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Synthesis, characterization of an AlPO-CJ_2 analogue containing heteroatomic Eu†

Lei Zhang, Caiyi Lu and Yingcai Long*
Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China. E-mail: yclong@fudan.edu.cn

Received (in Cambridge, UK) 30th May 2002, Accepted 2nd August 2002
First published as an Advance Article on the web 15th August 2002

An analogue of AlPO-CJ_2 microporous aluminophosphate containing heteroatomic Eu was hydrothermally synthesized *in situ* in the reactant system of carbamide–NH_4F–Al_2O_3–P_2O_5–H_2O, and characterization by ICP, powder XRD, Mössbauer spectra, ^{31}P MAS NMR and luminescent spectroscopy prove that Eu is incorporated into the framework.

It is an attractive topic to combine rare earth elements (RE) with porous materials for developing new types of functional materials. RE elements have been applied widely in the field of functional materials based on their unique optical and electronic properties. Porous materials, especially zeolite molecular sieves, are being used as hosts in nano-composite materials.[1–3] Traditionally, ion exchange is an easy way to approach the combination of RE and porous materials. Ozin and co-workers incorporated Eu into the cages of Y zeolite by ion exchange. Eu was used as a site-selective probe of extra-framework cations. Fluorescence spectra show that the local symmetries of the sites are of C_s, C_n or C_{nv} point group.[4] In the work of Rainho *et al.*, microporous titanosilicates ETS-10 ion exchanged by Eu was synthesized. The various local symmetries for Eu^{3+} sites in ETS-10 are assigned to C_1, C_2, C_s or C_{2v} point groups, based on the local field splitting of $^7F_{1,2}$ energy levels.[5]

Exploring new catalysts is another aim of the combination of RE and porous materials. RE ion exchanged zeolites are a typical example, with large-scale applications as catalysts, such as hydrocarbons cracking, isomerization and alkylation in the petro/chemical industry. However, because of weak interaction between RE ions and the framework of zeolites, the RE is easily washed away, which leads to a short life of the catalysts. Thus, the possibility of incorporating RE elements into the framework of porous materials is investigated. He and co-workers claimed that they incorporated La into the framework of a mesoporous molecular sieve MCM-41, which may be used as an excellent catalyst.[6]

However, it is relatively difficult to incorporate RE elements into the framework of zeolites since RE ions show strongly ionic bonding. As a result the tendency of incorporating RE into zeolite framework and forming covalent bond is very low. Generally, RE form covalent bond only under high temperature conditions. For example, Ce–O covalent bonds are found in the structure of Sr_2CeO_4, a new phosphor, prepared by high temperature solid reaction.[7]

AlPO-CJ_2, a microporous aluminophosphate, has been prepared using hexamethylenetetraamine as a template by Yu *et al.* in 1990.[8] The framework of AlPO-CJ_2 consists of AlO_5, AlO_5F and PO_4 units. Remarkably, there exist terminal O atoms because not all O atoms are shared in the framework. Such terminal oxygen atoms can absorb energy by charge transfer (CT) processes. Therefore, AlPO-CJ_2 is expected to be useful as a host in luminescent materials because the CT process is helpful in enhancing the luminescence of phophors.[9]

Eu_xAl_{1-x}PO-CJ_2 (sample S_{Eu}) was hydrothermally synthesized in a carbamide–NH_4F–Eu_2O_3–Al_2O_3–P_2O_5–H_2O reactant system at 170 °C. The molar ratio of the reactants for synthesis was: 2.0 NH_4F : 2.0 carbamide : 0.1 Eu_2O_3 : 0.9 Al_2O_3 : 1.0 P_2O_5 : 70 H_2O.

Fig. 1 presents the XRD patterns of sample S_{Eu} and AlPO-CJ_2 Here, the XRD pattern for the latter is obtained by computer simulation according to the data of single crystal structural analysis reported in ref. 8. The similar XRD patterns prove that the topography for sample S_{Eu} is close to that of AlPO-CJ_2, and no detectable Eu_2O_3 or other crystalline impurity phases exist. However, because the Eu–O bond is longer than that the Al–O bond, which leads to the MO_5 (M = Eu) polyhedra distorting substantially. As a result, the symmetry of AlPO-CJ2 with heteroatomic Eu may change. Furthermore, because Eu more strongly scatters X-rays, the structure factor of sample S_{Eu} must be different in comparison with that of AlPO-CJ_2. The above factors, as well as the crystalline orientation of samples, leads to differences of XRD patterns for the two samples.

