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The isopropylation of biphenyl over transition metal substituted aluminophosphates: MAPO-5 (M: Co and Ni)

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ABSTRACT

The isopropylation of biphenyl (BP) was examined over transition metal substituted aluminophosphates (MAPO-5; M: Co and Ni) with 12-membered (12-MR) oxygen ring pore-entrances of AFI topology. The MAPO-5 samples were synthesized by dry gel conversion method using trimethylamine as a structure directing agent, and their properties were characterized by XRD, XPS, SEM, N_2 adsorption, NH_3-TPD, pyridine adsorption, and *o*-xylene uptake. They are clear crystals without impurity phases and agglomerates, and found small amounts of Brønsted acid sites which are expecting active for acid catalysis. The isopropylation of BP over both of Co(5)APO-5 and Ni(5)APO-5 at 250 °C gave the high selectivities for 4,4′-DIPB: 65–75%. 4-IPBP is almost exclusive precursor of 4,4′- and 3,4′-DIPB. 3-IPBP was not significantly concerned even though 3-IPBP was predominant among IPBP isomers at the late stages: the MAPO-5 channels allow preferential access of 4-IPBP, and prevent the access of 3-IPBP due to reactant selectivity mechanism. The selective formation of 4,4′-DIPB occurred by preferential exclusion of bulkier 3,4′-DIPB and other isomers through the steric interaction of transition states with the channels by the restricted transition state selectivity mechanism. MAPO-5 (M: Co and Ni) has the same level of the selectivities for 4,4′-DIPB to SSZ-24 and other MAPO-5 (M: Si, Mg, and Zn), and these selectivities were originated by the AFI channels. The selectivities for 4,4′-DIPB were kept 65–75% at low and moderate temperatures over MAPO-5 (M: Co and Ni); however, they were decreased by the isomerization to stable 3,4′-DIPB with the increase in temperature.

1. Introduction

Shape selective catalyses in confined environments of ordered solid acids introduce a type of controls for the prevention of bulky products in their channels, resulting in the formation of the least bulky products which are not always kinetically and/or thermodynamically favored [1,2]. Ordered molecular sieves, such as zeolites, are the most favorable candidates for the purpose because their pores and channels are uniformly distributed, and their dimensions allow both reactants and products to enter, reside, and leave in the catalytic process [1].

Shape-selective catalyses over zeolites are based on the differentiation of reactants, products, and/or reaction intermediates according to shape and size in sterically confined environments [3]. If the zeolite pores and channels are small enough to accommodate both of reactants and products, the reactant conversion and product formation probabilities are determined by the molecular sizes and the configurations of the pores and channels. Only a reactant molecule smaller than the critical sizes against the pores, can enter in the pores, and reacts at the catalytic site in the channels. Furthermore, only a product molecule, which can diffuse out through the pores, appears as a product. Therefore, it is important to fit zeolites with the type of catalysis. In particular, the shape-selective catalysis appears through interaction of zeolites with reactants, transition

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states, and products by “reactant”, “product”, and “restricted transition state” selectivities [3].

Ordered microporous aluminophosphates (APO) were first synthesized by Wilson et al. in 1982 [4]. They have frameworks composed of networks of aluminum and phosphorous with similar topologies of zeolites. They are expected to work as molecular sieves for the catalysis, separation of organic compounds, *etc*. The drawback of these materials as catalytic materials, particularly for acid catalysis, is low acidity because of neutral tetrahedral framework composed of aluminum (three valence) and phosphorous (five valence); however, the introduction of the other metal cations to their frameworks enhances the appearance of acidities: typical examples are silicoaluminophosphates (SAPO) and other metalloaluminophosphates (MAPO) by Flanigen and her co-workers [5,6]. The valent imbalance by partial replacement of Al^{3+} by divalent cations or P^{5+} by tetravalent cations gives rise to Brønsted acid sites [7]. The addition of metal cations will expand the number and diversity of the APO, and afford new properties to the microporous materials, such as acid catalysis, oxidation, *etc*. depending on the types of metal species [9,10].

The isopropylation of biphenyl (BP) is a typical acid catalysis in Friedel–Crafts alkylation of aromatic hydrocarbons, which demonstrates the shape-selective nature of the molecular sieve [10–21]. 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 properly restricted by their channels [10–12,13].

