

## Ordered mesoporous carbon molecular sieves with functionalized surfaces

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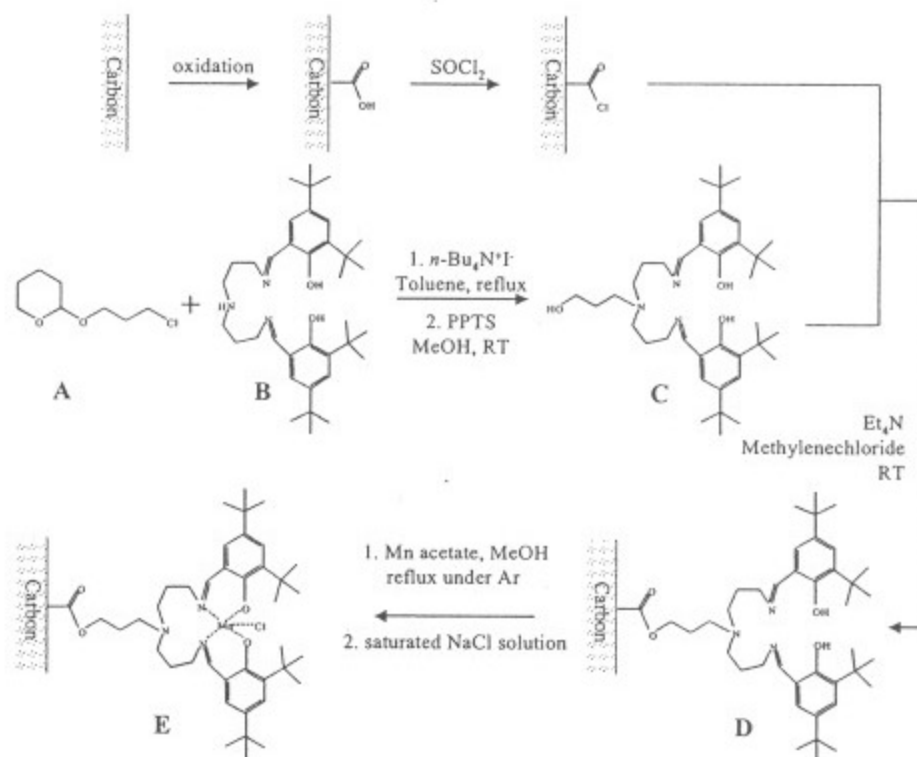
Ordered mesoporous carbon molecular sieves designated as CMK-1 and CMK-5 were synthesized by using nanocasting technique with the synthetic procedures reported previously. After carboxylic acid groups were generated on the carbon frameworks through the partial oxidation with nitric acid, pore walls of the mesoporous carbons were functionalized with various organic and organometallic functional groups using esterification and amidization reactions. Mn-Schiff base complex grafted on the mesoporous carbon surface by using ester bond formation showed remarkable catalytic activity for partial oxidation of cyclohexene. The mesoporous carbons were also functionalizable with tetraethylenepentamine (TEPA), which could be used for the effective removal of heavy metal ions.

### 1. INTRODUCTION

Recently, various types of ordered mesoporous molecular sieves composed of carbon frameworks have been synthesized by exploiting the "nanocasting" technique.<sup>1-3</sup> The mesoporous carbons have high specific surface areas, excellent mechanical and chemical stabilities, good electrical conductivity and capability of supporting platinum nanoparticles with excellent dispersions. With these remarkable properties, mesoporous carbons attract much scientific attention for the development of advanced separation systems, highly selective catalysts, hydrogen-storage systems, and catalysts for electrochemical energy conversion. Here we show that the pore walls of the mesoporous carbons can be functionalized with various kinds of organic and organometallic groups applying a general method that is commonly adopted for the surface modification of carbons. We believe that functionalized carbon materials could be used for various application even under hydrothermal condition.

### 2. EXPERIMENTAL

Two kinds of mesoporous carbons designated as CMK-1 and CMK-5 were prepared by synthetic procedures reported previously.<sup>1,3</sup> These carbons were treated with conc. HNO<sub>3</sub> for 15 min at 383 K to generate -COOH groups on the surface of carbon frameworks. This is the



Scheme 1. schematic representation of synthesis and grafting of manganese Schiff-base on carbon surface.

optimized condition for introducing acid groups as much as possible while the carbon framework remains intact.

