

Catalytic Active Sites on Mesoporous Molecular Sieves

The discovery of meso-structures of M41S family by the researchers of Mobil in 1992 has attracted much attention. Among them, MCM-41 of uniform hexagonal arranged tunnel-shaped pores with pore diameter ranging between 2-10 nm is most studied. The high surface area and highly ordered uniform pores in nanometer range make it a potential candidate for applications in sorption and catalytic conversions of bulky molecules encountered in the cracking of heavy crude oil and in the manufacture of fine chemicals and pharmaceuticals. Figure 1 compares the pore sizes of ZSM-5, Y-zeolite and MCM-41 molecular sieve and their applications as catalysts in petroleum processing of various components.

The substitution of hetero-elements into the framework of silica molecular sieves was essential in order to create acidic sites for catalytic reactions, while the incorporation of transition metal elements, such as Ti, V, Mn, Fe, Co, and Cu endows sites for redox reactions. Among the various analytical tools, X-ray absorption spectroscopy was found to be one of the most powerful techniques to examine the coordination environment of the catalytic active centers in the molecular sieves. For instance, the most applause results for characterization of Ti^{4+} , which is in d^0

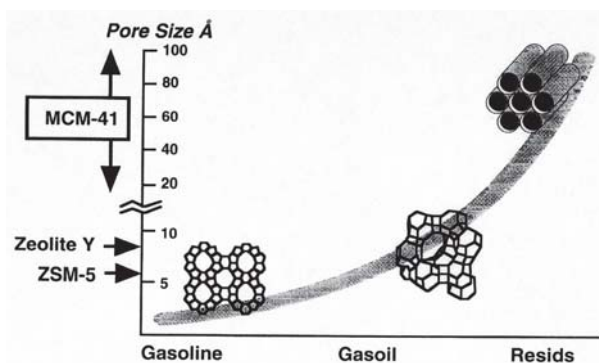


Fig. 1: The pore size distribution of various zeolites and molecular sieves and the range of component in petroleum processing catalyzed by them. (cited from a lecture given by N.Y. Chen, Mobil)

electron configuration, incorporated in zeolites were obtained from X-ray absorption spectroscopy. The near edge spectra associate with the transition of electrons in Ti^{4+} ion from $1s \rightarrow 3d$. By comparing the peak intensity and number of peaks, Ti can be identified to be in a tetrahedral or octahedral site based on the La Porte's selection rule. On the other hand, structural parameters, such as bond distance and coordination number, can be derived from Ti K edge EXAFS.

In the past few years, our laboratory has devoted a great effort to the synthesis and characterization of mesoporous molecular sieve materials, and developing their catalytic applications, especially in fine chemical synthesis. The Cu^{2+} -substituted MCM-41 synthesized by hydrothermal reaction was found to be an efficient catalyst in liquid phase oxidation of trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ). TMBQ is a key intermediate in making Vitamin E. The latter is expected to experience constantly increasing demand in the pharmaceutical and food industries in the coming decade. We found that Cu-substituted MCM-41 could efficiently catalyze the reaction with various oxidants in acid free solvents. Moreover, it was found that the catalytic activity was enhanced when a small amount of Al^{3+} was concomitantly incorporated in the framework of MCM-41.

Because Cu^{2+} contains an unpaired electron, the EPR spectra were measured using a Bruker ESP 300 X-band spectrometer. The g value was determined by using DPPH as the standard. Figure 2 compares the EPR spectra of the MCM-41 samples containing 1%Cu and 2%Al prepared by co-precipitation and impregnation, respectively. The spectra taken at ambient temperature show a broad peak at $g = 2.193$ for the co-precipitated sample but no peak other than that of DPPH at $g = 2.0036$ for the impregnated sample. When cooling the samples to liquid N_2 temperature, the broad peak of the co-precipitated sample was

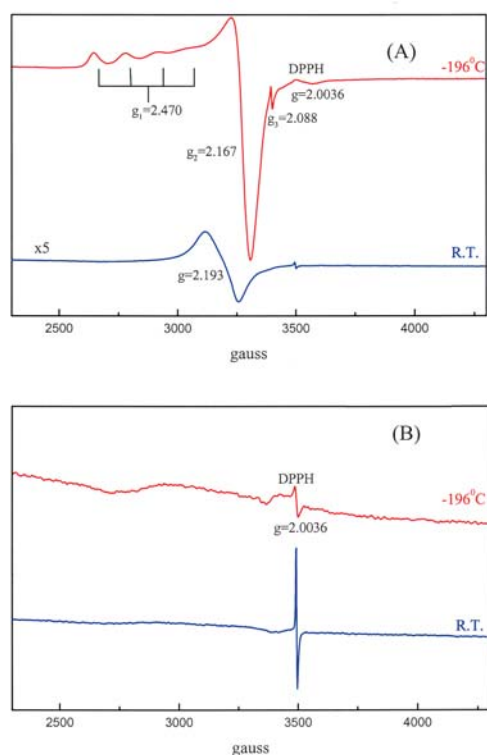


Fig. 2: EPR spectra of 1%Cu,2%Al-MCM-41 prepared by (a) co-precipitation and (b) impregnation; spectra taken at RT (blue) and liq. N₂ temperature (red).

