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Synthesis, characterization and catalytic properties of trivalent iron substituted hexagonal mesoporous aluminophosphates†

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Trivalent iron substituted hexagonal mesoporous aluminophosphate molecular sieve has been synthesized and characterized for the first time, which showed excellent catalytic activity and reusability for the cyclohexane oxidation reaction under mild conditions.

The incorporation of trivalent iron into silicate as well as aluminophosphate molecular sieves has drawn considerable interest due to their promise as redox heterogeneous catalysts. Several iron containing silicate and aluminosilicate materials, both microporous (silicalite,[1] LTL[2] and ZSM-5[2]) and mesoporous (MCM-41,[3] MCM-48[4] and HMS[5]), have been reported in the literature. However, one of the major problems of all these molecular sieves is the instability of Fe^{3+} ions in its tetrahedral framework during heat treatment. On the other hand, the flexibility of the aluminophosphate network may possibly favour the stabilization of Fe^{3+} ions in the matrix[6] and hence lead to good catalytic activity.[7] However, there is no report on the synthesis of trivalent iron substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves. In this communication, we report for the first time, the synthesis, characterization and catalytic properties of FeHMA.

The synthesis of FeHMA was carried out by the following procedure. Phosphoric acid (85%; Qualigens) was first diluted with water; to this aluminium isopropoxide (97%; Merck) was added under constant stirring followed by the addition of ferric nitrate (>98%, Aldrich) solution. The resulting mixture was stirred at 343 K for 1 h and then tetramethylammonium hydroxide (TMAOH; 25 wt% in water; Aldrich) was added dropwise. After a few hours of stirring, cetyltrimethylammonium chloride (CTAC; 25 wt% in water; Aldrich) was added dropwise and stirring was continued for another 12 h. The pH of the gel was maintained at 10. The final gel, having a molar composition of: $0.96\,Al_2O_3:P_2O_5:0.04\,Fe_2O_3:CTAC:2.8\,TMAOH:70\,H_2O$ ($[Al + P]/Fe = 49$) was kept in a Teflon-lined autoclave and heated in an air oven at 373 K for 6 days for crystallization. The resultant solid product was washed repeatedly with distilled water, filtered off and dried at 343 K for 12 h. Calcination was performed at 823 K for 1 h in a flow of N_2 followed by 2 h in air.

The as-synthesized as well as calcined samples were characterized by low angle powder X-ray diffraction (XRD, Rigaku-miniflex, Cu-Kα), inductively coupled plasma-atomic emission (ICP-AES, Labtam Plasma Lab 8440), diffuse reflectance ultraviolet-visible (DRUV-VIS, Shimadzu UV 260) and EPR (Varian) spectroscopic techniques. The Brunauer–Emmett–Teller (BET) surface area was measured on a Sorptomatic-1990 instrument. The pore size was calculated using the Horvath–Kawazoe (H–K) method. Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were recorded on a Philips 200 microscope operated at 160 kV. Absorption Mössbauer spectra were recorded at room temperature in constant acceleration mode with a driving unit MTV 100 from WissEL.

The XRD patterns of as-synthesized HMA as well as FeHMA show well resolved reflections corresponding to the mesoporous MCM-41 structure.[8,9] The increase in unit cell parameter of FeHMA (a_o = 47.3 Å; d_{100} = 41.6 Å) compared to HMA (a_o = 45.4 Å; d_{100} = 39.4 Å) indicates a possible substitution of Fe^{3+} in the aluminophosphate network due to the larger crystal radius of Fe^{3+} (0.63 Å) than Al^{3+} (0.52 Å) and P^{5+} (0.32 Å).[10] On the other hand, the diffraction patterns of calcined FeHMA and HMA show a single broad reflection (unit cell parameters a_o = 36.8 Å, d_{100} = 31.8 Å and a_o = 33.7 Å, d_{100} = 29.2 Å, respectively), corresponding to disordered mesoporous structures.[9,11] The presence of Fe^{3+}, however, reduces the shrinkage of the pore diameter in FeHMA (~22%) than HMA (~26%). The disordered arrangement is further confirmed by TEM (Fig. 1(a)) and ED (Fig. 1(b)) studies. The BET surface area (923 $m^2\,g^{-1}$), pore volume (0.48 $cm^3\,g^{-1}$) and average pore size (28 Å) of the calcined FeHMA are in the typically mesoporous range. ICP-AES analysis of calcined FeHMA shows 2.3 wt% of iron.

