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Journal of Molecular Catalysis A: Chemical 263 (2007) 238–246
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Shape-selective alkylation of biphenyl over metalloaluminophosphates with AFI topology

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Received 22 April 2006; received in revised form 25 August 2006; accepted 28 August 2006
Available online 1 September 2006

Abstract

Metalloaluminophosphates with AFI topology (MAPO-5; M: Mg, Ca, Sr, Ba, and Zn) synthesized by the dry gel conversion (DGC) method were used as catalysts for the alkylation of biphenyl (BP). MgAPO-5 and ZnAPO-5 had high catalytic activities of the isopropylation; however, activities of CaAPO-5, SrAPO-5, and BaAPO-5 were much lower than those of MgAPO-5 and ZnAPO-5. These results suggest that the catalytic activity of MAPO-5 molecular sieves was originated by the acidity due to the isomorphous substitution of M^{2+} for Al^{3+}. The selectivities for 4,4′-diisopropylbiphenyl (4,4′-DIPB) for all MAPO-5 molecular sieves are at the level of 70%. On the basis of various reaction behaviors, the predominant formation of 4,4′-DIBP was considered to be mainly due to the steric restriction on the transition state of the isopropylation to the least bulky isomer inside the channel of MAPO-5 molecular sieves.

The isopropylation of BP over MgAPO-5 and ZnAPO-5 was accompanied by the isomerization of 4,4′-DIPB to thermodynamically more stable isomers, 3,4′-DIPB at the higher temperatures; the decrease in the selectivity for 4,4′-DIPB was observed in both bulk and encapsulated products. These results show that 4,4′-DIPB formed inside channels was isomerized inside the channels in addition to external acid sites. The channels of MAPO-5 molecular sieves are large enough to allow the isomerization of 4,4′-DIPB especially at higher temperatures: this is quite different from those of H-mordenite.

The *sec*- and *tert*-butylations of BP over MgAPO-5 and ZnAPO-5 gave selectively the least bulky isomers, 4,4′-di-*sec*-butylbiphenyl (4,4′-DSBB) and 4,4′-di-*tert*-butylbiphenyl (4,4′-DTBB), respectively. The selectivity for the least bulky isomer increased with increasing the bulkiness of alkylating agents in the order: isopropylation < *sec*-butylation < *tert*-butylation. This order reflects the spatial constraints of the transition sates inside the AFI structure.

Keywords: Metalloaluminophosphate; AFI topology; Shape-selectivity; Biphenyl; Isopropylation

1. Introduction

Ordered microporous aluminophosphates were first synthesized by Wilson et al. in 1982 [1]. Thereafter, many types of aluminophosphate with different micropore size and topology have been synthesized by changing the templates and/or crystallization conditions. However, the main drawback of these molecular sieves as catalytic materials is low acidity because of neutral tetrahedral framework; they only provide low catalytic activity for acid catalysis. An important progress for catalytic materials was the synthesis of silicoaluminophosphates (SAPO) and other metalloaluminophosphates (MAPO) by Flanigen et al. [2,3]. The imbalance of valency by partial replacement of Al^{3+} by divalent cations or P^{5+} by tetravalent cations gives rise to Brønsted acid sites [4]. The addition of metal cations has expanded the number and diversity of the aluminophosphates, giving new properties to the microporous materials [5].

Molecular sieves such as aluminosilicates and metalloaluminophosphates are the most promising microporous crystals

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1381-1169/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.molcata.2006.08.078

for achieving highly shape-selective catalysis because their channels are uniformly distributed and have dimensions allowing both the reactants and products with a limited size to enter, to accommodate, and to leave [6,7]. Large-pore molecular sieves are useful in the alkylation of bulky polynuclear aromatics [8–10]. The isopropylation of biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating the shape-selective nature of the molecular sieve [8–10]. The selective formation of the least bulky 4,4′-diisopropylbiphenyl (4,4′-DIPB) should be facilitated over ordered microporous materials if the catalytic sites are sterically restricted. In the previous papers, we described that 4,4′-DIPB has been selectively produced from BP over dealuminated H-mordenite (H-MOR) [8–13]. Other relevant findings have been the shape-selectivity of CIT-5 [14], SSZ-24 [15,16], SAPO-5 [17], and SSZ-31 [18]for the isopropylation of BP. The high selectivity for 4,4′-DIPB suggests that catalytically active sites in H-MOR effectively restrict the transition state to form the least bulky 4,4′-DIPB [8–13]. We proposed the shape-selective isopropylation of BP over these molecular sieves occurred by the restricted transition state mechanism.

