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Determining roles of Cu⁰ in the chemosynthesis of diol via condensed diester hydrogenation on Cu/SiO₂ catalyst

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Abstract: Copper-based catalyst was applied in the condensed diester hydrogenation with unexpected high selectivity (~100%) to 1,6-hexanediol. On basis of the mass transfer analysis and kinetics results, the reaction rate of the condensed diester hydrogenation was deduced to be controlled by the activation of hydrogen on Cu⁰ sites, which was further demonstrated by the correlations between the catalytic activity and different copper species. Importantly, this catalysis mechanism is different with that of gas-phase diester hydrogenation, which is generally determined by the adsorption of ester on Cu⁺ species.

Diols is a kind of valuable fine organic chemical, which is widely used in polyesters, medicine, dye and many other fields^[1]. Among all kinds of diols, 1,6-hexanediol (HDO) is one of the most promising diols because it can be used for synthesizing polyurethane, UV paints and other fine chemicals^[2]. Recently, the hydrogenation of dimethyl adipate (DMA) is the most commonly used and studied route for HDO synthesis.

At present, there are two kinds of strategies for this reaction system: gas phase and liquid phase. For the gas-phase route, copper-based catalysts have been studied for decades^[3]. Violetta^[3b] found that Cu-Zn was better than conventional Cu-Cr due to its higher dispersion and stability in hydrogenation environment. And a highest DMA conversion of about 97% was achieved with HDO selectivity below 80%. Our previous work^[3c] reported a novel hierarchical porous copper catalyst (Cu/HPS) for the reaction with an extremely high space-time yield (STY) of hexanediol (0.72 h⁻¹) and HDO selectivity of 89%, which was attributed to highly dispersed Cu⁰ and Cu⁺ species as well as the enhanced mass-transfer due to the ordered mesoporous structure. Up to now, the bottleneck problem of the gas-phase hydrogenation of DMA is mainly the selectivity of HDO^[3b, 3c]. In addition, the essential high ratio of H₂/diester (generally, higher than 100) leads to high energy consumption.

Current reports on the hydrogenation of condensed DMA focused mainly on noble metal catalysts^[4]. Among these catalysts, Ru-Sn-Co/AIO(OH)^[4c] showed the highest conversion and HDO selectivity of 98% and 95%, respectively. However, the higher catalyst cost limits the application of noble metals.

Although the copper-based catalyst has been extensively studied and applied in gas-phase hydrogenation of esters with excellent catalytic performance, it has never been reported in the hydrogenation of condensed diesters to diols. And, the kinetics and the behaviors of copper species in condensed diester hydrogenation are totally unclear.

In this work, the condensed diester hydrogenation upon Cu/SiO_2 catalyst with DMA as the model reactant was studied, and the catalysis mechanism of copper species and the kinetics in this reaction system were discussed and clarified.

Firstly, we prepared Cu/SiO₂ catalyst by hydrolysis precipitation method (denoted as Cu-HP-N), which endowed the catalyst high dispersion of Cu⁰ and Cu⁺ as well as large mesopore size^[5]. As listed in **Table S1**, Cu-HP-N catalyst tested in a stirred tank reactor gives a significantly high selectivity of 100% and conversion of 94.7% at the optimized reaction conditions (Entry 4). Meanwhile, it also shows a STY of 1,6-hexanediol as high as 0.81 h⁻¹, which could open a gate for developing a new technology of condensed diester hydrogenation upon copper catalyst.



Figure 1. Mass transfer model for the hydrogenation of condensed DMA. I-gas phase; II-gas film; III, V-liquid film; IV-liquid phase.

In order to further study the catalytic system, the influence of mass transfer needs to be clarified firstly. Although the absence of external and internal diffusion limitations can be deduced according to the constant conversion results obtained by varying the stirring speed (**Figure S1**) and grain size of the catalyst (**Figure S2**), respectively, a detailed analysis should be further

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carried out. For this purpose, mass transfer criterion is applied in the system. As illustrated in supporting information, the simulation of diffusion resistance according to the Gas-liquidsolid diffusion model (Figure 1) reveals the absense of hydrogen-absorption resistance^[6]. And the diffusion limitation in liquid film (V) and pores have also been demonstrated to be eliminated by Carberry number (Ca)^[7] and Wheeler-Weisz group (W-W)^[8], respectively. These results further demonstrates that the reaction is mainly controlled by surface reaction rather than mass transfer. Thus, the intrinsic reaction and the role of copper species in this condensed diester hydrogenation can be further studied.