DRUV-VIS spectra (Fig. 2) of as-synthesized and calcined FeHMA samples show two prominent bands (a strong band at

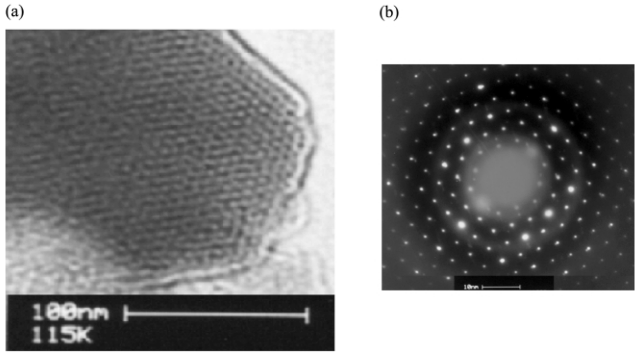

Fig. 1 (a) TEM image of calcined FeHMA and (b) ED pattern of calcined FeHMA.

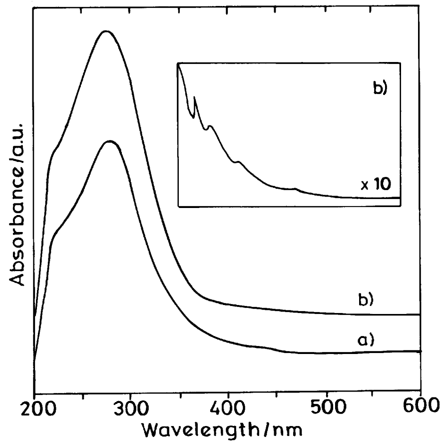

Fig. 2 DRUV-VIS spectra of: (a) as-synthesized FeHMA and (b) calcined FeHMA.

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† Electronic supplementary information (ESI) available: XRD patterns. See http://www.rsc.org/suppdata/cc/b2/b204215k/

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~290 nm associated with a shoulder at 230 nm) in the UV region arising from charge transfer transitions involving Fe^{3+} in $[FeO_4]^-$ tetrahedral geometry.[1] In addition, weak bands (see inset) in the range 350–500 nm, which originate from d–d forbidden transitions further supports the tetrahedral environment for trivalent iron.[1] Most importantly, unlike many silicate and aluminosilicate based systems,[1–5] no broadening of the spectrum corresponding to dislodgement of isolated framework Fe^{3+} ions was observed after calcination. Fig. 3 depicts the EPR spectra of FeHMA samples. The as-synthesized FeHMA showed a strong signal at $g_{\text{eff}} = 4.3$ assigned to high spin Fe^{3+} in distorted tetrahedral environment and a very weak (or absent) signal at $g_{\text{eff}} = 2.0$ attributed to high spin Fe^{3+} in symmetrical tetrahedral/octahedral coordination.[1,2] The intensity of the $g_{\text{eff}} = 4.3$ signal increases sharply at 77 K suggesting Fe^{3+} in isolated tetrahedral locations. It is also interesting to note that, unlike many ferrisilicates,[1–5] FeHMA does not show any dislodgement of Fe^{3+} from the matrix even after calcination and the results are in line with DRUV-VIS studies. The results are further confirmed by room temperature Mössbauer studies where the calcined FeHMA shows a strong symmetrical doublet (Fig. 4; IS = 0.16 mm s^{-1}; QS = 0.8 mm s^{-1}) corresponding to Fe^{3+} in distorted tetrahedral coordination[5,12] and a weak doublet attributed to Fe^{2+} in tetrahedral coordination originating from reduction of Fe^{3+} during synthesis.[13]