Most of previous works on the shape-selective alkylation of polynuclear hydrocarbons have used aluminosilicates as catalysts, and there are only a few works using aluminophosphate molecular sieves [18–21]. It would be interesting to explore the possibilities of shape-selective catalysis by large pore metalloaluminophosphates. Among them, we focused on the MAPO-5 molecular sieves (AFI topology), which are isostructural with SSZ-24 [22]. To demonstrate their shape-selective catalysis over these molecular sieves, we examine the alkylation (isopropylation, *sec*-butylation, and *tert*-butylation) of BP over MAPO-5 molecular sieves (M: Mg, Ca, Sr, Ba, and Zn), and discuss the catalysis in the channels of molecular sieves with AFI topology.

2. Experimental

2.1. Synthesis of MAPO-5 molecular sieves

The synthesis of metalloaluminophosphate with AFI topology (MAPO-5; M: Mg, Ca, Sr; Ba; and Zn) was carried out by the vapor phase transport (VPT) method, a type of dry-gel conversion (DGC) methods [19,20]. The molar composition of the starting gel was $1.0Al_2O_3$–$0.10MO$–$1.0P_2O_5$–$0.76Et_3N$–$45H_2O$. The typical procedures are shown for the synthesis of MgAPO-5. A 2.05 g of aluminum isopropoxide (5.0 mmol as Al_2O_3) was slurried in water (1.85 g). To this slurry, 1.15 g of 85% phosphoric acid (5.0 mmol as P_2O_5) diluted in water (2.0 g) was added dropwise over a period of 0.5 h with constant magnetic stirring. To the resulting solution, a 0.107 g of magnesium acetate (0.5 mmol as MgO) was added and the stirring was further continued for 0.5 h. The gels thus obtained were dried at 80 °C in an oil bath with continuous magnetic stirring to remove water. Finally, a mixture of 384 mg of triethylamine (3.8 mmol) and 150 mg of water was placed at the bottom of the autoclave so as to be supplied as vapor. The crystallization was carried out by heating the autoclave statically at 175 °C for 24 h in a convection oven. The autoclave assembled for the DGC method is shown in our previous paper [23].

After the crystallization, the products were washed with distilled water, separated by centrifugation, and dried at 100 °C overnight. The as-synthesized samples were calcined in a muffle furnace in a flow of air (flow rate: 50 ml/min) as follows: the temperature was raised from room temperature to 550 °C in 4 h, kept at this temperature for another 7 h, and finally cooled to room temperature in ambient conditions.

Other MAPO-5 molecular sieves were synthesized in a similar manner to MgAPO-5 [19,20].

2.2. Catalytic reaction over MAPO-5 molecular sieves

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave under a constant pressure of alkylating agent. Typical procedures of the isopropylation of BP are as follows: BP (7.7 g, 50 mmol) and MAPO-5 (250 mg) were mixed in an autoclave, which was flushed with nitrogen followed by heating to a desired temperature. Propene was then introduced to the desired pressure (0.8 MPa), and this pressure was maintained throughout the reaction period (4 h). After the reaction, the autoclave was cooled, and the catalyst was filtered and washed with toluene (50 ml). The solution (ca. 1.5 ml) was taken from the total bulk products and diluted with toluene (1.5–6.0 ml). The products obtained after the reaction were identified by gas chromatography–mass spectroscopy (GC–MS; QP5000, Shimadzu Corporation, Kyoto, Japan), and analyzed by a Shimadzu-14A gas chromatograph equipped with an Ultra-1 capillary column (25 m × 0.2 mm; Agilent Technologies, MA, USA).

The conversion of BP and the yield of each products were calculated on the basis of consumed BP. The selectivities for each diisopropylbiphenyl (DIPB) and isopropylbiphenyl (IPBP) isomer are expressed based on total amounts of IPBP and DIPB isomers, respectively.

$$\text{selectivity for a DIPB (IPBP) isomer (\%)} = \frac{\text{each DIPB (IPBP) isomer (mol)}}{\text{DIPB (IPBP) isomers (mol)}} \times 100$$

The products encapsulated inside the catalysts were analyzed as follows: after collection of the bulk products (as mentioned earlier), the catalyst was washed well with 200 ml of acetone, and dried at 110 °C for 12 h. Then 300 mg of resulting catalyst was carefully dissolved in 3 ml of aqueous hydrofluoric acid (47%) at room temperature. This solution was basified with solid potassium carbonate, and the organic layer was extracted three times with 20 ml of dichloromethane. After removal of the solvent *in vacuo*, the residue was dissolved in 5 ml of toluene, and then 10 mg of naphthalene was added as an internal standard. GC analysis was performed similarly to the case of bulk products.

The *sec*- and *tert*-butylations of BP were carried out in a similar manner as the isopropylation using 1-butene and 2-methylpropene as alkylating agents, respectively. Pressures of 1-butene and 2-methylpropene were set at 0.4 MPa.