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## Chiral Periodic Mesoporous Organosilicas for Asymmetric Catalysis

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### Introduction

The periodic mesoporous organosilicas (PMOs) with organic groups bridged in the framework are synthesized from the  $(RO')_3Si-R-Si(OR')_3$ .<sup>1-3</sup> In addition to the high surface areas and narrow pore size distributions, these novel materials have completely different adsorption properties from those of mesoporous silicas. Therefore, unique catalytic properties may be expected when they are combined with chiral ligand. Here, we report the synthesis and application of mesoporous organosilica with *trans*-(1R,2R)-diaminocyclohexane in the pore or in the framework. These novel materials with chiral ligands in the pore (after complexing with  $[Rh(cod)Cl]_2$ ) exhibit promising activity and enantioselectivity in the transfer hydrogenation of acetophenone. Compared with pure mesoporous silica counterparts, these mesoporous organosilicas are twice more active. The enhanced catalytic activity of the mesoporous organosilicas is mainly contributed to the specific adsorption and physical properties of the mesoporous networkbridged with ethane groups, particularly the hydrophobic properties. With benzyl group as a linker, *trans*-(1R,2R)-diaminocyclohexane was incorporated in the framework of mesoporous silica through one-step co-condensation of tetramethoxysilane (TMOS) with  $N,N'$ -bis[4-(trimethoxysilyl)benzyl]-(-)-(1R,2R)-diaminocyclohexane using cetyltrimethylammonium bromide as a structure directing agent under basic conditions. Coordinated with  $[Rh(cod)Cl]_2$ , the material exhibits TOF up to  $\sim 414\text{ h}^{-1}$  with 30% ee for the asymmetric transfer hydrogenation of acetophenone.

### Materials and Methods

EM-9-N with chiral ligand in the pore is synthesized from the co-condensation of  $N$ -[(triethoxysilyl)propyl]-(-)-(1R, 2R)-diaminocyclohexane with 1,2-Bis(trimethoxysilyl)ethane under basic conditions using C18TMACl as surfactant.  $TB_{benzyl-20-N}$  is synthesized from the co-condensation of  $N,N'$ -bis[4-(trimethoxysilyl)benzyl]-(-)-(1R,2R)-diaminocyclohexane with TMOS under basic conditions using C18TMACl as surfactant. The materials were characterized by X-ray powder diffraction patterns (Rigaku D/Max 3400 powder diffraction system using  $Cu\ K\alpha$  radiation), transmission electron microscopy (JEM-2010 at an acceleration voltage of 120 kV), nitrogen sorption isotherms (at 77 K on ASAP 2000 system in static measurement mode), and solid-state  $^{13}C$  (100.5 MHz) and  $^{29}Si$  (79.4 MHz) CP-MAS NMR (Bruker DRX-400 spectrometer).

### Results and Discussion

The results of X-ray diffraction (XRD), TEM and  $N_2$  sorption isotherms show that the materials have ordered mesoporous structure with high BET surface areas. The FT-IR and  $^{13}C$  and  $^{29}Si$  CP-MAS NMR spectra demonstrate that *trans*-(1R, 2R)-diaminocyclohexane moiety is successfully incorporated into the network of mesoporous silica and mesoporous materials.

Table 1 shows the catalytic properties of the mesoporous materials on the asymmetric transfer hydrogenation of acetophenone. All the catalysts with the ethane-bridged framework (EM-n-NRh) exhibit higher catalytic activity and enantioselectivity than the catalyst with the pure-silica framework (TM-9-N). The increased catalytic activity is mainly contributed to the enhanced surface hydrophobicity of EM-n-NRh with ethane moiety as an integrity part of the mesoporous framework. The mesoporous organosilicas with benzyl group as a linker (complexed with  $[Rh(cod)Cl]_2$ ) show remarkably high TOF of  $106\text{ h}^{-1} \sim 414\text{ h}^{-1}$  with ee up to 22%  $\sim$  30% for the asymmetric transfer hydrogenation of acetophenone. The linker with special rigidity and electron-withdrawing ability is favourable to the high catalytic activity and enantioselectivity (Table 1).

**Table 1. Physicoproperties and catalytic results of chiral PMOs for the asymmetric hydrogenation of acetophenone**

Sample	Conv. (%)	ee	BET (m <sup>2</sup> /g)	Rh (mmol/g)
homogeneous	89	21	-	-
TM-9-NRh <sup>a</sup>	48	14	890	0.27
EM-9-NRh <sup>b</sup>	82	19	851	0.12
$TB_{benzyl-20-N}^c$	93	27	908	0.29
$TB_{propyl-20-N}^d$	36	8	910	0.13

<sup>a</sup>, mesoporous silicas with chiral ligand in the pore; <sup>b</sup> mesoporous ethane-silica with chiral ligand in the pore; <sup>c</sup> mesoporous organosilicas with ligand in the framework using benzyl as a linker; <sup>d</sup> mesoporous organosilicas with ligand in the framework using propyl as a linker. After presentation of data, one would normally describe it and its relevance to the problem under study.

### Significance

The present synthetic strategy of chiral mesoporous organosilicas is a general method to synthesize mesoporous materials containing other chiral ligands. In addition, modulating the organic groups in the framework can change the surface properties of the mesoporous materials at molecular level. Thus, the mesoporous materials with different organic groups in the framework and chiral ligands in the mesopore are a new class of promising heterogeneous chiral catalysts.

### References

1. Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T., Terasaki, O. *J. Am. Chem. Soc.* 9611, 12 (1999). Knudsen, K.G., Cooper, B.H., and Topsoe, H. *Appl. Catal. A: General* 189, 205 (1999).
2. Melde, B. J., Holland, B. T., Blanford, C. F., Stein, A. *Chem. Mater.* 3302, 11 (1999).
3. Asefa, T., MacLachlan, M. J., Coombs, N., Ozin, G. A. *Nature* 867, 402 (1999).