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One-step synthesis of dimethyl ether from syngas on ordered mesoporous copper incorporated alumina[☆]

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ABSTRACT

Ordered mesoporous copper incorporated Al_2O_3 ($\text{Cu}/\text{Al}_2\text{O}_3$) with high Cu dispersion were prepared by a facile solution combustion synthesis method using aluminum nitrate and copper nitrate as oxidants and urea as fuel. It is a facile and green route to synthesize catalysts for dimethyl ether directly from syngas. $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts were characterized by XRD, N_2 adsorption–desorption, SEM-EDS, and H_2 -TPR. The results indicate that the catalysts obtain an ordered mesoporous structure and copper is homogeneously dispersed. The mesoporous $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts were utilized as bifunctional catalysts in syngas to dimethyl ether reaction (STD). The copper content affects the catalytic performance in STD reaction. The CO conversion and DME selectivity of $\text{Cu}/\text{Al}_2\text{O}_3$ with 15% copper molar ratio achieve 52.9% and 66.1%, respectively. Moreover, the mesoporous $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts show excellent stability in STD reaction.

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1. Introduction

Dimethyl ether (DME) is widely used as a basic intermediate for synthesis of important chemicals such as dimethyl sulfate, methyl acetate and acetaldehyde [1,2]. Meanwhile, DME is also a potential clean alternative diesel fuel or liquefied petroleum gas (LPG) with high cetane number and no soot, NO_x and SO_x emissions [3].

Conventionally, DME can be produced by a two-step process: methanol synthesized from syngas and followed by methanol dehydration to form DME. Compared with two-step process, a one-step process from syngas to DME in a single reactor, also known as STD reaction, has attracted growing interest because it is more thermodynamically and economically competitive [4]. The bifunctional catalysts for STD reaction usually comprise of a methanol synthesis catalyst (such as Cu/ZnO or Cr/ZnO) and a solid acid catalyst (such as Al_2O_3 or HZSM-5) [5,6].

Co-precipitation of methanol synthesis catalyst over methanol dehydration catalyst is a common preparation method for the preparation of the bifunctional catalysts for STD reaction. However,

the size of the precipitating particles and the subsequent aggregation are hard to be under control [7], which will affect the catalytic performance in the STD reaction. Physically mixing is another common method to synthesize the bifunctional catalysts for STD reaction: methanol synthesis catalyst and methanol dehydration catalyst are mechanically mixed [8]. However, it is difficult for the physically mixed catalysts to suppress the formation of undesired byproducts [9]. A series of capsule catalyst with a core-shell-like structure have been synthesized, which have shown excellent catalytic performance in the STD reaction [10,11].

However, the synthesis procedure for the capsule catalyst is usually complicated and must be operated very carefully, which severely confines its industrial preparation and application [9]. Recently, Jiang et al. used a solvent evaporation induced self-assembly (EISA) method for the synthesis of mesoporous $\text{Cu}-\text{Al}_2\text{O}_3$, and utilized this material as bifunctional catalyst for STD reaction [12]. This catalyst synthesized by EISA method without ZnO exhibited excellent catalytic performance, suggesting that ZnO might not be the essential component if copper is well dispersed on supports. However, this EISA method requires a strict control of experimental conditions and expensive Pluronic P123 as a structure directing agent which limits its industrial application.

Solution combustion synthesis (SCS) technique is a facile and effective route to synthesize Al_2O_3 based materials, which is capable of high output synthesis of fine and nanostructured materials [13,14]. The present work attempts to synthesize ordered mesoporous $\text{Cu}/\text{Al}_2\text{O}_3$ with high dispersion of copper via a facile SCS

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46 technique, and Cu/Al₂O₃ is characterized by XRD, SEM, EDS, N₂ 47 adsorption and H₂-TPR. The effects of calcination temperature and 48 copper content of this catalyst for catalytic performance are also 49 investigated in the present work.

