



Hydrogenation of diesters on copper catalyst anchored on ordered hierarchical porous silica: Pore size effect



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ABSTRACT

An ordered hierarchical porous silica (HPS) presenting both mesopores and micropores was fabricated and used for supporting copper catalysts (Cu/HPS). In the prepared Cu/HPS catalysts, high dispersion of both Cu⁰ and Cu⁺ species together with ordered porous structure were achieved. The anchoring effect of micropores hindered the agglomeration of copper species, while the formation of Cu–O–Si species, derived from the strong interaction between surface silica and copper precursor, was prompted by the ammonia evaporation approach. The Cu/HPS catalysts were tested in the hydrogenation of diesters to diols. It shows excellent activity on dimethyl adipate hydrogenation with a 1,6-hexanediol space-time yield of 0.72 g/(g·h) under WHSV = 1.2 h⁻¹. It was further investigated that the activity in dimethyl adipate hydrogenation, in contrast to that of dimethyl oxalate hydrogenation, would be readily limited by pore diffusion, due to the porous structure of HPS.

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1. Introduction

Diols, such as ethylene glycol (EG), 1,6-hexanediol (HDO), are value-added intermediates in the chemical industry. They have been applied in the synthesis of several polymers and fine chemicals, such as elastomers of polyurethane, adhesives, polyesters, plasticizers and pharmaceuticals [1–5]. Currently, HDO is mainly produced by hydrogenating carboxylic acids or their esters on industrial scale. In order to avoid the use of carboxylic acids which causes severe corrosion of the reactor and consequent catalyst deactivation, hydrogenation of dimethyl adipate (DMA) towards HDO attracted increasing interests from both fundamental research and industrial application. In a typical scaled-up operation, DMA hydrogenation takes place in the liquid phase, catalyzed by noble metals (Ru, Pd, Pt and Rh), facilitating the activation of C=O bond [1–4]. In addition to noble-metal catalysts, it has been further demonstrated that Co and Sn promote the reduction of ruthenium oxide to Ru(0) as the active species. The as-prepared Ru–Sn–Co/AlO(OH) catalyst showed excellent performance in the

hydrogenation of DMA with a conversion of 98% and the selectivity of HDO as high as 95% at 493 K under a hydrogen pressure of 5 MPa [6]. However, the high cost of noble metal catalysts, as well as the technical difficulties involved in liquid phase operation, limited the further development of above-mentioned process. Therefore, considerable efforts aiming for the substitution of noble metals with copper-based catalyst on catalytic long-chain alcohol formation have also been reported [7]. The two major bottlenecks are, (1) the severe conditions ($T = 523\text{--}623\text{ K}$ and $P(\text{H}_2) = 10\text{--}20\text{ MPa}$) and the low yield of alcohols; (2) the use of toxic Cr as a promoter in catalysis. Therefore, the development of highly active Cr-free catalysts in gas-phase DMA hydrogenation is of great significance. Yuan et al. [8] reported a Cu–Zn–Al catalyst for the hydrogenation of DMA and a 1,6-hexanediol yield higher than 95% was achieved at WHSV of 0.5 h⁻¹. They also proposed that Cu/Zn ratio played an important role in maintaining high activity. However, the structure effect of the catalyst on the hydrogenation of DMA was not yet revealed and the catalytic activity deserved a further improvement from an industrial point of view.

Examining other reaction systems involving C=O activation, the synthesis of EG via dimethyl oxalate (DMO) hydrogenation by using copper-based catalysts has attracted much attentions for the achievement of commercial scale [9–14]. As depicted in

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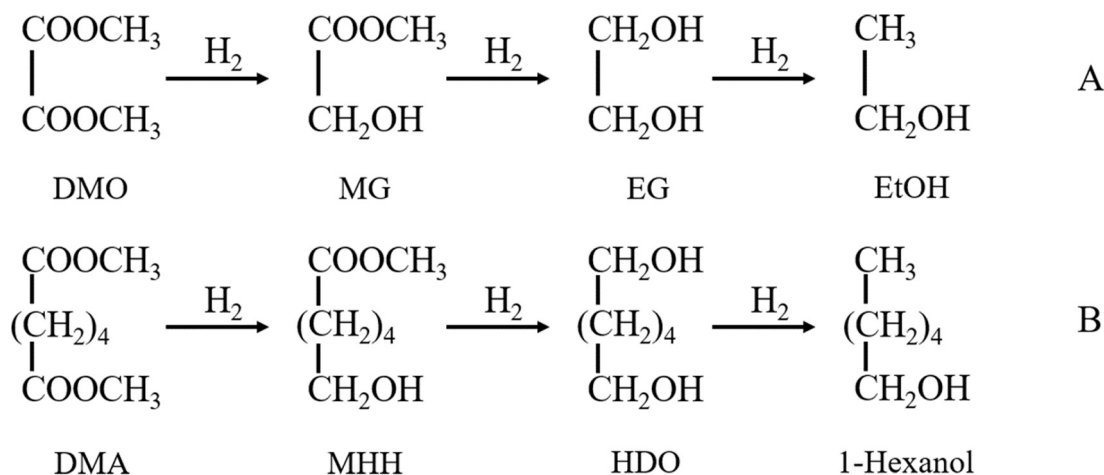
Notation