greatly intensified and split into several peaks, which were assigned as $g_1 = 2.470$, $g_2 = 2.167$ and $g_3 = 2.088$. In addition, hyperfine splitting of the g_1 peak into four peaks due to electron-nucleus ($I = 3/2$ for Cu) spin interaction is clearly seen. In contrast, the impregnated sample still did not show obvious peaks. These results are elucidated by that the Cu²⁺ ions on the impregnated sample are aggregated and form copper oxide, where the distances between Cu²⁺ ions are so close that the EPR signals are broadened out by the strong spin-spin interaction. On the other hand, the Cu²⁺ ions in the co-precipitated sample are well dispersed in MCM-41 with anisotropic coordination environment.

In order to further examine the nature of copper species in the co-precipitated sample, the Cu K-edge X-ray absorption spectra were obtained in an *in-situ* reactor. Spectra were taken in the transmission mode at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. The photon energies were calibrated using the known absorption edge of Cu foil. The Cu K-edge X-ray absorption spectra of the co-precipitated sample 2%Cu1%AlMCM-41 (Fig. 3a) were compared

with that of Cu²⁺ ion-exchanged 1%AlMCM-41 (Fig. 3b). CuO, Cu₂O and Cu foil were used as references for +2, +1 and 0 oxidation states, respectively, and their spectra are shown in Fig. 3c. Before reduction, the Cu K-edge spectra of 2%Cu1%AlMCM-41 and ion-exchanged sample were similar, and both edge energies were close to that of CuO, implying that the Cu species in both samples were in the +2 oxidation state. The reduction was performed with a 10% H₂/Ar flow in an *in-situ* reactor at 200 and 300 °C for the duration of 15 min and the samples were then frozen by liquid nitrogen. After reduction at 200 °C, the spectrum and the edge position were not much changed for ion-exchanged sample, while the co-precipitated sample had a small shoulder that appeared around 8983 keV. When the reduction temperature was raised to 300 °C, the ion-exchanged sample was reduced to copper metal and its spectrum was almost the same as that of copper foil. In contrast, for the co-precipitated sample 2%Cu1%AlMCM-41, the copper species were not completely reduced and the spectrum was a mixed pattern of those of Cu²⁺ and Cu⁺. In conclusion, the Cu²⁺ ions exchanged on AlMCM-41 would be reduced to copper metal at 300 °C, while that substituted in MCM-41 retained in a mixture of +1 and +2 oxidation states. These results confirmed that the Cu²⁺ ions incorporated in MCM-41 by co-precipitation were likely isomorphously substituted in the silica framework,

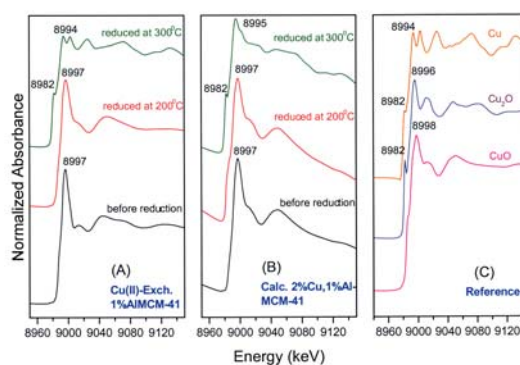


Fig. 3: Cu K-edge X-ray absorption spectra of (a) Cu²⁺-exchanged 1%AlMCM-41, (b) calcined 2%Cu1%Al-MCM-41: before reduction (black), and reduction with 10% H₂/Ar at 200 °C (red), 300 °C (green). (c) references: CuO (magenta), Cu₂O (violet) and Cu foil (orange).