ICP measurements prove that sample S_{Eu} contains a certain amount of Eu. The atomic ratio of P : Al : Eu is 1 : 0.917 : 0.058, and (Al + Eu)/P = 0.975 ≈ 1, implying a possibility that Eu is incorporated into the framework of sample S_{Eu} and partly replaces Al.

The Mössbauer spectrum of sample S_{Eu} is shown in Fig. 2. The result of fitting shows that there is only one type of local environment of Eu in sample S_{Eu}. The isomer shift (I.S.) is 0.22 ± 0.01 mm s^{-1}, confirming the valence of Eu in sample S_{Eu} is +3. The value of the quadrupole interaction (Q.I.) is 6.24 ± 0.01 mm s^{-1} and indicates a deviation of Eu site from high symmetry even if the contribution of ligand to Q.I. is considered.[10] Because the I.S. of Eu_2O_3 is at 0.88(1) mm s^{-1} (cubic) or 1.09 mm s^{-1} (monoclinic), the possibility of a Eu_2O_3 phase existing in sample S_{Eu} is ruled out completely.[11]

The ^{31}P MAS NMR spectrum of sample S_{Eu} is shown in Fig. 3 in which two strong peaks occur at −21.2 and −10.2 ppm, almost at the same positions as those of AlPO-CJ_2.[12] Addition-

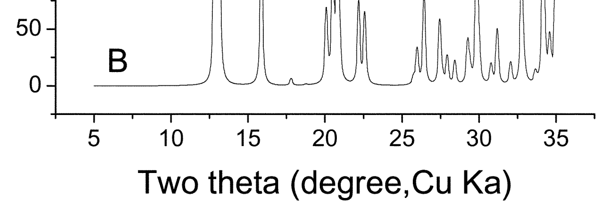

Fig. 1 The XRD patterns for S_{Eu} (A) and AlPO-CJ_2 (B).

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† Electronic supplementary information (ESI) available: SEM photographs; Mössbauer data; ^{27}Al MAS NMR spectrum; characterization and synthesis details. See http://www.rsc.org/suppdata/cc/b2/b205254g/

DOI: 10.1039/b205254g

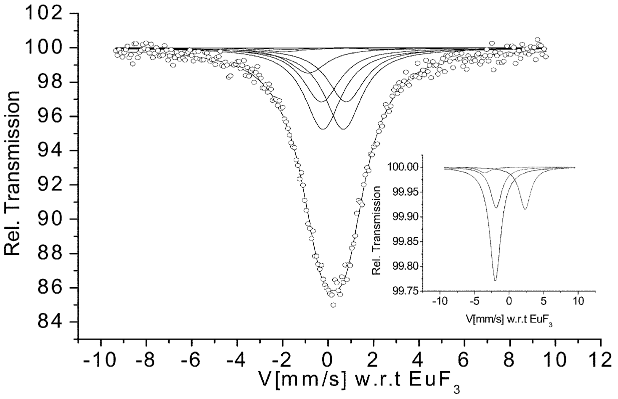

Fig. 2 Mössbauer spectrum of sample S_{Eu}, Circles denote the experimental data and the full line shows the fitting to nine expected lines. The inset shows a zoom of four weak sub-spectrum lines; range of relative transmission is 99.75–100.