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Figure 2. Kinetics results for hydrogenation of condensed DMA. Conditions for (a) and (b): T=483 K, P=5 MPa; conditions for (c) and (d): T=483 K, P=3~6 MPa.

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able 1. Physicochemical properties of catalysts								
	Catalyst	S _{BET} (m ² /g)	D _{Cu} (nm) ^[a]	D _{Cu2} O (nm) ^[a]	D _{TEM} (nm)	Cu ⁺ /Cu ⁰	S _{Cu⁰} (m ² /g) ^[b]	$S_{Cu^{+}} (m^{2}/g)^{[c]}$
	Cu-HC	342	3.9	3.1	5.3	0.50	33.3	16.6
	Cu-AE-3H	440	ND	3.3	4.5	0.67	43.3	29.0
	Cu-AE-12H	435	ND	3.1	4.4	0.39	53.4	21.0
	Cu-HP-B	498	ND	3.6	4.2	0.66	33.8	20.4
	Cu-HP-N	542	ND	3.2	4.0	-	-	-

[a] nanoparticle size obtained from XRD results. [b] measured by N₂O-titration. [c] calculated by Cu⁺/Cu⁰ × S_{Cu}⁰. ND cannot be detected by XRD.

According to the XRD patterns of calcined catalysts (Figure S5a), all the catalysts have similar diffraction peaks which could be ascribed to the chrysocolla (JCPDS27-0188). The small nanoparticle size of Cu and Cu₂O (Table 1) on the reduced catalysts (Figure S5b) demonstrates the coexistence of highly dispersed Cu⁰ and Cu⁺. TEM images of reduced catalysts (Figure S6) show that all the catalysts are amorphous except for the Cu-HC with nanotube structure. And, the size of copper nanoparticles is almost identical for all the catalysts, which is consistent with the XRD results.



Figure 3. XPS (a) and Cu LMM Auger (b) spectra of reduced catalysts.

hydrogenation of esters has been widely accepted^[5, 9], in which hydrogen and esters should be adsorbed on two different active sites before the reaction. And, only one of them is the controlling-step. For the condensed diester hydrogenation on Cu/SiO₂ catalyst, both the DMA conversion and HDO yield (Y_{HDO}) exhibit linear correlation with reaction time (Figure 2). Considering the much higher and constant hydrogen pressure (5 MPa), as well as the big decrease of DMA concentration with the reaction time, we speculate that the reaction is zero order with respect to DMA. According to the law of mass action^[10], the apparent reaction rate can be expressed by equation (1) and (2), in which x and y are the reaction order of H₂ and DMA, respectively. The hydrogenation rates (conversions are all controlled below 20%) with different reactant concentration have been obtained and shown in Figure 2c and 2d. Obviously, the reaction is first order with respect to hydrogen, but zero order to DMA. It demonstrates that the rate-controlling step of the condensed DMA hydrogenation is the activation of hydrogen instead of DMA.

Recently, the synergy mechanism of the copper catalyst in the

$$R_{A} = k c_{H}^{x} c_{DMA}^{y} (1)$$

$$lnR_{A} = x lnc_{H} + y lnc_{DMA} + lnk (2)$$

To obtain further insight into the catalysis mechanism in hydrogenation of condensed DMA, several Cu/SiO₂ catalysts with different Cu⁰ and Cu⁺ surface areas were prepared by different methods, including ammonia evaporation method (AE)^[11], hydrothermal crystallization method (HC)^[12] and hydrolysis precipitation method (HP)^[5].

According to the results of N2-adsorption (Figure S4), all these catalysts are demonstrated to be mesoporous structured materials. The BET surface areas vary from 342 m²/g to 542 m²/g (Table 1), but their mean pore diameter and volume exhibit little difference (Table S3). In addition, the W-W numbers of all catalysts are below 0.1 (Table S4), excluding the possible influence of pore diffusion on the reaction rates.

