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Thermally stable trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves: Synthesis, characterization, and catalytic properties

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Dedicated to Professor Hemant V. Keer on the occasion of his 70th birthday.

Abstract

Thermally stable trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves were synthesized and systematically characterized using analytical and spectroscopic techniques, including XRD, TEM, ICP–AES, TGA–DTA, N_2 sorption, DRUV–vis, EPR, and Mössbauer spectroscopy. The characterization studies showed that framework substitution of trivalent iron in tetrahedral framework position of the mesoporous aluminophosphate has taken place. Mössbauer revealed the presence of a small amount of divalent iron. This material has high thermal stability with regard to the dislodgement of trivalent iron from the framework structure on calcination and showed excellent activity in the liquid-phase oxidation of cycloalkanes such as cyclohexane, cyclooctane, and cyclododecane in presence of molecular oxygen or air under mild reaction conditions. FeHMA behave as a heterogeneous catalyst; the catalytic activity was practically unaffected by recycling experiments. Furthermore, the oxidation was successful for the bulkier cycloalkane molecules. A comparative study with selected iron-containing molecular sieve-based catalysts indicated that FeHMA is a promising heterogeneous catalyst with respect to its microporous analogue (FeAPO-5) as well as the silicate analogues, microporous FeS-1 and mesoporous FeMCM-41.

Keywords: Mesoporous; Aluminophosphates; Iron; FeHMA; Oxidation; Cycloalkanes; Cyclohexane; Cyclooctane; Cyclododecane

1. Introduction

The importance of trivalent iron complexes in biological oxidation as well as their use as catalysts in conjunction with a variety of oxidants in organic synthesis has prompted extensive studies under homogeneous reaction conditions [1–8]. However, these homogeneous catalyst systems are often impracticable because of easy deactivation, difficulties in regeneration, and separation of the catalyst. This has led to the development of cleaner, environmentally benign heterogeneous catalytic routes, which may replace conventional stoichiometric or homogeneously catalyzed organic synthesis. Over the years, various supported catalysts have been suggested for this purpose; however, the leaching of active metal ions resulted in a short catalyst lifetime [9]. Trivalent iron-substituted molecular sieves (silicates, aluminosilicates, and aluminophosphates) have attracted considerable attention. Although the fact that trivalent iron occupies the tetrahedral site in zeolitic framework was established long ago, McNicol and Pott [10] showed in 1972 that the iron impurities in faujasite occupy the substitutional framework sites. A detailed synthesis, characterization, and description of the catalytic properties of a ferrisilicate with MFI structure were first published in 1985 [11]. The isomorphous substitution of trivalent iron in the framework structure of many silicate and aluminosilicate topologies, including ZSM-5, ZSM-11, ZSM-12, ZSM-23, EU-1, EU-2, zeolite-L, sodalite, beta, faujasite, and mordenite have also been reported [12,13]. The isomorphous substitution of trivalent iron in aluminophosphate molecular sieves with APO-5, APO-11, and VPI has also been published [14–17]. All of these catalysts have been used in

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numerous catalytic reactions, including the oxidation of cyclohexane and phenol and the Prins condensation reaction [18–22].

The small pore opening of these microporous materials restricts their use in processes with bulky molecules, however. Although the trivalent iron-substituted mesoporous silica molecular sieves [23–33] showed much promise for large molecules, they have the same disadvantages as the microporous materials. A major problem with both microporous and mesoporous molecular sieve-based materials is the instability of trivalent iron in the tetrahedral framework during heat treatment. This problem is well documented in the literature and, hence the application of iron-substituted molecular sieves has been limited, in contrast to many other transition metal-containing molecular sieves. To the best of our knowledge, no one has reported the synthesis of trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves. These sieves are similar to the mesoporous silicates/aluminosilicates in that they have the MCM-41 structure [34–38]. Compared with the silicates/aluminosilicates, the low pH synthesis and the flexible network of HMA are the main factors favoring stabilization of large amounts of trivalent iron in the matrix. Here we give a detailed account of the synthesis, characterization, and catalytic properties of FeHMA. A preliminary description of this work was given elsewhere [39]. For comparison, we also studied mesoporous iron-substituted silicate (FeMCM-41) as well as microporous iron-substituted aluminophosphate (FeAPO-5) and silicate (FeS-1) catalysts.