The liquid phase oxidation of cyclohexane was carried out at 373 K using 50 mg FeHMA, 18 mmol of cyclohexane (99.5%; Merck), 5 mmol of 2-butanone (99.5%; S.D. fine chemicals) and 18 mmol aq. H_2O_2 (30 wt%; S.D. fine chemicals) in 10 ml acetic acid (99.9%; SISCO) for 12 h under atmospheric pressure. The reaction products were analyzed by gas chromatography (GC, Nucon 5700) using Carbowax column. The catalyst showed good conversion (84%) with cyclohexanol (66%), cyclohexanone (27%) and cyclohexyl acetate (7%) as products. It is also to be noted here, that using HMA or no catalyst (blank), the reaction shows only ~10% conversion. Thus, the observed high activity of FeHMA can be attributed to the presence of isolated tetrahedral Fe^{3+} in the HMA matrix. Furthermore, the catalyst was recycled three times without losing the activity (Fig. 5). Thus, the results indicate FeHMA is a promising heterogeneous catalyst under mild conditions compared to many other reported catalysts.[14]

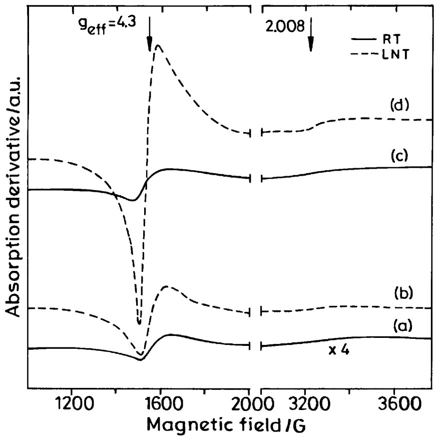

Fig. 3 EPR spectra of: (a), (b) as-synthesized FeHMA and (c), (d) calcined FeHMA.

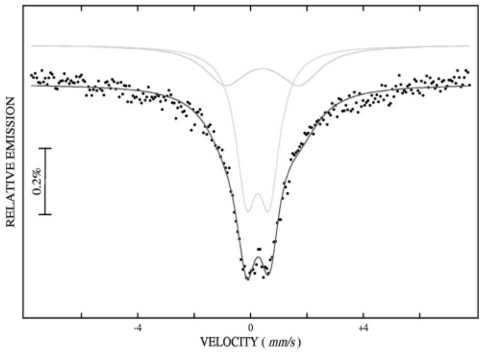

Fig. 4 Mössbauer spectrum of calcined FeHMA.

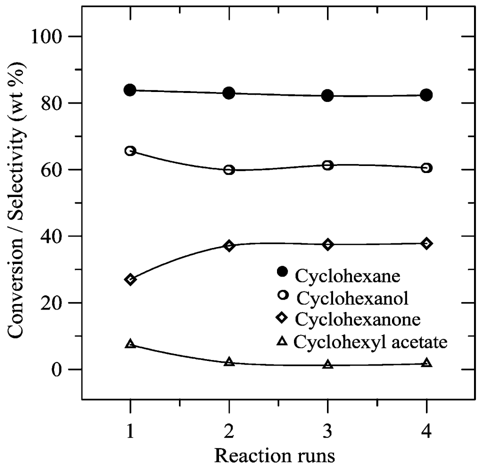

Fig. 5 Recycling studies over calcined FeHMA.

In conclusion, for the first time, Fe^{3+} substituted mesoporous aluminophosphate molecular sieves have been successfully synthesized. Various characterization techniques suggest the presence of isolated Fe^{3+} in distorted tetrahedral framework sites. Further, dislodgement of tetrahedral Fe^{3+} was not observed during heat treatment indicating the stability of Fe^{3+} in the matrix. The catalyst showed excellent activity and recyclability for the oxidation of cyclohexane under mild conditions.

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