S_{BET}	BET surface area (m^2/g)	u	the linear velocity of the gas in catalyst bed (m s^{-1})
V_{meso}	mesopore volume (cm^3/g)	r_{obs}	apparent reaction rate ($\text{mol L}^{-1} \text{s}^{-1}$)
V_{micro}	micropore volume (cm^3/g)	$D_{\text{eff},i}$	effective diffusivity in the pores of the catalyst ($\text{m}^2 \text{s}^{-1}$)
D	average pore diameter (nm)	R	the radius of the catalyst pellet (m)
D_{Cu}	copper particle diameter (nm)	C_i^s	concentration of specie i at the particle surface (mol m^{-3})
Disp_{Cu}	dispersion of metallic copper in the catalyst (%)	T	temperature of catalyst bed (K)
$S_{\text{Cu}(0)}$	specific surface area of Cu^0 (m^2/g)	V_i	the atomic diffusion volume of specie i (cm^3/mol)
$X_{\text{Cu}(I)}$	the ratio of $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^0)$ (%)	$D_{p,i}$	the diffusion coefficient in the pores ($\text{m}^2 \text{s}^{-1}$)
$S_{\text{Cu}(I)}$	specific surface area of Cu^+ (m^2/g)	$D_{k,i}$	the Knudsen diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
C_{DMA}	DMA conversion (%)	d_p	pore diameter of the catalyst (m)
S_{HDO}	HDO selectivity (%)	$D_{i,j}$	binary diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
C_{DMO}	DMO conversion (%)	M_i	the molecular weight of the specie i (kg mol^{-1})
S_{EG}	EG selectivity (%)	y_i	mole percent content of the diffusing specie i (dimensionless)
r_{site}	the conversion rate of the diesters normalized by reaction time and number of active sites (h^{-1})	P	reaction pressure (Pa)
N_{w-p}	Weisz-Prater criterion	I	species ($i = \text{H}_2, \text{DMA}, \text{HDO}, \text{Ethanol}$)
Ca_{gs}	Carberry number	θ	porosity of catalyst bed
a_s	the external surface area of the catalysts ($\text{m}^2 \text{L}^{-1}$)	μ	molecular viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
$k_{g,i}$	the gas-solid diffusion coefficient of the catalysts ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)	ρ_g	density of gas (kg m^{-3})
Sc	Schmidt number	ε	porosity of porous medium (dimensionless)
$D_{B,i}$	the bulk diffusivity of specie i ($\text{m}^2 \text{s}^{-1}$)	τ	tortuosity factor (dimensionless)
Re	Reynolds numbers		
J_D	Colburn J factor		

Scheme 1, the hydrogenation of both DMO and DMA involves similar reaction sequences. The hydrogenation of DMO first generates methyl glycolate (MG), which can be subsequently hydrogenated to EG and ethanol via two-step hydrogenation. Similarly, the hydrogenation of DMA forms methyl 6-hydroxyhexanoate (MHH), HDO and 1-hexanol as the main products. Normally, it is proposed that there are two different active sites responsible for DMO hydrogenation, namely Cu^0 and Cu^+ . The former mainly contributes to H_2 activation, while the latter acts as Lewis acid site to activate $\text{C}=\text{O}$ bond in carbonyl group [15]. In our previous work on Cu-MCM-41 catalyzed DMO hydrogenation, Cu—O—Si unit, generated from interaction between Cu and the support MCM-41, is demonstrated for its crucial roles on the formation and dispersion of Cu species, resulting in its high catalytic activity [16]. Copper phyllosilicate generated during the preparation of Cu/SiO₂ was also reported to contribute to the formation of Cu^+ species and improve the copper species dispersion [9,17].

For the rational catalyst design for DMA hydrogenation, in order to simultaneously activate the carbonyl functional group and hydrogen, one should be interested in a delicate Cu—O—Si unit or copper phyllosilicate to enhance the formation of Cu^+ and high dispersion of Cu^0 species. However, compared to DMO, the significant larger molecular size of DMA might lead to lower rate of reagents' diffusion. Moreover, the preparation of copper catalyst supported on mesoporous silica by conventional impregnation approach resulted in rare interaction between SiO₂ support and Cu species, leading to lack of accessible active sites.

Herein, series of well-ordered hierarchical porous silica (HPS) with tunable pore size, featured by the co-presence of both mesopores and micropores, were prepared. Further incorporation of Cu species by ammonia evaporation allows the formation of Cu—O—Si unit, while the agglomeration of copper species is hindered by the micropores in HPS. Meanwhile, the mesoporous structure of HPS was also successfully maintained after loading the copper species.



Scheme 1. Main reaction pathway for the hydrogenation of (A) DMO and (B) DMA.

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