Before grafting various functional groups,  $\text{-COOH}$  groups were first converted to more reactive acyl chloride ( $\text{-COCl}$ ) through the reaction with thionyl chloride ( $\text{SOCl}_2$ ) in dichloromethane at room temperature. A Schiff base ligand, 3-[N,N'-bis-3-(3,5-di-tert-butyl salicylidenamino) propyl] hydroxypropylamine [C in Scheme I] was grafted onto the carbons through the esterification between  $\text{-COCl}$  and compound C. In the synthesis, 3-[N,N'-bis-3-(3,5-di-tert-butyl salicylidenamino) propyl] amine [B] was prepared via the condensation reaction between 3,3'-diaminopropylamine (Aldrich) and 3,5-di-tert-butyl salicyladehyde (Aldrich).<sup>4,5</sup> Compound B was reacted in excess under reflux condition in toluene solution with A, which was prepared by reacting 3-chloropropanol with tetrahydropyran to protect the alcohol group. The product was purified through usual workup and chromatographic separation and then protection group in the product was removed by cleaving ether linkage with methanol. After grafting C onto carbons, the product (D) was complexed with a  $\text{Mn}^{2+}$  ion using  $\text{Mn}(\text{acac})_2$  (Aldrich) in methanol at 355 K under argon. The  $\text{Mn}^{2+}$  complex was subsequently oxidized to  $\text{Mn}^{3+}$  in saturated NaCl solution in air. Products were thoroughly washed with methanol and water in order to remove species physically adsorbed. The catalytic activity of the carbon-supported Mn Schiff base was measured for the partial oxidation of cyclohexene with tetrabutylhydroperoxide. The reaction was started with 0.1 g catalyst, 20 mL  $\text{CH}_2\text{Cl}_2$ , 0.5 mL cyclohexene (freshly distilled after purchase, Acros 99%) and 0.4 mL tetrabutylhydroperoxide (5.5 M solution in decane, Aldrich) under reflux conditions at 333 K in argon. Gas chromatographic analysis (HP 5890, Carbowax 10M column) of the reaction mixture was performed to check the conversion of the reaction.

The functionalization of the mesoporous carbons for metal chelation has been performed with amines, using the same amidization procedure reported in a previous work on carbon fibers.<sup>6,7</sup> CMK-1 was reacted with tetraethylenepentamine [HN(CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>, Aldrich, TEPA for brevity] under reflux condition at 463 K for 15 h after the partial oxidation with HNO<sub>3</sub>. This carbon was immersed in a sufficiently large amount of 0.01 M Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution for 24 h. After filtered, thoroughly washed with distilled water and dried, the copper content was analysed by ICP.

### 3. RESULTS AND DISCUSSION

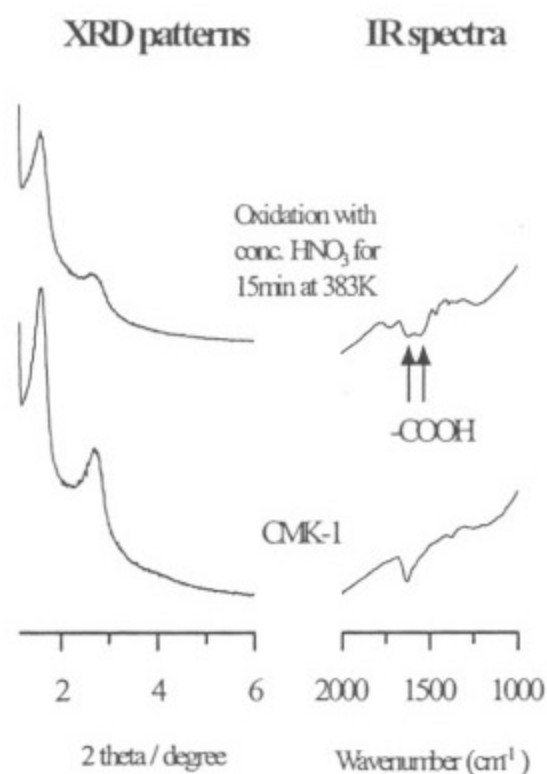


Fig. 1. XRD and FT-IR spectra of CMK-1 before and after carbon surface.

compared to 48  $\mu\text{mol g}^{-1}$  of MCM-48 catalyst synthesized by the same method reported previously<sup>4,5</sup>.

