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RESEARCH PAPER

Synthesis of MgAPO-11 Molecular Sieves and the Catalytic Performance of Pt/MgAPO-11 for *n*-Dodecane Hydroisomerization

YANG Xiaomei[1,2], XU Zhusheng[1], MA Huaijun[1,2], XU Yunpeng[1], TIAN Zhijian[1,*], LIN Liwu[1,3]

[1] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
[2] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[3] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

Abstract: A series of MgAPO-11 molecular sieves have been synthesized by varying the crystallization time, the P/Al molar ratio, and the Mg source. X-ray diffraction, X-ray fluorescence spectroscopy, and temperature-programmed desorption of NH_3 have been used to characterize the crystalline phase, the Mg content, and the acidity of MgAPO-11, respectively. The results show that the synthesis conditions have an effect on the crystalline phase, the Mg content, the acidity, and thereby the catalytic performance of Pt/MgAPO-11 in the hydroisomerization of *n*-dodecane. The reaction data reveal that the activity of Pt/MgAPO-11 is dependent on the number of strong acid sites of MgAPO-11. Short crystallization time, P/Al molar ratio of 1.0, and $Mg(NO_3)_2$ as the Mg source favor the increase in the number of the strong acid sites of MgAPO-11 and hence promote the catalytic activity of Pt/MgAPO-11 for the hydroisomerization of *n*-dodecane.

Key Words: platinum; MgAPO-11; supported catalyst; *n*-dodecane; hydroisomerization; crystallization time; P/Al ratio; magnesium source

The MgAPO-11 molecular sieve synthesized in 1986 is a member of AEL structured molecular sieves [1], which is formed by the isomorphous substitution of Mg^{2+} for Al^{3+} in the framework of the AlPO-11 molecular sieve [2]. Isomorphous substitution of Al^{3+} with Mg^{2+} leads to a negatively charged framework. When the negatively charged framework is balanced with protons, strong Brønsted acid sites of bridged MgP–OH are formed. Additionally, because the covalent P–O bond is strong and the Al–O interaction in AlPOs is essentially ionic [3], the Lewis acid sites associated with Mg^{2+} ions are also formed when Mg^{2+} ions replace Al^{3+} ions [4]. Consequently, the number of both Lewis acid sites and strong Brønsted acid sites are increased after substitution of Mg^{2+} into the framework of the AlPO-11 molecular sieve. This extends the application area of the AlPO-11 molecular sieve as a solid acid catalyst in heterogeneous reactions [5].

Hydroisomerization of long-chain *n*-alkanes is an important petrochemical process and plays an important role in the production of diesel fuels with improved cold flow properties and lubricate base oils with high viscosity index [6–8]. The isomerization reaction usually takes place over bifunctional catalysts composed of acid supports and noble metals. It has been found that MgAPO-11 as well as SAPO-11 exhibit excellent catalytic performance in the hydroisomerization of long-chain *n*-alkanes. Moreover, because of the acid strength of MgP–OH is higher than that of SiAl–OH, MgAPO-11 is more active compared with SAPO-11 [9]. In the hydroisomerization of long-chain *n*-alkanes, the catalyst performance is dependent on the properties of the molecular sieves to a large extent, which are related to the conditions of the synthesis. Therefore, in this study, the authors synthesized a series of MgAPO-11 molecular sieves through a hydrothermal method and investigated the influence of the crystallization time, P/Al molar ratio, and the Mg sources on the crystalline phase, the acidity, and the catalytic performance of the MgAPO-11 molecular sieves for the hydroisomerization of *n*-dodecane.

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*** Corresponding author.** Tel: +86-411-84379151; E-mail: tianz@dicp.ac.cn

1 Experimental

1.1 Synthesis of the molecular sieve and preparation of the catalysts

The following materials were used to synthesize MgAPO-11 molecular sieves: phosphoric acid (85% H_3PO_4, AR), pseudoboehmite (78.4% Al_2O_3), di-*n*-propylamine (n-Pr_2NH, AR, Fluka), $Mg(NO_3)_2 \cdot 6H_2O$ (AR), $Mg(CH_3COO)_2 \cdot 4H_2O$ (AR), anhydrous $MgSO_4$ (AR), MgO (CP), and deionized water. The synthesis gels were formed following the molar ratio of $0.03MgO:1.0Al_2O_3:xP_2O_5:1.2n\text{-}Pr_2NH:50H_2O$. The gels were transferred into a stainless steel autoclave lined with polytetrafluoroethylene and crystallized at 200°C. The solid products recovered by centrifugation were washed with deionized water, dried overnight at 110°C, and then calcined at 560°C in air to remove the template. The molar ratio of the gels used for the synthesis of AlPO-11 was $1.0Al_2O_3:1.0P_2O_5:1.2n\text{-}Pr_2NH:50H_2O$. The MgAPO-11 powder was pressed, crushed, and sieved to obtain particles with sizes of 20–40 mesh. The Pt/MgAPO-11 catalysts with a Pt loading of 0.5% were obtained by the impregnation of MgAPO-11 particles with an aqueous H_2PtCl_6 solution in vacuum. After impregnation, the materials were dried at 120°C and then calcined at 480°C for 8 h. Prior to the reaction, the catalysts were reduced in situ in hydrogen at 400°C for 4 h.