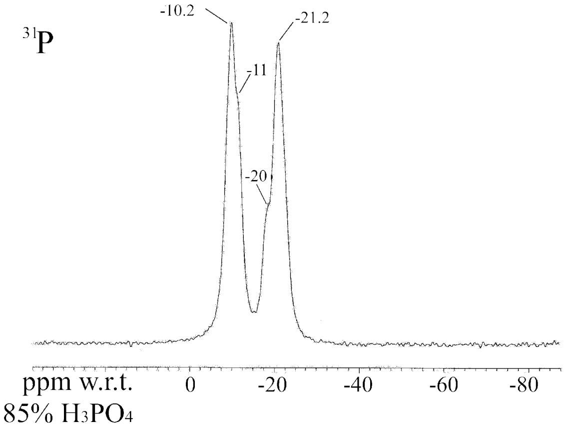

Fig. 3 7.0 T ^{31}P MAS NMR spectrum of sample S_{Eu}, spinning speed 10 kHz. Besides the main signals of P1 (−10.2 ppm) and P2 (−21.2) ppm, two shouder peaks appear at −11 and −20 ppm.

ally, two shoulders appear at about −11 and −20 ppm. The difference between ^{31}P MAS NMR spectrum of sample S_{Eu} and AlPO-CJ_2 should be caused by the replacement of Al by Eu statistically. There are two different crystallographic positions for P atoms in an asymmetric unit of AlPO-CJ_2. Of these the P(1) atom is connected to two AlO_5 groups and two AlO_6 (or AlO_5F) groups while P(2) connects with one AlO_5 group and two AlO_6 (or AlO_5F) groups. When Eu is in the site of Al(v) statistically, the chemical environment of the affected P atoms must change. Correspondingly, the chemical shift of the affected P atoms change, which are shown to be shoulder peaks in the ^{31}P MAS NMR spectrum.

The fluorescent spectra of sample S_{Eu} are shown in Fig. 4. One peak at 579 nm ($^5D_0$–$^7F_0$), three peaks at about 590 nm ($^5D_0$–$^7F_1$) and five peaks at about 610 nm ($^5D_0$–$^7F_2$) are observed in the emission spectrum of sample S_{Eu}. The splitting of $^7F_{1,2}$ energy levels indicates that Eu is located in a rather low symmetric environment that should belong to one of C_1, C_s and C_2 point groups. Since C_1, C_s and C_2 point groups have no inversion center, we conclude that Eu should replace Al on Al(v) sites.

The excitation spectrum of S_{Eu} displays a broad maximum at 280 nm and some sharp lines. The broad band excitation can be assigned to ligand-to metal charge transfer from O^{2-}–Eu^{3+}. As mentioned above, terminal oxygen atoms exist in the framework of AlPO-CJ_2, and the bond formed by the terminal O and Al is shorter by about 0.1 Å than that formed by the shared O and Al. Therefore, it is possible that the electrons of the terminal oxygen atoms transfer from the outer orbit of O to that of Eu when absorbing radiation energy, and form the CT state (with Eu^{2+}–O^{-} characteristics). This type of CT process has been applied on some luminescent materials to enhance the luminescence, and even led to luminescence occurring in some materials without luminescent centres.[7,13,14]

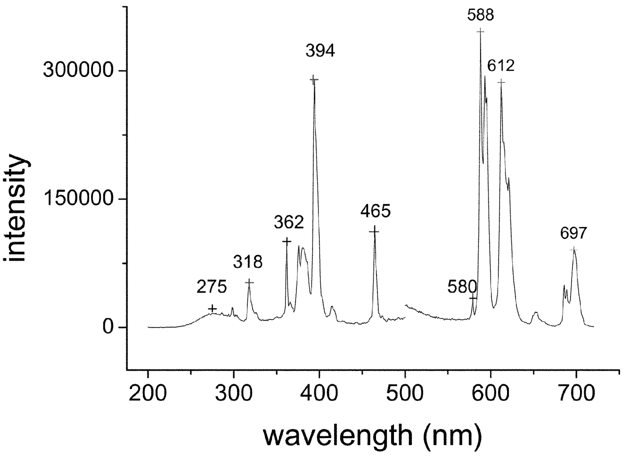

Fig. 4 Fluorescent spectra of sample S_{Eu}. The excitation spectrum was recorded under 610 nm and the emission spectrum was recorded under 254 nm.

This work is supported by Project 20073010 of National Natural Science Foundation of China. We thank Prof. Guan Yan Hong in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences for his help with the measurement and explanation of the fluorescence spectra. We also thank Prof. Zi Gao in Fudan University, Professor Y. F. Xia and Master X. F. Sun in Nanjing University for their help in the measurement and interpretation of Mössbauer spectra.

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