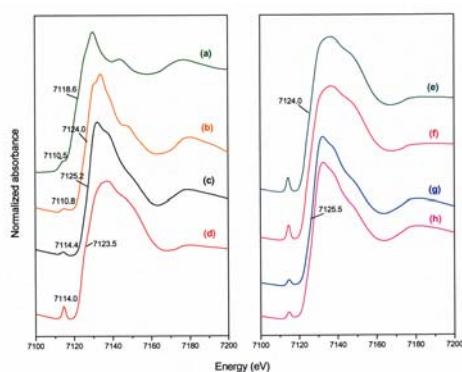


Fig. 4: XANES of Fe K-edge: (a) FeO, (b) Fe₂O₆, (c) 1%FeAPO-5, (d) 1%FeAPO-5 dried at 200 °C, (e) 1%FeZSM-5, (f) 1%FeZSM-5 dried at 200 °C, (g) 3%FeMCM-41, and (h) 3%FeMCM-41 dried at 200 °C.

instead of at the extra-framework ion-exchange sites.

Industrially, pinacolone is prepared through pinacol (2,3-dimethyl-2,3-butanediol) rearrangement in large-scale processes using strong acids such as, H₂SO₄, H₃PO₄ or AlCl₃ as catalysts. The reaction will be much cleaner and more environmentally friendly if the corrosive acids can be replaced by solid catalysts. Our previous study found that pinacol rearrangement proceeded at relatively mild temperature in solution over metal-substituted aluminophosphate molecular sieves. Moreover, among the first row transition metal elements substituted in AFI crystal structure, Fe³⁺, Cu²⁺ and Ni²⁺ in order are the three which gave the highest pinacol conversion and pinacolone selectivity. The redox capability of the transition metal center was proposed to be responsible for the catalytic activity. Three different Fe-substituted molecular sieves, saying AlPO₄-5, ZSM-5 and MCM-41, was compared in order to understand the effect of pore size and zeolitic structure on the catalytic rearrangement reaction. The pore diameters of these three molecular sieves were ca. 7.5, 5.5 and 26 Å, respectively.

X-ray absorption spectra of Fe in the molecular sieves were taken in order to understand its oxidation state and coordination environment. Fig. 4 shows the X-ray absorption near-edge spectra (XANES) of the Fe-incorporated molecular sieves before and after heating at 200 °C in N₂, in comparison to those of FeO and Fe₂O₃ standards. The edge-energies determined from the inflections of the absorption edges were 7118.6 eV for FeO and

7124.0 eV for Fe₂O₃. That of 1%FeAPO-5 was 7125.2 eV, indicating that Fe was in the +3 oxidation state. After heating 1%FeAPO-5 at 200 °C under N₂ in an *in-situ* reactor, the absorption peak became broader and the edge-energy shifted slightly to 7123.5 eV. Moreover, an apparent increase in the intensity of the pre-edge peak was seen. Judging from the edge energy, iron in the dried 1%FeAPO-5 should retain in the +3 oxidation state, but its coordination environment was changed. The pre-edge peak is assigned to the 1s→3d electron transition. In octahedral coordination environment, this transition is La Porte forbidden. However, in a non-central symmetric or tetrahedral coordination, this transition is allowed. The change of coordination environment of Fe³⁺ from octahedral to tetrahedral elucidates the increase in intensity of the pre-edge peak after heating of FeAPO-5. The Fe³⁺ which substitutes Al³⁺ in the AlPO₄-5 framework should be in tetrahedral coordination. The octahedrally coordinated Fe³⁺ observed before heating is attributed to the fact that water molecules are coordinated to Fe³⁺ centers through dative bonding. However, the water molecules are ready to be removed by heating or evacuation. Figure 4 also shows the XANES of 1%FeZSM-5 and 3%FeMCM-41 before and after heating at 200 °C in N₂. FeZSM-5 has a broader absorption edge and a strong pre-edge peak, while FeMCM-41 has a sharper edge peak and a weak pre-edge. Different from that observed on FeAPO-5, heating the samples does not change both of the spectra. The strong pre-edge confirms that Fe³⁺ in ZSM-5 is in tetrahedral coordination. Moreover, Fe³⁺ incorporated in the framework of ZSM-5 is hydrophobic. In contrast, Fe³⁺ in MCM-41 was in octahedral coordination and no transformation to tetrahedral was observed when the sample was heated at 200 °C in N₂. This phenomenon is elucidated by the fact that the water molecules coordinated to the Fe³⁺ centers in MCM-41 are not as easily removed as that on AlPO₄-5 framework. It explains why among the three Fe-substituted molecular sieves, FeAPO-5 was the most efficient in catalyzing the pinacol rearrangement of 2,3-dimethyl-2,3-butanediol (generally named pinacol). FeZSM-5 showed null catalytic activity due to its pore diameter, which is