1.2 Characterization of the molecular sieve

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro diffractometer using Cu K_α radiation (λ = 0.15404 nm). The samples were scanned from 5° to 50° at 40 kV and 40 mA. Chemical compositions of the samples were determined using a Philips Magix X-ray fluorescence spectrometer at 60 kV and 40 mA.

Temperature-programmed desorption (TPD) of NH_3 was carried out using a homemade apparatus. Prior to the measurement, 0.1 g sample was treated in helium (40 ml/min) at 350°C for 30 min. Ammonia was then adsorbed at 100°C until saturation. The sample was then held at 100°C for 30 min. The desorption process was monitored using a thermal conductivity detector (TCD) in a temperature range from 100°C to 600°C at a heating rate of 20°C/min. The distribution of acidic sites on the MgAPO-11 molecular sieve was deconvolved by simulating TPD plots through Gaussian curves [10, 11]. The Gaussian peaks were categorized into two groups according to the temperature of the peaks. The group with peak temperatures lower than 300°C corresponds to weak acid sites, and the other group with temperatures higher than 300°C corresponds to strong acid sites. The total number of the acid sites was calculated on the basis of the amount of ammonia desorbed.

1.3 Catalyst testing

Hydroisomerization of *n*-dodecane (n-C_{12}) was carried out at atmospheric pressure in a fixed-bed stainless steel reactor under H_2 (25 ml/min) with a $H_2/n\text{-}C_{12}$ molar ratio of 15 and WHSV of 1 h^{-1}. The amount of catalysts was 0.75 g. After reaction for 1 h, the products were analyzed using an online gas chromatograph (Varian CP-3800) equipped with a flame ionization detector (FID) and a PONA capillary column (100 m).

2 Results and discussion

2.1 Effect of the crystallization time

Crystallization time is an important parameter in the synthesis of molecular sieves. The effect of the crystallization time on the properties of the MgAPO-11 molecular sieves was investigated. Fig. 1 shows the XRD patterns of the MgAPO-11 molecular sieves synthesized with different crystallization times. It can be seen that the relative crystallinity of the sample reached 80% after crystallization for 4 h. At the same time, a small amount of MgAPO-41 (AFO phase) and MgAPO-31 (ATO phase) was cocrystallized with MgAPO-11, which was probably because of the fact that both the synthesis conditions (materials, gel compositions, and synthesis media) and the structure (one-dimensionally tubular channel) of the two samples were very similar. By prolonging the crystallization time, the crystallinity increased slowly until it reached 100% at the crystallization time of 48 h. The crys-

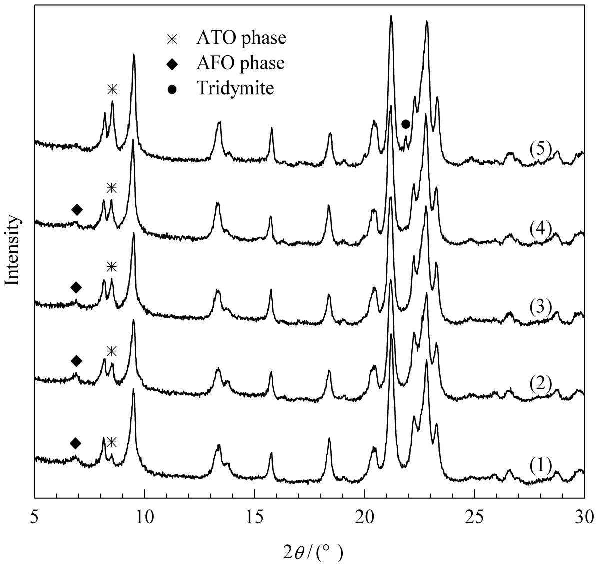

Fig. 1 XRD patterns of MgAPO-11 synthesized with different crystallization times

(1) 4 h, (2) 10 h, (3) 24 h, (4) 48 h, (5) 72 h

(The P/Al molar ratio in the gels is 1.0, and the Mg source is $Mg(NO_3)_2$.)