dried overnight in an oven at 80 °C, and calcined in a muffle furnace at 500 °C for 6 h to remove the organic templating agent. The prepared sample was named SAPO-11-P.

Oxalic acid was selected to treat the SAPO-11-P sample according to the following procedures: firstly, a certain weight of the sample and solid oxalic acid were thoroughly mixed in a solid pulverizer (the mass ratios of solid oxalic acid to SAPO-11-P were selected as 5%, 10%, and 15%); thereafter, the mixed powder was transferred into a stainless steel reaction vessel with a polytetrafluoroethylene liner and reacted at 100 °C for 6 h. The reacted SAPO-11 samples were named SAPO-11-5%, SAPO-11-10%, and SAPO-11-15%.

The bi-functional catalysts were loaded with 0.5 wt% Pt with an H₂PtCl₆·6H₂O aqueous solution by the incipient wetness impregnation method and named as Pt-SAPO-11-P, Pt-SAPO-11-5%, Pt-SAPO-11-10%, and Pt-SAPO-11-15%.

2.2. Hydroisomerization reaction

The catalyst powder was compressed into tablets under a pressure of 20 MPa using a tablet pressing machine. After crushing in an agate mortar, the particles were passed through a stainless-steel sieve with 20–40 nm mesh sizes. The catalyst particle was packed in a fixed bed reactor and reduced in a hydrogen atmosphere at 350 °C for 6 h under atmospheric pressure. After the catalyst was reduced, the fixed bed reactor was adjusted to the reaction conditions. *n*-Dodecane was added to the fixed bed reactor using a pump. The liquid product was collected by a condensate tank, and the liquid product was analyzed by a GC-2014C gas chromatograph. The conversion and selectivity of *n*-dodecane was calculated as follows: conversion of *n*-dodecane = (moles of converted *n*-dodecane) ÷ (moles of the initial *n*-dodecane) × 100%; selectivity of *i*-dodecane = (moles of *i*-dodecane) ÷ (moles of the initial *n*-dodecane) × 100%.

2.3. Catalyst characterization

The crystal structures of the samples were characterized using an X-ray diffractometer (XRD, Rigaku, Ultima IV). The crystal morphologies of the samples were observed using a

Fig. 1. XRD patterns of the SAPO-11 samples before and after treatment.

scanning electron microscope (SEM, Zeiss SUPRA 55 SAPHIRE). The surface area and pore volume of the samples were determined by the Brunauer-Emmett-Teller (BET) and t-plot methods, and pore sizes in the ranges of 0–2 nm and 2–50 nm were calculated by the Horvath-Kawazoe (HK) method and the Barre-Joyner-Halenda (BJH) method, respectively. The elemental compositions of the samples were analyzed by X-ray fluorescence spectroscopy (XRF, Bruker S4PIONEER). The types and number of acid sites were estimated based on the Py-IR spectra (EQUINOX 70, Bruker, Germany). Solid-state MAS NMR experiments were performed at 5 kHz on a Bruker AVANCE 400 spectrometer operating at frequencies of 79.5 and 104.22 MHz for ^{29}Si and ^{27}Al , respectively.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD patterns of the SAPO-11 samples before and after oxalic acid treatment. All the crystal samples have diffraction peaks at 2θ of 8.1° , 9.4° , 13.1° , 15.6° , 20.3° , 21.2° , and 22.1° – 23.2° , which are attributed to the typical SAPO-11 phase with the AEL topology. However, the peak intensities of different peaks change to a certain extent. The relative crystallinities of the samples were calculated using the diffraction peak area method in a specific diffraction angle range ($2\theta = 5^\circ$ – 50°). Compared to that of the parent sample, SAPO-11-P (100%), the relative crystallinities of the treated samples were 98.1%, 95.3%, and 92.1% for SAPO-11-5%, SAPO-11-10%, and SAPO-11-15%, respectively. The elemental analysis results in Table 1 also indicate that the molar composi-

Fig. 2. Peak area ratio of the three crystal faces in different SAPO-11 samples.

tions of the prepared samples changed slightly after treatment. With increasing the oxalic acid content, the relative crystallinity decreased gradually, although no impurity phase peaks were observed even with 15% solid oxalic acid, indicating that the pure SAPO-11 crystal was well-persevered after the treatment. Three crystal faces, (200), (020), and (002), were marked. Based on the peak area of the three characteristic peaks, the peak intensity ratios of the three crystal faces in the samples were calculated, as shown in Fig. 2. The results indicated that more (002) crystal faces were exposed, implying that more pores of the crystal could be exposed; thus, more acid sites were provided for the reaction [34]. As indicated by the pore mouth and key-lock mechanism, changing this crystal face may improve the hydroisomerization performance.

