
Study of Supercritical-Phase CO₂ Dried Cu/ZnO Catalyst for Low-Temperature Methanol Synthesis from Syngas

Prof. Jian MENG, State Key Laboratory of Rare Earth Resource Utilization,
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China

Methanol, as the main products of the C1 chemistry, is a kind of chemical feedstock which has broad applications. Currently, the commercial methanol synthesis method uses copper-zinc-based oxide catalyst developed by ICI Co. Ltd. under high temperature and high pressure (523 – 573 K, 50 – 100 bars). However, the efficiency of methanol synthesis is severely limited by thermodynamics because it is an extremely exothermic reaction. In order to solve this problem, the present authors developed a new low-temperature process for methanol synthesis by using alcohol as both solvent and promoter over Cu/ZnO catalyst at 443 K and 5.0 MPa from syngas containing CO₂.

The catalyst was prepared by co-precipitation method. The swelled precursor experiences remarkable sintering during the drying in air at 393 K. The sintering of the precursor is caused by large liquid-vapour interfacial forces, which destroy the delicate surface structure during an evaporative drying procedure. Recently, a new drying technique, supercritical drying, has been developed. The supercritical drying is using another solvent, which is above the critical point of the mixture of two solvents, to extract the solvent involved in the swelled catalyst. Theoretically, the skeletal structure of the swelled catalyst can be maintained through supercritical drying. Alcohol and carbon dioxide are usually used as supercritical drying media, and the latter has a relatively low critical temperature ($T_c = 31^\circ\text{C}$) and is not flammable. In this work, we used the supercritical fluid of CO₂ to extract the solvent from the catalyst precursor to avoid the agglomeration of the surface structure of the Cu/ZnO catalyst. The influence of the supercritical fluid drying preparation method to methanol synthesis was also investigated and discussed.

The Cu/ZnO catalysts were prepared by a co-precipitated method. An aqueous solution containing copper, zinc nitrates with a molar ratio of 1:1, and an aqueous solution of sodium carbonate were added simultaneously the deionized water with constant stirring. The obtained precipitate was aged overnight, filtrated, and washed with adequate deionized water. The deposit was dried at 393 K for 12 h. For the catalyst prepared by SCF-CO₂ drying, the deposit was dried by 7.5 MPa or 8.0 MPa SCF-CO₂ at desired temperature fore different period. The precursors as mentioned above were then calcined in air, reduced by a flow of 5 % hydrogen, and successively passivized by 1 % oxygen.

The BET surface area of Cu/ZnO catalyst was measured by N₂ adsorption method. Specific copper surface areas were determined by a well-known decomposition method that N₂O reacts with surface Cu⁰.

A semi-batch type reactor was employed in the experiment. 3.0 g of the catalyst and 40 ml of 2-butanol were poured into the reactor. After purging the system with syngas (CO/CO₂/Ar/H₂ = 31.8/5.21/3.04/59.95) at room temperature, the internal pressure of the reactor increased to 5.0 MPa. The experiment was conducted at 443 K with the feeding gas of 20 ml/min under continuous stirring. The products were collected after 20 h semi-batch activity test, and then analyzed by Shimadzu

GC320 and GC-8A with FID detector.

The catalytic activity, the BET surface area and the specific copper surface area of the prepared Cu/ZnO catalysts for MeOH synthesis at low-temperature from CO₂ containing syngas using alcohol as promoter, as proposed in our previously work, are listed in the Table 1. At 443 K, the prepared Cu/ZnO catalyst without SCF-CO₂ drying exhibited the lowest total conversion, i.e. 35.1 %, and MeOH selectivity, i.e. 96.3 %, among all of the catalysts. The BET surface area and Cu-specific surface area of Cu/ZnO catalyst were 53.1 m²/g and 18.7 m²/g, respectively. For the catalysts dried by SCF-CO₂ during the preparation, both the total conversion and the MeOH yield increased indicating that the SCF-CO₂ drying improved their catalytic performance.

The influence of the various SCF-CO₂ drying conditions was also evaluated in Table 1. For the catalyst precursor dried by SCF-CO₂ at 308 K for 1, 3 or 5 h, only the precursor dried by SCF-CO₂ for 3 h presented the highest catalytic activity, i.e. MeOH yield of 44.8 %, as well as the biggest specific-Cu surface area of 23.3 m²/g. Here, with the prolonged drying period, the BET surface area also increased. Nevertheless, when the SCF-CO₂ drying temperature increased from 308 to 363 K, the MeOH yield, the BET surface area, and the specific-Cu surface area decreased, simultaneously. It suggests that high SCF-CO₂ drying temperature might sinter the catalyst precursor leading to the suppressed BET surface area as well as the specific-Cu surface area. Also, the specific-Cu surface area was an important factor for the catalytic activity for the SCF-CO₂ prepared catalyst. The bigger specific-Cu surface area is the higher MeOH synthesis activity. Moreover, the catalyst precursor dried by SCF-CO₂ at 7.5 MPa and 443 K for 3 h was also investigated. Compared with the catalyst SCF-CO₂ dried at 8.0 MPa, the BET surface area of the catalyst dried at 7.5 MPa increased from 58.0 to 63.9 m²/g, while that of the MeOH yield decreased from 44.8 to 42.1 %, and the specific-Cu surface area decreased a little from 23.3 to 22.7. It indicates that the BET surface area didn't directly affect the catalytic activity of the catalysts, while the increase of the specific-Cu surface area, which correlated to the number of the active species, i.e. Cu⁰, on the catalyst, could enhance the catalytic activity.

Table 1 Catalytic performance of the Cu/ZnO catalysts with the various SCF-CO₂ treatment.

SCF-CO ₂ conditions ^a	Total conversion (%)	MeOH selectivity (%)	MeOH yield (%)	BET surface area (m ² /g)	Specific-Cu surface area (m ² /g)
0 ^b	35.1	96.3	33.8	55.0	18.9
308 K, 8 MPa, 1 h	37.1	96.0	35.6	52.1	16.8
308 K, 8 MPa, 3 h	46.4	96.6	44.8	58.0	23.3
308 K, 8 MPa, 5 h	39.2	96.2	37.7	63.5	18.7
323 K, 8 MPa, 3 h	37.4	94.9	35.5	55.9	18.8
343 K, 8 MPa, 3 h	36.9	95.3	35.2	55.0	18.5
363 K, 8 MPa, 3 h	36.4	94.7	34.5	53.8	18.5
308 K, 7.5 MPa, 3 h	42.7	98.6	42.1	63.9	22.7

^a the flow rate of SCF-CO₂ was 5 ml/min. ^b the catalyst without SCF-CO₂ treatment.