



Full Length Article

Effect of ethanol on the surface properties and n-heptane isomerization performance of Ni/SAPO-11



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ABSTRACT

Effect of ethanol on SAPO-11 and Ni/SAPO-11 catalysts was systematically investigated. The pore structure and surface acidity of the SAPO-11 are sensitive to the impregnation solvents. Ethanol was less destructive to the pore structure compared with water, and more surface moderate acid sites were presented on the SAPO-11 treated with ethanol. The Ni/SAPO-11 catalysts were prepared via impregnation method. The solvent effect was also exhibited. The sample prepared with ethanol exposed a higher metal dispersion on the surface and larger micro-pore volume than that of prepared with water. There were more moderate acid sites over the catalyst when the ethanol was used as the solvent. The higher metal dispersion and rich moderate acid sites contributed higher i-heptane selectivity and yield to the catalyst prepared with ethanol. Of note is that the selectivity of the SAPO-11 can be shown in the isomerization of n-heptane and the amount of supported Ni for the catalysts should be paid more attention to.

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1. Introduction

The isomerization of n-alkanes has been attracting a great interest in increasing the octane number of gasoline [1]. The popular catalysts used in such reactions are bifunctional, comprising by metal sites for dehydrogenation/hydrogenation activities and surface acid sites for skeletal isomerization [2–4]. Noble metals (e.g., Pt, Pd) based isomerization catalysts present the optimal performance. While they are restricted due to the high cost and sensitivity to poisons [1]. It arouses much more attention to the non-noble metal based isomerization catalysts. Of pity is that these catalysts bear the low metal dispersion ascribing to high supported metal amount, which can accelerate the aggregation of metal species during the thermal treatment, especially with a support providing a low surface area [5–7]. The low metal dispersion imposes less metal active sites on the surface which leads to the restrictions on the catalyst optimization. So far, it is agent to improve the metal dispersion for isomerization catalysts.

As a bifunctional catalyst, the catalytic performance was strongly influenced by the surface acidity. Wild acid sites are prefer-

able for the isomerization reaction, while strong ones enhance the cracking selectivity. It means that the selectivity of the n-alkanes isomerization intimates with the acidity. The acid property of the bifunctional catalysts is mainly determined by the support. Besides, the isomerization selectivity is also affected by the pore structure of support. Among the numerous catalytic materials, SAPO-11 is widely used as the acid support of bifunctional catalysts, due to its unique pore structure and moderate acidity [8–10]. Whereas, these properties mentioned above are changed during the preparation of the catalysts [5,6,11].

Solvent has a key role in improving the metal dispersion for the catalysts prepared by impregnation method. It has been observed that water used as the solvent is not preferable due to the higher polarity. This property of water always leads to the aggregation of metal species on the surface of catalysts during the thermal treatment [12,13]. Researchers have tried some other solvents to improve the metal dispersion of the catalysts. Variava et al. [14] observed that smaller particle size of nickel on the multiwalled carbon nanotubes could be obtained via ethanol as the impregnation solvent, which presented a high conversion in the methanation of CO. Ho et al. [15] compared the dispersion of Co on the surface of Co/SiO₂ catalyst prepared by ethanol or water as the solvent. They observed that ethanol gave the higher dispersion of Co species. Carvalho et al. [16] showed that higher dispersion of Pt on Al₂O₃ was obtained through ethanol rather than water or acetone. The

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similar result was reported by Tao [13] who got a higher nickel dispersion on SiO₂ with ethanol as the impregnation solvent for CO methanation reaction.

It is worth noting that SAPOs are more sensitive to solvent destruction compared with aluminosilicate zeolites or amorphous oxides. The destructive effect from water molecule may lead to the destruction of the framework. It is proposed that liquid water is more destructive than the gas phase [17]. Many research groups have investigated this phenomenon and proposed potential mechanism like Al–O bonds opening [18–20]. Parlitz's research indicated that SAPOs such as SAPO-5, SAPO-17 and SAPO-44 were vulnerable to the destruction from water in the temperature from 50 to 200 °C [21]. The similar behavior was observed on SAPO-34 when water molecule existed [22].

Water used as the impregnation solvent is not preferable to get a high metal dispersion, and properties of SAPOs molecular sieves are sensitive to water. However, seldom work has been carried out to investigate the effect of solvent on Ni/SAPO-11 catalyst for *n*-alkane isomerization. In this study, Ni/SAPO-11 catalysts were prepared via impregnation method with ethanol and water as the solvent respectively. The effect of solvent on the nickel dispersion was investigated, and the pore structure, surface acidity of SAPO-11 and Ni/SAPO-11 were studied simultaneously. The catalytic performance of Ni/SAPO-11 was assessed by the isomerization of *n*-heptane as a model reaction.