3.2. Morphology

The SEM images of all the samples are shown in Fig. 3. SAPO-11-P (Fig. 3(a)) has spherical particles with sizes in the range of 4–6 μm with a compact packing structure formed by the accumulation of flaky crystals around a fixed center. Expectedly, it is difficult for the *n*-dodecane molecules to interact with the crystals inside the particles due to the limitation of the diffusion. For SAPO-11-5% (Fig. 3(b)), SAPO-11-10% (Fig. 3(c)), and SAPO-11-15% (Fig. 3(d)), SAPO-11-P was reacted with different amounts of solid oxalic acid at a microscopic scale. The three samples exhibited no obvious change in morphology according to the SEM images, which also indicate that the primary crystal structure was retained after the mild solid oxalic acid treatment.

Table 1

Textural properties of the samples from N_2 adsorption and desorption isotherms and X-ray photoelectron spectroscopy.

Sample	Molar composition ^a	Surface area (m^2/g)				Pore volume (cm^3/g)			
		Total	Micropore	External	R_b	Total	Micropore	Mesopore	R_b^c
SAPO-11-P	$\text{Si}_{0.092}\text{Al}_{0.457}\text{P}_{0.452}\text{O}_2$	213	107	106	50.2%	0.165	0.055	0.11	33.3%
SAPO-11-5%	$\text{Si}_{0.091}\text{Al}_{0.458}\text{P}_{0.453}\text{O}_2$	224	138	86	61.6%	0.166	0.071	0.095	42.8%
SAPO-11-10%	$\text{Si}_{0.092}\text{Al}_{0.459}\text{P}_{0.451}\text{O}_2$	210	147	63	70.0%	0.153	0.076	0.077	49.7%
SAPO-11-15%	$\text{Si}_{0.093}\text{Al}_{0.460}\text{P}_{0.449}\text{O}_2$	200	127	73	63.5%	0.144	0.065	0.079	45.1%

^a The molar compositions of the SAPO-11 samples before and after treatment, calculated by X-ray fluorescence spectroscopy.

^b The ratio of the micropore to the total specific surface area.

^c The ratio of the micropore to the total pore volume.

Fig. 3. SEM images of the SAPO-11 samples. (a) SAPO-11-P; (b) SAPO-11-5%; (c) SAPO-11-10%; (d) SAPO-11-15%.

3.3. Pore structure

N_2 adsorption and desorption isotherms for different SAPO-11 samples are presented in Fig. 4(a). All the samples exhibit the type IV isotherm with an H4-type hysteresis loop. The sharp increase in adsorption at a relative pressure of $10^{-6} < P/P_0 < 0.01$ is attributed to micropore filling, indicating the presence of microporous structures in the samples [35]. Simultaneously, the adsorption amount is significantly increased and the hysteresis loop appears near the saturation pressure ($0.4 < P/P_0 < 1.0$), which proves the existence of mesoporous and macroporous structures [36]. Generally, the intracrystalline mesopores in the samples are possibly generated by the lamination of the layered structure demonstrated by SEM images (Fig. 3).

Table 1 lists the BET data results. All the samples contain microporous and mesoporous structures, although mesoporous structures are dominant. The micropore and mesopore distribution curves of the samples are shown in Figs. 4(b) and 4(c). The micropore size is concentrated at about 0.5 nm for all the samples, and the mesopore size of SAPO-11-P is concentrated at about 3.8 nm and increases to about 4.0 nm for the samples after acid treatment. Meanwhile, the micropore and mesopore volumes of the samples changed accordingly, as shown in Table 1. Interestingly, there is no obvious difference

between the pore volume and surface area of the samples after oxalic acid etching, due to the mild post-treatment condition. However, with the increase in the amount of oxalic acid, the samples possess relatively high ratios of the micropore surface area to the total specific surface area (R_a), and the micropore volume to the total pore volume (R_b), as shown in Table 1. The SAPO-11-P sample has a compact packing structure (Fig. 3), which causes the pores at the mutual contact faces of the crystals to be clogged. The pore volume and specific surface area of the contact surface cannot be effectively measured. When oxalic acid is etched to these contact faces, more micropores are released, which is consistent with the data in Table 1. The BET surface area, total pore volume, and micropore volume of SAPO-11-10% are 210 m^2/g , 0.153 cm^3/g , and 0.076 cm^3/g , respectively; moreover, SAPO-11-10% has the largest R_a and R_b values among the samples.

