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学位の種類	博士(工学)
学位記番号	富理工博甲第70号
学位授与年月日	平成26年3月21日
専攻名	ナノ新機能物質科学専攻
学位授与の要件	富山大学学位規則第3条第3項該当
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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学位論文の要旨

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).

ナノ新機能物質科学専攻

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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.

【論文審査の結果の要旨】(曾 春陽)

当学位審査委員会は本論文を詳細に審査し、かつ論文審査会を平成 26 年 1 月 28 日公開で開催し、その発表と質疑応答について審査した。その審査結果を下記のようにまとめる。

本論文は C 1 化学に関する新触媒ならびに新プロセスの開発に関する内容である。

第一章では C 1 化学の背景、展望に関するものである。

第二章では新規低温メタノール合成に応用される銅一酸化亜鉛触媒の新規調製方法として、窒素あるいはアルゴンといったイナートな雰囲気でのゾルーゲル自己燃焼法を開発し、従来固体金属触媒調製工程において不可欠であった還元ならびに表面不動化処理を省略でき、直接還元済状態である金属触媒を得られた。新規調製法で得られた触媒が高い活性を示した。更に各種の物理・化学分光手法を用いて新規触媒調製法のメカニズム、並びに触媒反応のメカニズムを解明した。

第三章では自己燃焼法銅一酸化亜鉛触媒の調製において使われる有機カルボン酸に関する研究内容である。金属硝酸塩とキレートを形成するカルボン酸がクエン酸であったが、炭素原子 6 個を有するため、自己燃焼において燃焼しきれず、触媒表面へ炭素析出がしばしば起き、触媒の金属面露出に不利であった。ここでは炭素一炭素結合を持たないギ酸を代わりに投入し、触媒表面へ炭素析出問題を解決した。更に上記第二章で研究した窒素あるいはアルゴンといったイナートな雰囲気での自己燃焼方法と異なり、空気中での自己燃焼法を研究し、銅一酸化亜鉛触媒の新規調製方法を確立した。これらの新触媒の新規低温メタノール合成において高い活性を確認するとともに、各種の物理・化学分光手法を用いて新規触媒調製法のメカニズム、並びに触媒反応のメカニズムを解明した。

第四章では、二酸化炭素を含む合成ガス（一酸化炭素と水素の混合ガス）からジメチルエーテル(DME)の一段合成用 Cu/ZnO/HZSM5 触媒に関する内容である。従来の触媒調製法では、硝酸銅と硝酸亜鉛を HZSM5 ゼオライト触媒表面へ担持するが、金属イオンが還元されず、触媒活性がほとんどなかった。本研究では金属銅と金属亜鉛を同時にスパッタリング法によって HZSM5 ゼオライト表面へ担持し、困難な還元問題を解決でき、高い DME 合成活性を実現した。各種の物理・化学分光手法を用いて新規触媒調製法のメカニズム、並びに触媒反応のメカニズムを解明した。

第五章では液化天然ガス(LNG)に関する世界唯一な転換研究である。エネルギー密度の低い在来型天然ガスと異なり、液体ケージ構造を有する LNG では

エネルギー密度が高く、高圧反応に類似した状態である。ここでは液化空気も LNG に同伴させ、液中プラズマ放電を導入し、ラジカル励起反応によって選択的にエチレン、合成ガスを生成した。

第六章では F T 合成におけるバイモダル触媒挙動に関するシミュレーションである。メソポアにマイクロポアを有するバイモダル触媒はメソポアに起因する快速物質移動と、マイクロポアに由来する高触媒表面積を同時に有するため、極めて高い F T 合成反応活性を示した。本研究では反応-拡散モデルを立て、数値解析を行い、メソポア或いはマイクロポアのみを有する触媒よりバイモダル触媒の高い活性と選択率について、定量的に解明した。

第七章は上記内容のまとめである。

上記の内容は国際学術専門誌に原著論文 10 報（関連論文 4 報、参考論文 6 法）として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、エネルギー、無機化学合成、触媒調製、ナノ科学、プロセスシミュレーション諸分野において、学術的価値のある知見を与えていると判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。