

# Preparation of Mesoporous Base Catalysts from Uniform Layered Double Hydroxide Nanoparticles

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Layered double hydroxides (LDHs) are of great importance as precursors of basic mixed metal oxides (MMOs) used as solid base catalysts. Because the porosity of MMOs depends on the textural properties of LDHs, the control of porous structures of LDHs is important. Here, we report the preparation of highly active solid base catalysts using uniform Mg–Al LDH nanoparticles (LDHNPs) as precursors. As we have reported [1], the particle size of LDHNPs is finely controllable, using tripodal ligands as surface stabilizing agents. Mesoporous MMOs were prepared by assembling LDHNPs with a block copolymer template, followed by thermal decomposition.

The LDHNPs were prepared by mixing an aqueous solution of metal salts ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and that of a tripodal ligand (tris(hydroxymethyl)aminomethane), followed by heating at 80 °C for 24 h. The LDHNPs were washed and dispersed in an aqueous solution of a block copolymer template (Pluronic F127). The mixture was filtered, dried, and calcined at 450 °C. The samples prepared without template are denoted as MMO(X) (X = average particle size). Those prepared with templates are denoted as MMO(X)-F127 (X = average particle size). The catalytic test was carried out for Knövenagel condensation of ethyl cyanoacetate (2 mmol) and benzaldehyde

**Table 1.** Porosities and catalytic activities of mesoporous MMO catalysts.

Sample	Surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore size (nm)	Yield of product (%) <sup>[a]</sup>
MMO(12)	243	3.9	44
MMO(26)	203	4.4	26
MMO(60)	210	3–100	25
MMO(100)	137	>50	12
MMO(12)-F127	400	15	>99
MMO(26)-F127	330	18	90
MMO(60)-F127	239	33	33

[a] Yield after 10-min reaction.

(3 mmol) dissolved in toluene (4 mL), using a mesoporous MMO catalyst (60 mg) at 60 °C.

Uniform LDHNPs, whose sizes were 10 nm, 26 nm, and 60 nm, were obtained when the concentrations of the tripodal ligand were 0.5 M, 0.25 M, and 0.10 M, respectively. MMOs were formed by calcination of these LDHNPs. Relatively larger surface areas and pore sizes were obtained from smaller LDHNPs (Table 1). When the MMOs were prepared by using a F127 template, MMOs with much larger surface areas and pore sizes were obtained. In these cases, the surface areas and pore sizes are more dependent on the particle sizes of LDHNPs because many surfaces became accessible by the formation of large interparticle mesopores.

The catalytic activities of MMO catalysts were assessed by the yield of the product by the Knövenagel condensation after short reaction time (Table 1). MMO catalysts prepared from LDHNPs showed much higher activities than the conventional MMO(100) catalyst, prepared from LDH particles 100 nm in size. The activities roughly depended on the surface areas of the MMO catalysts. These results suggest that the mesoporous MMO catalysts, especially MMO(12)-F127, are effective as solid base catalysts and catalyst supports.

In conclusion, the uniform LDHNPs stabilized with a tripodal ligand are useful as precursors of MMOs with high activity for Knövenagel condensation. The use of a block copolymer template is effective to improve surface areas and catalytic activities.

## REFERENCES

[1] Y. Kuroda, et al, Chem. Mater., 25 (2013) 2291.