3.4. Acidity

Py-IR was used to evaluate the acidity of the SAPO-11 samples [37]. Figs. 5(a) and 5(b) show the infrared absorption spectra of pyridine at 200 and 350 °C of the samples, separately. The wave number regions of 1540–1548 and 1445–1460 cm^{-1} are the infrared absorption peaks of pyridine at the Brönsted acid sites and Lewis acid sites, respectively [38]. Table 2 shows the intensity distributions of the number of acidic sites with the samples; the total Brönsted and Lewis acid sites were measured at 200 °C, and the medium and strong Brönsted and Lewis acid sites were measured at 350 °C. According to the results, the samples contained mainly medium and strong acid sites. In addition, with the increase in oxalic acid content, the total number of Brönsted acid sites increased first and then decreased. This is because, at a relatively low oxalic acid content, the acidic sites of the overlapping portions of the flaky crystals inside the SAPO-11 sample particles are exposed, resulting in an increase in the number of acid sites. At a relatively high oxalic acid content, the crystal structure is partially destroyed, resulting in an overall decrease in the number of acid sites. The SAPO-11-10% sample has the maximum number of total Brönsted acid sites and the minimum proportion (66.5%) of medium and strong Brönsted acid sites when compared to those of the other SAPO-11 samples. Fig. 6(a) and 6(c) presents the ^{27}Al and ^{29}Si MAS NMR spectra of SAPO-11-P and SAPO-11-10%. Fig. 6 shows that both samples have a tet-

Fig. 4. N_2 adsorption and desorption isotherms (a), micropore size distributions (b), and mesopore size distributions (c) of the SAPO-11 samples.

Fig. 5. IR spectra of the pyridine absorbed from the SAPO-11 samples at 200 (a) and 350 °C (b).

Table 2

Acid site distribution of the samples ($\mu\text{mol/g}$).

Sample	Total acid sites (200 °C)		Medium and strong sites (350 °C)	
	B	L	B	L
SAPO-11-P	108.9	22.8	77.3	20.1
SAPO-11-5%	113.8	21.4	76.4	21.2
SAPO-11-10%	161.6	29.8	107.5	23.0
SAPO-11-15%	115.7	26.0	80.9	22.7

ra-coordinated framework of Al atoms, which was indicated by the resonance peak at about 54.5×10^{-6} [39]. The pentacoordinated Al resonance peak at about 21×10^{-6} resulted from the coordination of the template to the Al framework [40,41]. The

hexacoordinated Al resonance peak at about 0×10^{-6} is associated with the interaction between the tetra-coordinated Al species and water molecules [41]. Meanwhile, the signals of hexacoordinated Al of SAPO-11-10% is stronger than that of SAPO-11-P, which indicates that the acid treatment induces dealumination of the silicoaluminophosphate framework of SAPO-11. Fig. 6(c) and 6(d) exhibit a broad band ranging between -80 and -120×10^{-6} . The values, -87 (peak 1), -94 (peak 3), -102 (peak 4), -107 (peak 5), and -112×10^{-6} (peak 6), are indicative of Si(4Al), Si(3Al,1Si), Si(2Al, 2Si), Si(1Al, 3Si), and Si(4Si), respectively, in the SA domain, and -91×10^{-6} (peak 2) represents Si(4Al) in the SAPO domain [38]. The original data were deconvoluted into six peaks using Gaussian curves; the results are provided in Table 3. The decrease in the Si(4Al) peaks in the SAPO and SA domains demonstrates the destruc-

Fig. 6. ^{27}Al and ^{29}Si MAS NMR spectra of SAPO-11-P (a, c) and SAPO-11-10% (b, d).

Table 3Deconvolution results of the ^{29}Si MAS NMR spectra of SAPO-11-P and SAPO-11-10%.

Sample	SAPO domain			SA domain		
	Si(4Al) (-91×10^{-6})	Si(4Al) (-87×10^{-6})	Si(3Al,1Si) (-94×10^{-6})	Si(2Al,2Si) (-102×10^{-6})	Si(1Al,3Si) (-107×10^{-6})	Si(4Si) (-112×10^{-6})
SAPO-11-P	20.3%	8.3%	6.5%	63.6%	0.4%	0.9%
SAPO-11-10%	8.1%	2.6%	1.8%	66.6%	11.3%	9.6%

tion of the SAPO-11 crystal structure, as shown in Fig. 1, which also implies that the Al species are very sensitive to acid treatment. The skeletal isomerization of hydrocarbons was promoted by the medium and strong Brönsted acid site distributions in Si(1Al) and Si(2Al) in the SA domains, and Si(3Al) located at the interface between the SA and SAPO domains [42]. Thus, the SAPO-11-10% sample with a high Si($n\text{Al}$) ($0 < n < 4$) has more medium and strong Brönsted acid sites than those of the SAPO-11-P sample, which is in accordance with the Py-IR characterization results (Table 2).