The catalytic activities of Mn Schiff-bases grafted on different supports are represented in Figure 2. Interestingly, the catalytic activities of the carbon catalysts reduced by Mn content were at least twice as much as that of an MCM-48 silica catalyst. The higher catalytic activity of the mesoporous carbons may be related to the increased concentration effect of the reactants in the case of the more hydrophobic carbon catalysts. All the carbon catalysts exhibited highly reproducible catalytic activities even after the reaction was repeated 5 times. The carbon catalysts retained the structural order and catalytic activities even after boiling in water for 10 days while the MCM-48-based catalyst lost structural order and catalytic

Figure 1 shows the XRD patterns and FT-IR spectra of CMK-1 before and after surface oxidation. From XRD patterns, we could recognize that, mesoscopic order was not impaired significantly even after oxidation and the FT-IR peaks appearing around 1750 and 1650  $\text{cm}^{-1}$  confirmed the presence of COOH group. By using the general titration method with standard NaOH solution, the amount of acid groups introduced was calculated as  $1 \times 10^{-3}$  mol per g CMK-1.

Through the ester bond formation with the acid group produced, we grafted Mn Schiff-base onto mesoporous carbon surface. In the case of the CMK-5 carbon, the grafting experiment could be also performed onto the carbon/silica composite during the carbon synthesis. Subsequent removal of the silica framework with HF gave a CMK-5 sample containing the Schiff-base complex selectively grafted inside the nanopipes. From the inductively coupled plasma emission (ICP) analysis data, Mn contents for different catalysts are as follows; 20  $\mu\text{mol g}^{-1}$  for CMK-1, 42  $\mu\text{mol g}^{-1}$  for CMK-5 (20  $\mu\text{mol g}^{-1}$  for inside-selective grafting)

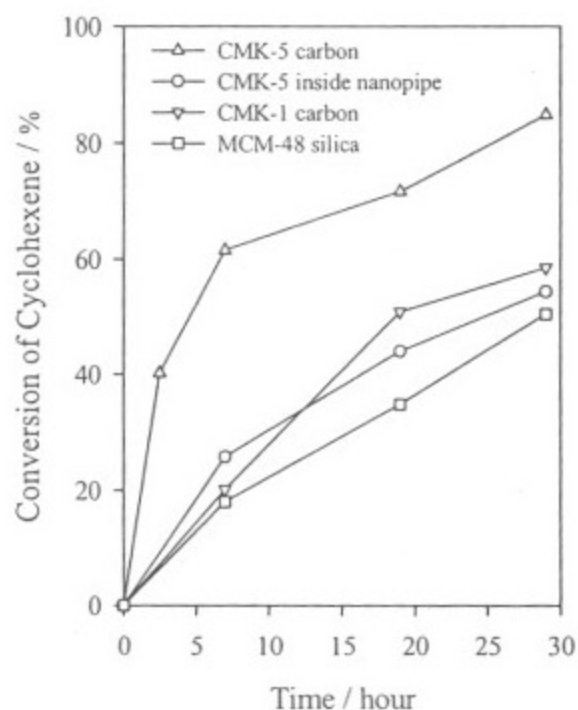


Fig. 2. Conversion of cyclohexene for partial oxidation of cyclohexene plotted with reaction time: ( $\Delta$ ) CMK-5, ( $\circ$ ) CMK-5 functionalized selectively inside the nano-pipes, ( $\nabla$ ) CMK-1 carbon and ( $\square$ ) MCM-48 silica.

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activities almost completely.

Finally, TEPA-functionalized CMK-1 adsorbed 0.4 mmol  $\text{Cu}^{2+}$  per g carbon, whereas the original CMK-1 exhibited undetectable copper adsorption. It is noteworthy that this adsorption capacity for  $\text{Cu}^{2+}$  was much higher than the value of 0.1 mmol  $\text{Cu}^{2+}$  per g, which was reported with molecular-imprinting functionalization of MCM-41 silicas with ethylene-diamine.<sup>8</sup> The metal chelating effect may be useful for water treatments, since the carbons functionalized in this way can remove heavy metals and organic pollutants simultaneously.

While the pore-wall functionalization is a well-known strategy used for MCM-41 silicas, low hydrothermal stability has been a serious problem with the silica-based mesoporous materials. The functionalization of the mesoporous carbons exhibiting much higher hydrothermal and acid-base stabilities could offer a remarkable advantage especially for the applications under hydrothermal conditions.