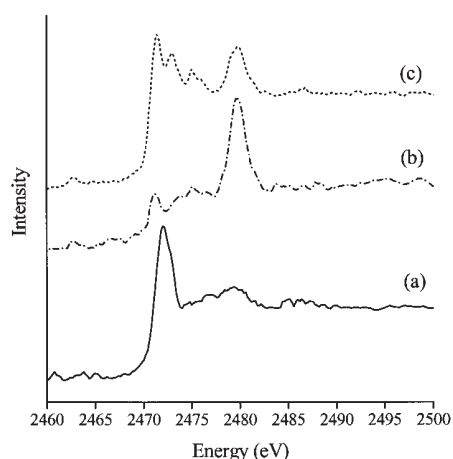


Fig. 5: S K-edge XANES spectra of thiol functionalized MCM-41 materials (a) before oxidation, (b) after oxidation, and (c) sample with incomplete oxidation of thiol groups.

too small for pinacol to diffuse in freely. The higher activity of FeAPO-5 in comparison to that of FeMCM-41 is attributed to the more facile removal of coordinated water molecules from Fe^{3+} centers on AlPO4-5 than on MCM-41. As a result, the reactants can be adsorbed on the Fe^{3+} active centers more easily on FeAPO-5 molecular sieve.

In spite of having large pore dimensions, the acidity of mesoporous materials like AlMCM-41, is much weaker than that of microporous zeolites. In order to overcome this drawback, a great effort has been focused on introducing strong acid sites on the mesoporous materials. The hybrid inorganic-organic mesoporous materials with alkylsulfonic acid groups were synthesized and reported to behave as a strong acid catalyst in the condensation reactions and also in the esterification reactions. Bisphenol-A is an important raw material for polymer and resin production, and it is produced industrially using ion-exchange resins like Amberlyst. However, thermal stability and fouling of the resins were the major problems for resin catalysts and the search for thermally stable and regenerable solid acid catalyst still continued. We found that sulphonic acid functionalized mesoporous MCM-41 silica could be an efficient catalyst for the condensation of phenol and acetone at relatively low temperature to synthesize Bisphenol-A with a very high selectivity. Surface functionalization with sulphonic acid groups was carried out by grafting method. Typically, the

freshly calcined MCM-41 molecular sieve was evacuated and then an excess of 3-mercaptopropyltrimethoxysilane (MPTS) in dry toluene was introduced. The surface -SH groups were converted into the -SO₃H groups by mild oxidation with H₂O₂.

For obtaining good catalytic activity it is imperative that the thiol groups are to be effectively oxidized to the active sulphonic acid groups. Sulphonic acid groups anchored to the surface of mesoporous MCM-41 silica have been identified with S K-edge XANES spectra. The XANES experiments were performed at Beam line 15B at National Synchrotron Radiation Research Center facility at Hsinchu, Taiwan. Standard operating conditions were 1.5 GeV and 200 mA beam current and the photon energies were calibrated using the L-edge of pure Mo foil. Figure 5 shows the S K-edge XANES spectra of the thiol functionalized samples before and after H₂O₂ oxidation. It has been reported that both the energy position (E_k) and intensity of the S s→p transition peak (white-line) are sensitively related to the oxidation state of the S atom. Studies with model compounds showed an increase of E_k and amplitude of the white-line with increasing formal oxidation states of S. Thus, for un-oxidized sample containing thiol groups the white-line appears at 2472 eV corresponding to sulfur in reduced state. After H₂O₂ oxidation the white-line shift to higher energy side to 2481 eV, which corresponds to sulfonic acid with S in +5 state. It can be seen from Fig. 5 that major part of the anchored thiol groups has been oxidized to the sulphonic acid group under the oxidation conditions mentioned earlier. It is noticed that optimization of the oxidation process in preparation of MCM-SO₃H is essential to achieve high catalytic activity. For samples with similar sulfur loadings but with incompletely oxidized thiol groups (dotted line in Fig. 5) the activity was found to be much lower. XANES spectra of the samples with incompletely oxidized sulfur species showed a number of peaks around 2472 eV, suggesting the presence of lower valent sulfur species like sulfides and disulfides. It has also been observed that at higher sulfur loadings (above 1.5 meq/g solid) part of the sulfur remains in reduced form even after prolonged oxidation process, probably due to formation of sulfides and disulfides.

In summary, X-ray absorption spectroscopy is a powerful technique in identification of the catalytic active sites in the molecular sieve materials. *Ex-* and *In-situ* experiments can be utilized to identify the oxidation state, coordination environment and the chemical nature of the catalytic active centers.

Beamlines:

15B1 Tender X-ray beamline

17C1 W20/XAS beamline

Experimental Station:

EXAFS end station

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