3.5. Catalytic performance

The catalytic performance of the catalysts toward the hydroisomerization of *n*-dodecane was investigated. The reaction pressure was 2.0 MPa; the temperature range was 280–360 °C, and the GHSV was 1.2 h⁻¹. Fig. 7(a) (temperature-conversion diagram) clearly illustrates that the conversion of *n*-dodecane increases with increasing temperature. Additionally, the con-

version of *n*-dodecane increases in the following order: Pt-SAPO-11-P < Pt-SAPO-11-5% < Pt-SAPO-11-15% < Pt-SAPO-11-10%. Over the entire reaction temperature range, Pt-SAPO-11-10% exhibits a much higher conversion than those of the other samples. In addition, Fig. 8(a) shows that the reaction conversion of the catalyst increases as the number of Brönsted acid sites in the SAPO-11 samples increases. The mechanism of hydroisomerization of long-chain alkanes over bifunctional catalysts indicates that under conditions of sufficient hydrogenation sites, the reaction rate-determining step is a rearrangement of carbonium at the Brönsted acid sites, including the skeletal rearrangement or carbon-carbon bond rupture [17]. The Brönsted acid sites catalyze the alkane carbon skeletal isomerization reaction; the higher the Brönsted acid content, the higher the reaction conversion rate, which is consistent with the experimental result shown in Fig. 8(a). As indicated in Table 2, the SAPO-11-10% sample (161.6 $\mu\text{mol/g}$) has the highest number of Brönsted acid sites compared to those of the other SAPO-11 samples. Fig. 7(b) shows the

Fig. 7. Conversion of *n*-dodecane (a), isomers selectivity (b), and isomer yield (c) over Pt-SAPO-11-P, Pt-SAPO-11-5%, Pt-SAPO-11-10%, and Pt-SAPO-11-15% catalysts as a function of the reaction temperature.

Fig. 8. (a) Conversion at different reaction temperatures against the number of Brönsted acid sites; (b) the selectivity at different reaction temperatures against the R_a value of the catalysts.

Table 4Performance of the prepared catalysts toward *n*-dodecane hydroisomerization at 300 °C.

Catalyst	Conversion (%)	S_T^a (%)	S_{Mo}^b (%)	S_{Multi}^c (%)	S_{Mo}/S_{Multi}
Pt-SAPO-11-P	57.8	88.3	58.2	32.1	1.8
Pt-SAPO-11-5%	52.6	80.0	69.4	10.6	6.6
Pt-SAPO-11-10%	81.1	93.7	80.3	13.4	6.0
Pt-SAPO-11-15%	54.0	88.9	73.5	15.4	4.8

^aThe selectivity of the total isomers.^bThe selectivity of the mono-branched isomers.^cThe selectivity of the multi-branched isomers.

changes in selectivity as a function of temperature. Normally, the selectivity decreases as the temperature increases due to the production of more cracking products at a relatively high temperature, which is consistent with the previous reports [28,30,32]. More interestingly, we found that the *R_a* value is positively correlated with the reaction selectivity indicated by the curves in Fig. 8(b). The pore mouth and key-lock mechanism of the alkane hydroisomerization reaction indicated that the main part of the alkane carbon skeletal isomerization occurs near the pores of the SAPO-11 molecular sieve. Even if the alkane reaches the depth of the pore by diffusion, the reaction would still be difficult to occur owing to the presence of space resistance, which causes the alkane carbon skeletal to crack easily. Therefore, the more micropore specific surface areas and (002) crystal faces of the SAPO-11 molecular sieve crystal are exposed, the more efficient reaction sites are exposed, which improve the selectivity of the hydroisomerization reaction [43]. Fig. 7(c) shows the isomer yield of the catalysts at different temperatures, and the best isomer yield performance is recorded at 320 °C. The total yield of the isomers displays a volcanic type profile, and the highest yield of 80.1% appears for Pt-SAPO-11-10%, which is much higher than that of the parent Pt-SAPO-11-P sample (55.34%). Moreover, an excellent hydroisomerization performance requires not only high conversion and high isomer yield, but also high mono-branched selectivity to maintain its high viscosity index [30]. Table 4 lists the isomer product selectivity of the catalyst at 300 °C; the selectivity of the mono-branched isomer increases after the post-treatment; however, the selectivity of multi-branched isomers decreases simultaneously. Consequently, the S_{Mo}/S_{Multi} ratio increases significantly (more than 3 times) after the oxalic acid treatment. Among all the prepared catalysts, Pt-SAPO-11-10%, having a higher *n*-dodecane conversion, higher isomer yield, and higher selectivity of mono-branched isomers, is the best catalyst. Based on the above experimental results, the hydroisomerization performance could be enhanced significantly over the bifunctional catalysts after subjection to facile solid oxalic acid treatment.