2. Experimental section

2.1. Synthesis of SAPO-11

In a typical synthesis of SAPO-11, 4.37 g pseudoboehmite (70.0 wt% Al₂O₃, Yantai Henghui Petrochemical Co., Ltd.) was hydrolyzed in deionized water under stirring. Ortho-phosphoric acid (85.0 wt% H₃PO₄, XiRong Petrochemical Co., Ltd.) was added to the mixture and homogenized under stirring for 2 h. Then, Dipropylamine (DPA, Sinopharm Chemical Reagent Corporation) was added and stirred for another 2 h, followed by the addition of silica sol (30.0 wt% SiO₂, Qingdao Haiyang Petrochemical Co., Ltd.). The final molar composition of the synthesis sol was 1.0 Al₂O₃: 1.0 P₂O₅: 1.1 DPA: 0.4 SiO₂:50.0H₂O. After that, the hole mixture was homogenized for 2 h, and then dried in water-bath at 353 K. The obtained pre-dried gel powder was transferred into a weighing bottle located at the bottom of a Teflon-lined stainless steel autoclave. A certain amount of deionized water (0.3 g per gram of dried gel powder), separated from the powder by the weighing bottle, was added to the bottom of the autoclave. Finally, the autoclave was subjected to crystallization under autogenous pressure at 473 K for one day to form a precursor gel. After crystallization, the as-synthesized solid product was washed with deionized water, dried overnight at 373 K, and calcined at 873 K for 4 h in air to remove the organic template.

2.2. Preparation of Ni/SAPO-11

A series of Ni/SAPO-11 catalysts were prepared by the impregnation method with ethanol as the solvent and nickel nitrate as the metal precursor. The pre-synthesized catalysts were dried at 383 K for 2 h, then calcined in air atmosphere at 673 K for 4 h. The resulting samples were denoted as xNi/SAPO-11(ET) with x indicating the nickel content (2.0, 4.0, 6.0 and 8.0 wt%). As comparison, water was also used to dissolve nickel nitrate for the impregnation of SAPO-11, with the same subsequent steps as mentioned above. These catalysts were noted as xNi/SAPO-11(W) with x standing for 4.0, 6.0 and 8.0 wt%.

2.3. Treatment of SAPO-11

The effect of impregnation solvent on the supports during the synthesis of catalysts was investigated. The sample preparation process was the same as Ni/SAPO-11, but no metal precursor was dissolved in the solvent. The resulting samples treated by ethanol and water were labeled as SAPO-11(W) and SAPO-11(ET), respectively.

2.4. Characterizations

X-ray diffraction (XRD) patterns were recorded with an X' Pert PRO MPD diffraction meter with Cu K α radiation. It was operated at 40 kV and 40 mA, with a scanning speed of 10° min⁻¹. N₂ adsorption-desorption isotherms were measured on an Tristar-3000 (Micromeritics, USA) analyzer at 77 K, after samples were outgassed at 573 K under vacuum for 4 h. The surface area was determined by the Brunauer-Emmett-Teller (BET) method, while the micro-pore surface area (S_{micro}) and micro-pore volume (V_{micro}) of the samples were obtained by t-plot analysis. The total volume were estimated at $P/P_0 = 0.98$. To characterize the acidity, temperature programmed desorption of ammonia (NH₃-TPD) was carried out at a dynamic chemisorption analyzer (Micromeritics ASAP 2920). Prior to NH₃ adsorption at 343 K for 0.5 h, the sample was pretreated in helium flow at 823 K for 0.5 h. After that, the physically adsorbed NH₃ was removed in a flow of helium for 0.5 h, followed by heated to 873 K with a rate of 10 K min⁻¹. The signals were recorded by monitoring the desorption of ammonia with a TCD detector. The ²⁷Al, ²⁹Si and ³¹P magic-angle-spinning nuclear magnetic resonance (MAS NMR) were collected on a Bruker Advance 400 spectrometer. The chemical shift was referenced to AlK(SO₄)₂·12H₂O (0.21 $\mu\text{g g}^{-1}$), tetramethylsilane (TMS) and phosphoric acid (85.0 wt%). X-ray fluorescence (XRF) characterization was carried out to collect the information about the bulk composition of SAPO-11 and samples treated with water or ethanol. The XRF measurements were conducted on a ZSX-100e instrument (Rigaku, Japan) using Rh and Au excitation tubes operated at 30 kV. The NiO particle sizes were examined by transmission electron microscopy (TEM) using a JEM 2100UHR (JEOL Japan) microscope. Pyridine-adsorbed infrared (Py-IR) was used to discriminate the acid type of samples on a Nicolet-6700 FTIR spectrometer. Samples were pre-dehydrated prior to the adsorption of pure pyridine vapor under room temperature for 24 h. After reaching equilibrium, the pyridine-adsorbed system was evacuated at 423 K for 3 h, and finally, the IR spectra were recorded. Temperature programmed reduction (TPR) was performed by the same chemisorption analyzer with NH₃-TPD. In typical runs, sample was heated to 473 K (10 K min⁻¹) under He flow and kept at this temperature for 2 h, followed by cooling down to room temperature. After introducing the reduction agent of 10 vol% H₂/Ar, the temperature was programmed to rise to 1073 K and the signals of H₂ consumption were recorded by the TCD detector. The reduction degree analysis of the pre-reduced catalysts was also carried out by the same chemisorption analyzer. The oxidized catalysts were pre-reduced in the micro-reactor under the hydrogen atmosphere, then cooled down to the room temperature. The pre-reduced catalysts were transformed into the chemisorption analyzer intermediately. After introducing the 10 vol% H₂/Ar, the temperature was programmed to rise to 1073 K and the signals of H₂ consumption were recorded by the TCD detector.

2.5. Catalytic performance assessment

The isomerization of *n*-heptane (*n*-C₇, Sinopharm Chemical Reagent Co., Ltd.) as a model reaction was carried out in a fixed-bed micro-reactor. In each run, 0.7 g of the catalyst was loaded into

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