50 2. Experimental

51 2.1. Synthesis of catalyst

52 The bifunctional catalysts Cu/Al₂O₃ were synthesized by a so- 53 lution combustion synthesis procedure using analytical reagent 54 Al(NO₃)₃·9H₂O (Kermel, 99%) and Cu(NO₃)₂·3H₂O (Kermel, 99%) as 55 the oxidant and carbamide (urea, CO(NH₂)₂) (Kermel, 99%) as the 56 fuel. In a typical synthesis procedure, 95 mmol carbamide, 2 mmol 57 Cu(NO₃)₂·3H₂O, and 38 mmol Al(NO₃)₃·9H₂O were dissolved into 58 10 mL deionized water under magnetic stirring. The obtained so- 59 lution was poured into ceramic carrier and placed into a tubular 60 furnace to be calcined from room temperature to 400 °C, 600 °C, 61 800 °C or 1000 °C at a heating rate of 3 °C/min in air for 2 h. Af- 62 ter calcination, the obtained samples were granulated into a 20- 63 40 mesh grain before used as catalysts for STD reaction. The total 64 amount of metal species was kept constant (40 mmol), and 65 Cu/Al₂O₃ with 5%, 10%, 15%, 20% and 25% copper contents was syn- 66 thesized, respectively. The final samples were denoted as xCA-800, 67 x indicating copper molar percentage, C indicating copper, A indi- 68 cating aluminum and 800 indicating the calcination temperature. 69 For example, 5CA-800 refers to Cu/Al₂O₃ with 5% molar fraction of 70 copper and calcined at 800 °C. For investigating the effect of cal- 71 cination temperature on the structure of Cu/Al₂O₃ and catalytic 72 performance, 15CA (Cu/Al₂O₃ with 15% copper molar contents) 73 with different calcination temperatures (400 °C, 600 °C, 800 °C or 74 1000 °C) was synthesized denoted as 15CA-400, 15CA-600, 15CA- 75 800 and 15CA-1000 °C, respectively.

76 2.2. Characterization of catalyst

77 Powder X-ray diffraction patterns were recorded on a Shimadzu 78 XRD-6000 diffractometer using Ni-filtered Cu K α (0.154 nm) radi- 79 ation. The catalysts were characterized in terms of their specific sur- 80 face area (BET), total pore volume and average pore diameter. The 81 average pore diameter was calculated using the Barrett-Joyner- 82 Halenda (BJH) pore size model applied to the adsorption branch 83 of the isotherm. Measurements were carried out by N₂ adsorp- 84 tion-desorption using a NOVA 1200e gas sorption analyzer. The 85 morphology and elemental distributions of the catalyst's surface 86 were analyzed by a HITACHI S-4800 scanning electron microscope 87 equipped with energy dispersive spectroscopy (SEM-EDS).

88 Temperature-programmed reduction (TPR) was performed on 89 Chemisorb 2720 loaded with 50 mg of sample. The sample was 90 first purged with He gas at 300 °C for 1 h, then cooling to 50 °C 91 and switching to a gas mixture of 10% H₂ in argon at a flow of 92 30 mL/min. The temperature was raised from 50 °C to 500 °C or 93 700 °C with a heating rate of 10 °C/min.

94 NH₃-TPD experiments were conducted by the following pro- 95 cedure: 40 mg sample was activated in flowing He at 300 °C for 96 1 h and then exposed to 5% NH₃ in N₂ at 60 °C for 0.5 h. Then, 97 the sample was purged with He at 60 °C for 1 h to remove the 98 physisorbed NH₃. The TPD measurements were performed with 99 He flow (30 mL/min) from 60 °C to 800 °C, with a heating rate of 100 10 °C/min. The TPD signals were recorded by a thermal conductiv- 101 ity detector (TCD).

102 X-ray photoelectron spectroscopy (XPS) was conducted using 103 ESCALAB 250 spectrometer with a mono-chromatized Al K α source 104 (1486.6 eV) at constant analyzer pass energy of 30.0 eV. The bind- 105 ing energy is estimated to be accurate within 0.1 eV. All binding

energies (E_b) were corrected, referencing to the C 1s (284.6 eV) 106 peak of the contaminant carbon as an internal standard. 107

108 Before the reaction, 1 g catalyst was first reduced in situ at 109 280 °C in a fixed-bed stainless steel reactor (internal diameter: 110 8 mm; length: 120 mm) by a 5% H₂ in nitrogen flow (50 mL/min) 111 for 4 h. After reduction, the syngas (H₂/CO=2) was introduced into 112 the reactor at 5 MPa with a gas hourly space velocity (GHSV) of 113 1500 mL/(h·g_{cat}) and at a temperature of 260–320 °C. The effluent 114 products were analyzed by an online GC (Shimadzu, TCD). The CO 115 conversion and products selectivity were calculated based on the 116 total carbon balance. All analysis lines and valves were heated to 117 prevent possible condensation of the products before entering the 118 gas chromatograph, ensuring a reliable materials balance.