4. Conclusions

In this work, a facile solvent-free post-treatment process was developed for SAPO-11 based on a novel melting-assisted post-synthesis using solid oxalic acid. After loading Pt (0.5 wt%), the performance of the prepared bifunctional catalysts toward the hydroisomerization of *n*-dodecane was investigated.

The treated SAPO-11 samples had more Brönsted acid sites, which significantly contributed to improved reaction conversion, higher micropore specific surface area ratio, and increased (002) crystal face ratio that enhanced the reaction selectivity, simultaneously. The isomeric product yield over Pt-SAPO-11-10% reached 80.1% compared to that over Pt-SAPO-11 (55.3%). Based on these results, the melting-assisted solvent-free synthesis method not only reduces wastewater but also optimizes the physicochemical properties of the catalyst; thus, an efficient and environmentally friendly method for enhancing hydroisomerization performance is provided.

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Graphical Abstract

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Melting-assisted solvent-free synthesis of SAPO-11 for improving the hydroisomerization performance of *n*-dodecaneGan Yu, Xinqing Chen *, Wenjie Xue, Lixia Ge, Ting Wang, Minghuang Qiu, Wei Wei, Peng Gao, Yuhua Sun *
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SAPO-11 zeolite with high crystallinity and a suitable number of Brønsted acid sites is post-treated via a novel melting-assisted solvent-free route using solid oxalic acid, and it shows promise as a catalyst in normal paraffin hydroisomerization.

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无溶剂熔融辅助法合成SAPO-11及其在长链烷烃加氢异构反应的应用

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摘要: 长链正构烷烃加氢异构化是润滑油基础油生产的有效方法, 可有效改善润滑油的低温物理化学性质。在具有酸位点的载体上负载具有加氢脱氢功能的贵金属制备双功能催化剂得到了广泛研究。SAPO-11分子筛具有一维的孔结构和适宜的酸度, 在加氢异构反应中扮演着重要角色。根据加氢异构反应的孔口机理和锁钥机理, 位于分子筛晶体外层附近的Brønsted酸位点, 对正链烷烃碳骨架的异构化起主要作用。因此, 优化分子筛载体的物理化学性质是提高加氢异构性能的关键。近年来, 以酸或碱作为蚀刻剂的后处理方法已被广泛用于改变分子筛的物理化学性质。然而, 目前的后处理方法主要涉及酸性或碱性水溶液, 产生大量废水。此外, 蚀刻溶液的使用也导致分子筛的低产率。鉴于此, 我们提出了采用无溶剂熔融辅助合成法来处理SAPO-11分子筛, 并将其应用于加氢异构反应。该方法以固体草酸作为蚀刻剂, 通过与分子筛原粉机械搅拌混合均匀后, 直接在水热反应釜中反应, 处理过程不会有废水产生。本文以不同量的固体草酸处理原粉, 处理得到的样品负载0.5 wt% Pt金属制备一系列贵金属/分子筛双功能催化剂, 以正十二烷作为模型反应物, 研究制备的催化剂在不同实验条件下的加氢异构化性能。

XRD和SEM表征结果表明, 处理前后的SAPO-11分子筛保持了高的结晶度和比较完整的形貌。XRF数据表明处理前后分子筛的元素组成变化不明显。基于特征峰的峰面积计算结果表明, 处理后SAPO-11分子筛暴露出更多(002)晶面, 有利于更多的分子筛孔口进行加氢异构反应。BET和Py-IR表征表明, 经过草酸处理后, SAPO-11原粉颗粒内部的片状晶体的重叠部分被暴露出来, 这导致处理后的样品的微孔孔容占比和Brønsted总酸量的增加。加氢异构反应数据表明, n -C₁₂转化率随着SAPO-11分子筛样品Brønsted总酸量的增加而增加, i -C₁₂选择性随SAPO-11分子筛样品的微孔孔容占比的增大而增大。该无溶剂熔融辅助合成法同时优化了Pt-SAPO-11催化剂的酸性质和微孔孔结构性质, 提高了反应转化率和选择性, 正十二烷异构体的产率从55.3%大幅提高到80.1%, 催化性能显著提高。该方法在双功能催化剂加氢异构反应中具有广泛的应用前景。

关键词: 加氢异构; 分子筛; SAPO-11; 无溶剂熔融辅助; 后处理; 双功能催化剂

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