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Cu⁰ and Cu⁺ surface areas have been obtained by combining the XPS and N₂O-titration results. As illustrated in **Figure 3a**, the photoelectron peaks at about 952.2 eV and 932.4 eV can be assigned to the binding energy of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ respectively, and the absence of shoulder peak between 942 eV to 944 eV suggests that the Cu²⁺ in all samples has been totally reduced to Cu⁰ or Cu^{+[13]}. In addition, the peaks at 572.7 eV and 570.0 eV in **Figure 3b** can be assigned to the binding energy of Cu⁺ and Cu⁰, respectively^[14]. The Cu LMM spectra were deconvoluted and the ratio of Cu⁺/Cu⁰ were calculated. Finally, Cu⁺ surface areas were calculated by combining the ratio of Cu⁺/Cu⁰ with the Cu⁰ surface areas (measured by N₂O-titration). The results are shown in **Table 1**, in which the big difference in both S_{Cu⁰} and S_{Cu⁺} should be attributed to the different coppersilica interaction induced by the various preparation methods^[5].



Figure 4. The correlation between catalytic performances and copper species. $STY-S_{Cu^{0}}(a)$; $TOF_{Cu^{0-}}S_{Cu^{+}}(b)$.

Figure 4a presents an approximately linear correlation between STY and the surface areas of Cu⁰. Moreover, as shown in Figure 4b, the turnover frequency (TOF) of Cu⁰ exhibits a constant value (about 3.23 h⁻¹) with the increase of Cu⁺ surface areas. These results indicate the number of Cu⁺ sites on these catalysts are sufficient for DMA adsorption. On the contrary, no regular correlation between STY and Cu⁺ surface areas or between TOF of Cu⁺ and Cu⁰ surface areas is observed (Figure S7), which further identify that Cu⁺ site is not the determining factor for the condensed DMA hydrogenation. Therefore, it can be concluded that the hydrogen activation controlled by Cu⁰ sites is the rate-determining step in the hydrogenation of condensed DMA to HDO on Cu/SiO₂ catalyst. Certainly, it does not mean that Cu⁺ site is useless, only that Cu⁰ acts as more important roles than Cu⁺ at the given conditions. It is noteworthy that above findings are different with those previous reported catalysis mechanism in gas-phase esters hydrogenation on copper catalyst, in which the adsorption of ester on Cu⁺ site is always the controlling step ^[5, 15]. Although it has been confirmed that the carbonyl group of esters can be easier adsorbed on Cu+ than Cu⁰ site ^[16], the weak adsorption of DMA molecular on the Cu⁰ surface ^[17] could be serious in the condensed DMA hydrogenation system. As a result of the competitive adsorption between DMA and H₂, the adsorption of H₂ on Cu⁰ site could be inhibited. Therefore, the adsorption of H₂ instead of diester becomes the rate-determining step in the condensed diester hydrogenation system. This finding could provide an important clue for the rational design of efficient catalyst and the development of new technology for diester hydrogenation.

In summary, the roles of Cu/SiO_2 in the condensed diester hydrogenation was studied for the first time. The Cu/SiO_2 catalyst exhibited significantly higher diol selectivity of 100% and space-time yield of 0.81 h⁻¹ at the conversion of 95%. On basis of the mass transfer analysis and kinetic study, the condensed DMA hydrogenation is first order with respect to H₂, but zero order to DMA. It indicates that the concentration of hydrogen in the liquid phase is the key factor for the condensed DMA hydrogenation. Furthermore, the rate-determining step of this reaction system was demonstrated to be the activation of hydrogen, which depends on the adsorption ability of Cu^0 species on the catalyst. These results give crucial important guidance to the development of highly efficient catalyst for the hydrogenation of condensed diesters.

Experimental Section

The details of the synthesis, characterization and evaluation of the catalyst are provided in the electronic supporting information.

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Keywords: Hydrogenation • Diester • Condensed phase • Copper • Kinetics.

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Entry for the Table of Contents



A significantly high hexanediol selectivity of 100% is achieved in the condensed diester hydrogenation on Cu/SiO_2 catalyst. The determining-step of this system is the activation of hydrogen on Cu^0 sites, which is different with that in gas-phase hydrogenation of diesters.