119 3. Results and discussion

120 Fig. 1(a) presents the small angle XRD patterns of Cu/Al₂O₃ 121 with different copper contents. All of the catalysts show a diffrac- 122 tion peak at 1.0°, indicating the presence of uniform mesoporosity 123 on Cu/Al₂O₃. The catalyst 15CA-800 exhibits the strongest diffrac- 124 tion peak among the catalysts; meanwhile, 5CA-800 and 10CA-800 125 show relatively low order of pore structure. It is noted that the 126 existence of uniform mesoporosity on Cu/Al₂O₃ after calcined at 127 800 °C, indicated the excellent thermal stability of the mesoporous 128 Cu/Al₂O₃. Weak peaks at 37.5°, 45.8° and 66.8° are observed on the 129 wide angle XRD pattern of 5CA-800 and 10CA-800 (Fig. 1b), which 130 indicates the formation of crystalline Cu- γ -Al₂O₃ [12,15,16].

131 The characteristic peaks of CuAl₂O₄ spinel (JCPDS No. 33-0448) 132 at 31.3°, 36.8°, 45.1°, 59.4° and 65.3° are observed on the samples, 133 and the intensity of these peaks increases along with the increas- 134 ing copper content. No diffraction peak of CuO is detected on the 135 samples. All the XRD results indicate that copper is incorporated 136 into the alumina matrix, suggesting that copper is well dispersed 137 on the samples.

138 Fig. 2(a) presents small angle XRD patterns of 15CA at different 139 calcination temperatures. Along with the calcination temperature 140 increasing from 400 °C to 800 °C, the intensity of the peak becomes 141 less defined and the peak is not present any more when calcina- 142 tion temperature is 1000 °C. The results indicate that the order of 143 mesoporosity is obviously lost with increasing calcination temper- 144 ature. As shown in Fig. 2(b), the XRD patterns of 15CA-400 and 145 15CA-600 display the characteristic peaks of CuAl₂O₄, and the in- 146 tensity of the peaks becomes stronger along with calcination tem- 147 perature increasing. Further increasing calcination temperature to 148 1000 °C, the characteristic peaks of α -Al₂O₃ (JCPDS No. 046-1212) 149 and θ -Al₂O₃ (JCPDS No. 023-1009) can be observed obviously on 150 15CA-1000 [17]. Meanwhile, the characteristic peaks of CuAl₂O₄ at 151 31.3°, 36.8°, 45.1°, 59.4° and 65.3° are not present but a new char- 152 acteristic peak of CuAl₂O₄ at 55.7° (422) can be observed. More- 153 over, no diffraction peaks of CuO are detected on all of the sam- 154 ples. Again, all the XRD results indicate that copper is incorporated 155 into the alumina matrix, suggesting that copper is well dispersed 156 on these samples as well.

157 Fig. 3 shows N₂ adsorption-desorption isotherms (a) and the 158 corresponding pore size distributions (b) of Cu/Al₂O₃ with differ- 159 ent Cu contents. The isotherms of the samples are type IV with 160 H1 hysteresis loops, which indicates the mesoporosity of the sam- 161 ples. The corresponding pore size distributions reveal that all the 162 samples obtain ordered pore distributions and average pore size 163 distribution centers between 3.7–6.3 nm. The pore structure pa- 164 rameters of Cu/Al₂O₃ with different Cu contents are summarized 165 in Table 1. With different copper contents, BET surface areas vary 166 from 128.8 m²/g to 237.8 m²/g, and BET surface areas decrease 167 along with the increasing copper contents from 5% to 25%. The 168 total pore volumes are between 0.21 cm³/g to 0.27 cm³/g. The aver- 169 age pore diameters are between 3.7 nm to 6.3 nm.

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