The development of environmentally benign catalytic oxidation processes with eco-friendly oxidants such as hydrogen peroxide, molecular oxygen, and air under mild reaction conditions is of immense industrial importance [40,41]. In recent years, several groups have described a number of promising heterogeneous catalysts for the oxidation of cyclohexane [42–45]. No reports are available on the oxidation of higher cycloalkanes such as cyclooctane and cyclododecane, in contrast to homogeneous catalysts for the oxidation of these bulky cycloalkane molecules. But low yields, longer reaction periods, deactivation of the catalysts through the oxidative degradation of ligands, problems with separation, and the production of hazardous byproducts have made these catalysts uninteresting [46–48]. In this investigation, we used trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves for the selective oxidation of cycloalkanes under mild reaction conditions. A preliminary account of the work has been published elsewhere [39].

2. Experimental

2.1. Starting materials

We used phosphoric acid (85%; Qualigens), aluminium isopropoxide (97%; Merck), tetramethyl ammonium hydroxide (TMAOH, 25 wt% in water; Aldrich), cetyltrimethylammonium chloride (CTAC, 25 wt% in water; Aldrich), CABOT fumed silica (99.8%; Aldrich), cetyltrimethylammonium bromide (CTAB, 99%; Aldrich), sodium hydroxide (NaOH, 98%; Loba), ferric nitrate (>98%; Aldrich), triethylamine (99.5%; Thomas Baker), pseudoboehmite (70%; Vista), tetrapropylammonium bromide (TPAB, 98%; Lancaster), cyclohexane (99.5%; Merck), *tert*-butyl hydroperoxide (TBHP, 70% aqueous solution; Lancaster), cyclooctane (99%; Lancaster), cyclododecane (99%; Lancaster), methyl ethyl ketone (MEK, 99.5%; SD fine), and glacial acetic acid (>99%; Fischer).

2.2. Hydrothermal synthesis

2.2.1. FeHMA

The synthesis was carried out as follows. Phosphoric acid (1.4 mL) was diluted with 11.7 mL of water. Then 4.08 g of aluminium isopropoxide was added under vigorous stirring, followed by the addition of an iron nitrate solution (0.378 g in 5 mL of water). The mixture was stirred for 1 h at 343 K, after which TMAOH (7.3 mL) was added dropwise. The slurry was stirred for few hours, then drops of CTAC (13.2 mL) were added and the mixture was stirred for another 12 h. The pH of the gel was maintained at 10. The final gel, with a molar composition of $(1-x)$ Al_2O_3:P_2O_5:x Fe_2O_3:CTAC:2.8 TMAOH: 70 H_2O, was kept in a Teflon-lined autoclave and heated in an air oven at 373 K for 6 days until crystallization. The resultant solid was washed repeatedly with distilled water, filtered, and dried at 343 K for 12 h. Calcination was performed at 823 K for 1 h in a flow of N_2 and for 2 h in air. By varying the value of x, we prepared samples of varying molar ratios ($[Al + P]/Fe$): FeHMA(200), FeHMA(100), FeHMA(50), and FeHMA(25).

2.2.2. FeMCM-41

The synthesis was carried out as described previously [24]. First, TMAOH was dissolved in water, and the mixture was stirred for 15 min. Fumed silica was added slowly (solution A). Another mixture was prepared by mixing CTAB and NaOH in distilled water and stirring it for 30 min (solution B). Solution A was then added dropwise to solution b, and the resulting gel was stirred for 1 h to achieve homogenization. Acidified ferric nitrate solution was added dropwise to the gel to prevent the precipitation of iron; the pH of the gel was maintained at about 11.3–11.5. The final (molar) gel composition was 1 SiO_2:0.27 CTAB:0.26 NaOH:0.26 TMAOH:60 H_2O:0.01 Fe_2O_3 ($Si/Fe = 50$). The gel was transferred to Teflon-lined stainless steel autoclaves and kept in an air oven for crystallization at 423 K for 216 h. The solid products were washed, filtered, and dried in an oven at 353 K for 12 h. The as-synthesized samples were calcined at 823 K in a flow of N_2 for 2 h and in air for 8 h.

2.2.3. FeAPO-5

The synthesis was performed according to the following procedure. Pseudoboehmite (13.1 g) was hydrolyzed in 20 mL of distilled water for 2 h until a slurry was obtained. Phosphoric acid (13.2 mL) was added dropwise to this slurry, which was stirred for 2 h until a homogeneous gel was obtained. During stirring, 1.84 g of ferric nitrate, dissolved in 10 mL of acidified water, was added dropwise to the homogeneous gel for 1 h. The organic template, 36 mL of TEAOH, was added dropwise, and the mixture was stirred vigorously for 3 h. The final gel (0.09 Al_2O_3:0.1 P_2O_5:0.1 TEAOH:0.0038 Fe_2O_3:4 H_2O; [Al +