

## The Potential Industrial Application of Mesoporous Silicate in the Catalytic Oxidation of Aromatics under Room Temperature

Niankai Li, Yan Kong\*, Cheng Wu, Yingjie Zhang, Dandan Chen, Peng Sun and Jun Wang  
State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China  
\*kongy36@njut.edu.cn

### Introduction

Mesoporous silicates supported with different active component exhibited excellent catalytic activity in many reactions [1]. However, they were not put into practical use due to their poor hydrothermal stability. Although much efforts have been devoted to the improvement of their hydrothermal stability, their surface structures and catalytic activities were changed simultaneously.

In our lab, these kinds of catalysts were used in the direct oxidation of aromatics by hydroperoxide under room temperature. Considering that most of the oxidative reactions are exothermic, the equilibrium constants under lower temperature must be larger than those under higher temperature on the view of thermodynamics. It is possible to enhance both the catalytic activities and the stabilities of mesoporous materials in these reactions under room temperature. Also, lower temperature reaction means requiring much less energy and producing fewer by-products. The problems were how to accelerate the reaction at a lower temperature and avoid the lost of active species in liquid reaction.

In the present work, MCM41s incorporated with high contents of different kinds of heteroatoms such as Cu, Fe, V, Co and Ti [2-4] in the framework were synthesized. The statuses and the coordination environment of different heteroatoms were identified by lots of modern techniques. Their catalytic activities, especially Fe-MCM41 in the direct oxidation of phenol and V-MCM41 in the direct oxidation of benzene under room temperature were evaluated.

### Materials and Methods

The catalysts were synthesized by traditional sol-gel method. In order to incorporate high content of heteroatoms into the framework of mesoporous silicates, the synthesis conditions such as pH, aging temperature and time, stirring rate were controlled strictly. Meanwhile, auxiliary surfactant and reagent were also used. The structures of the materials were identified by using XRD, FT-IR, N<sub>2</sub> adsorption isotherms, HRTEM, XPS, UV-vis, H<sub>2</sub>-TPR, ESR and <sup>29</sup>Si MAS NMR techniques. Catalytic tests were performed in self-made reactor.

### Results and Discussion

Figure 1 showed the XRD patterns of some samples. An intense (100) peak at about  $2\theta = 2^\circ$  together with two weak (110) and (200) peaks in the small angle range suggested the MCM41-type structures were still maintained after high amount of heteroatoms were incorporated into the framework of the mesoporous materials. The regular mesoporous structures and the narrow pore size distributions were confirmed by the type IV isotherms and the HRTEM images.

It was important to distinguish whether the heteroatoms in the framework or on the surface of the mesoporous materials. In our opinion, three kinds of methods can be used. First,

wide angle XRD patterns, HRTEM images and other techniques could be used to differentiate if there were large crystalline particles of metal oxides existence or not. Second, the formation of M-O-Si bonds could be found from the variations of the spectra of silicon, oxygen and metal oxides. For example, the binding energy of O<sub>1s</sub> decreased with the increase of copper contents (Fig.2) in the framework of MCM41, due to the formation of Cu-O-Si bonds, which caused the decrease of the density of the lining electron cloud of oxygen atoms. [2] The existence of V-O-Si or Ti-O-Si bond can also be confirmed from the LRS spectra of V or Ti-MCM-41. And the third, the heteroatoms in the framework or on the surface of the mesoporous materials caused the different variations of the structure parameters, such as the special surface area, the average pore size, the thickness of pore wall, etc[3,4].

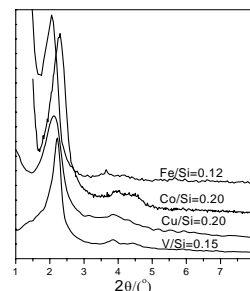


Figure.1 XRD patterns of some samples.

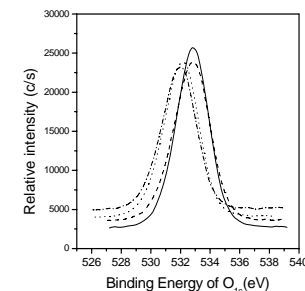


Figure.2 Binding energy of O<sub>1s</sub> (from right to left) of 5Cu, 10Cu, 20Cu and 30Cu samples

The selectivity of product and the stability of catalyst were important for the industrial use of a new technique. Some catalytic performances of our catalysts under lower temperature were given in table 1. The selectivity was all high and the mesoporous structures of all the catalysts were still maintained after reused for many times. Especially for Fe-MCM41 in the direct oxidation of phenol by H<sub>2</sub>O<sub>2</sub>, the catalytic activity did not declined after reused for ten times at 298K, and it declined sharply after reused for four times at 333K.

Table 1 Catalytic activity of some mesoporous materials

Reaction	Heteroatom(M)	Content of M(%)	Con.(%)	Sel. (%)
Benzene to phenol	Cu	17.92	33	100
	V	14.5	15.1	100
	Co	11.1	35.4	100
Phenol to diphenol	Fe	9.0	21.3	92

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