In the previous papers, we described that 4,4′-DIPB has been selectively produced from BP over dealuminated H-mordenite (MOR) [12,13]. We also found SSZ-24 with AFI topology has high potentials for the shape-selective formation of 4,4′-DIPB [14–16]. However, most of previous works on the alkylation of polynuclear hydrocarbons have used zeolites as catalysts, and there are only a few works using MAPO [18–21]. It is interesting to explore the possibilities of shape-selective catalysis by large pore MAPO. Among them, we focused on the MAPO-5 of AFI topology, which are isostructural with SSZ-24 [22]. We found MAPO-5 (M: Si, Mg, and Zn) for aluminophosphate version and SSZ-24 for aluminosilicate version gave the almost same levels of the selectivities for 4,4′-DIPB [14–16,18–20]. These results indicate that shape-selective natures of these materials are due to AFI topology based on their oxygen rings.

In this paper, we examined the isopropylation of BP over transition metal substituted APO-5 (MAPO-5; M: Co and Ni) in order to clarify the influence of transition metals in the acid catalysis. This is the first example succeeding in shape-selective catalysis for transition metal substituted APO-5.

2. Experimental

2.1. Reagents

Aluminum triisopropoxide, cobalt(II) acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$), and nickel(II) acetate tetrahydrate ($Ni(OAc)_2 \cdot 4H_2O$), and phosphoric acid (85%), trimethylamine (Et_3N), BP, and other organic chemicals were obtained from Sigma–Aldrich. 4,4′-Diisopropylbiphenyl (4,4′-DIPB) was purchased from Tokyo Chem. Ind., Tokyo, Japan.

2.2. The synthesis of MAPO-5 (M: Co and Ni)

The synthesis of CoAPO-5 was carried out by dry gel conversion method (vapor phase transfer method) [23]. The gel composition for the synthesis of Co(5)APO-5 was as follows: $1.0Al_2O_3$-0.03-0.40CoO-$1.0P_2O_5$-$0.76Et_3N$-$45H_2O$. The typical procedures are as follows: 2.05 g of aluminum triisopropoxide (5.0 mmol as Al_2O_3) was slurred 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 cobalt acetate (0.5 mmol as CoO) 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. When the gel became thick and viscous, it was homogenized manually using a Teflon rod and this was continued until it dried. The gels in Teflon cups were placed in the autoclaves (23 ml, Parr Instrument Co., IL, U.S.A.), and, finally, a mixture of 384 mg of Et_3N (3.8 mmol) and 150 mg of water was taken at the bottom so as to be supplied as water 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 synthesis is shown in our previous paper [22].

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.

NiAPO-5 was synthesized in a similar manner to CoAPO-5 using nickel acetate as NiO precursor.

The resultant aluminophosphates are expressed as M(x)APO-5, where M is transition metals, and *x* is input percentage of substituted metal (mol) with aluminum (mol) (see Table 1).

2.3. The isopropylation of BP over MAPO-5 (M: Co and Ni)

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave (Nitto Koatsu, Tsukuba, Japan) under a constant pressure of propene. Typical procedures of the isopropylation of BP are as follows: BP (3.84 g, 20 mmol) and Co(5)APO-5 (100 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 the reaction started by the agitation. The 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 (10 ml). The solution (*ca*. 1.5 ml) was taken from the total bulk products and diluted with toluene (1.5 ml). The products were identified by gas chromatography–mass spectroscopy on Shimadzu GC–MS; QP5000, and analyzed by a Shimadzu 2010plus gas chromatograph equipped with an Ultra-1 capillary column (25 m × 0.2 mm; film thickness: 25 μm; Agilent Technologies).

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

The products encapsulated in the catalysts were analyzed as follows: after collection of the bulk products (as mentioned earlier), the catalyst was washed 5 times with 20 ml of acetone, and dried at 110 °C for 12 h. Then 20 mg of resulting catalyst was carefully dissolved in 0.5 ml of concentrated hydrochloric acid (35%) at room temperature. This solution was basified with solid potassium carbonate, and the organic layer was extracted three times with 2 ml of dichloromethane. After removing of the solvent *in vacuo*, the residue was dissolved in 0.5 ml of toluene. GC analysis was performed similarly to the case of bulk products.

2.4. The characterization of MAPO-5 (M: Co and Ni)

Crystallinity and phase purity of MAPO-5 were confirmed on a Rigaku Ultima III X-ray diffractometer with Cu Kα radiation