

学位論文題目: New Catalyst and New Process for C₁ Chemistry (C₁化学の新触媒と新プロセス).

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New Catalyst and New Process for C₁ Chemistry

Recent years, dimethyl ether (DME) and methanol are widely used as feedstock in chemical and energy industries. DME, the simplest ether, is widely used in a lot of fields, cooking fuel, spray-can propellant, or diesel fuel oil. And it can replace LPG with similar chemical and physical property. And methanol is also one of the most important liquid fuels that can be supplied to the modified internal combustion engines or fuel cells via either reforming to hydrogen or the methodology of direct methanol fuel cell. In this thesis, the Cu/ZnO catalysts used for methanol and DME synthesis, prepared by different methods, are employed. Besides, natural gas, as an important energy resource in production of clean transportation fuels and other chemicals such as hydrogen, syngas, higher hydrocarbons, and organic oxygenates, has attracted great interest in recent years. Furthermore, natural gas needs to be liquefied to liquid natural gas (LNG) for facilitating the transporting and storage in the industrial application. Numerous studies are carried out on methane conversion, which focus on mainly two processes such as direct and indirect conversion of methane. Direct conversion of LNG to syngas and ethylene using non-equilibrium pulsed discharge is also studied here.

In chapter 1, different methods for preparation of Cu/ZnO catalysts are introduced. Metallic catalysts are widely used in the industrial catalytic processes, as hydrogenation, dehydrogenation, isomerization, reforming, selective hydrocarbon oxidation catalysts and so on. General methods for the synthesis of metallic catalysts often reduce metal oxides with H₂ or CO at high temperature. However, the extra cost for reduction energy and engineering makes the whole catalyst preparation process

inefficient.

Methanol with a worldwide demand of ~50 Mtons per year is industrially produced under high-temperatures and elevated pressures (523-573 K, 5-10 MPa), mainly using Cu/ZnO/Al₂O₃ catalysts developed by ICI Co. However, the efficiency of methanol synthesis is severely limited by thermodynamics because it is an extremely exothermic reaction. One pass conversion of ICI plant is limited to only 14% and it will become zero if synthesis temperature is lower than 473 K. Therefore, developing a low-temperature process for methanol synthesis that can make higher one-pass CO conversion becomes a reality and greatly reduces the production cost.

DME is synthesized through two main routes: one is the direct dehydration of methanol. Another is through a tandem catalysis process, from syngas via methanol as an intermediate, named as syngas to DME (STD) reaction. Different from the DME synthesis using methanol as feedstock, the STD process can be directly conducted in a one-step process from syngas containing CO₂, which also has higher maximum theoretic one-pass CO conversion than methanol synthesis due to the thermodynamics equilibrium shift effect.

In chapter 2, a novel sol-gel auto-combustion method is developed in an argon atmosphere to synthesize metallic Cu/ZnO catalysts which are directly used in low-temperature methanol synthesis without further reduction. However, carbonic residues, from the decomposition of citric acid on the surface of the as-burnt catalysts identified by FT-IR and Raman analysis, will greatly influence the hydrogenation ability of ethyl formate, resulting in low methanol selectivity (37.6%). In this study, the calcination atmosphere is improved from argon to air. The influence of carbonic residues and amorphous carbon is eliminated. The Cu/ZnO catalysts prepared by traditional solid-state and sol-gel combustion methods are employed as references here to compare. Compared with the reaction results from the references and previous reports, the activity (60.7%) and methanol selectivity (93.0%) are significantly increased. The main advantages of the proposed citric acid assisted solid-state method are that: 1) The whole catalyst preparation process is easily-operated with inexpensive metal nitrates and citric acid as raw materials, while typical preparation method of

industrial Cu/ZnO catalyst produces a lot of waste water containing Na^+ and NO_3^- ; 2) It is environmentally friendly because no water is used and no waste water is produced during the whole catalyst-preparation process; 3) Compared with traditional solid-state and sol-gel auto-combustion methods, as-prepared Cu/ZnO catalysts exhibit much higher activity and methanol selectivity.

In chapter 3, account of our precious work in a new low-temperature methanol synthesis is presented. The efficiency of conventional methanol synthesis is severely limited by thermodynamics because it is an extremely exothermic reaction. We proposed a new method of low temperature synthesis of methanol from $\text{CO}/\text{CO}_2/\text{H}_2$ on Cu/ZnO based catalyst using alcohol as a catalyst and solvent, by which methanol was produced at 443 K and 5.0 MPa. As the used alcohol solvent contained a small amount of water, it was considered that this new low-temperature process could directly use low-grade syngas containing CO_2 and H_2O , without purification. The effects of the amounts of the different solvent, the effects of different feed gases, the mechanism of low-temperature methanol synthesis and the kinetics analysis are critically studied.

In chapter 4, we report that Cu/ZnO methanol synthesis catalyst components are directly loaded onto acidic zeolite catalyst by physical sputtering, forming Cu/ZnO/zeolite composite catalyst to accomplish direct synthesis of DME from syngas. The intimate contact between these two catalysts improves this consecutive STD reaction efficiency, achieving high DME selectivity. Conventional wet impregnation method to prepare this kind of catalyst will make Cu cations adsorbed onto zeolite sites very strongly, which are almost impossible to be reduced due to the very strong interaction from zeolite surface. To solve this problem, we propose a new physical sputtering method to directly load metallic Cu and Zn clusters simultaneously onto acidic zeolite catalyst surface, to readily obtain highly selective and multifunctional Cu/ZnO/zeolite metallic catalyst. In the sputtered catalyst, very strong acidic sites of the zeolite are selectively diminished by the sputtered metal, stopping the side reaction of DME dehydration to light hydrocarbons.

In chapter 5, this work firstly reports non-catalytic direct conversion of liquid

natural gas (LNG) to ethylene and syngas using pulse discharge technology, which is completely different from the reaction pathway of gaseous methane conversion. Large amounts of ethylene are formed while no formation of acetylene is observed in the discharge region, indicating that the activation of CH_2 to CH radicals is completely suppressed whereas the dimerisation of CH_2 radicals is promoted, when gaseous CH_4 molecules are liquefied. The operational factors such as electric current, voltage, discharge distance and input power alter obviously the LNG conversion and yield of hydrogen, while affect slightly the product distribution. CO_2 formation is also suppressed due to the low temperature of LNG and the cage effect of high-density LNG.

In chapter 6, for slurry-phase Fischer-Tropsch Synthesis (FTS), the catalyst with distinct bimodal pore structure has excellent advantages because of higher diffusion efficiency and highly dispersed active sites. In this study, the zirconia-silica bimodal catalyst is prepared by introducing zirconia sol into the large pores of silica gel. The internal pore diffusion/reaction is simulated on the basis of the catalyst properties and catalytic performances. The modeling of this bimodal catalyst is established to elucidate the kinetics and pore size effects. As compared with uni-large-pore or uni-small-pore catalyst, the zirconia bimodal catalyst significantly enhances FTS activity because the presence of macropores greatly enhances the mass transfer of reactants and products, while the mesopores improve the dispersion of the active metal, which is consistent with the simulation results.