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Highlight

ZnO-ZrO₂ solid solution catalyst for highly selective hydrogenation of CO₂ to methanol

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The issue of CO₂, that causing global environmental change has become a worldwide concern. Meanwhile CO₂ is a sustainable carbon resource. It is highly desired to develop technologies to convert CO₂ into valuable chemicals. CO₂ hydrogenation to methanol is one of the promise processes to realize the technologies. Methanol is not only an excellent fuel, but also can be transformed to olefins and other high-value added chemicals. It should be emphasized that the needed hydrogen can be produced from water using any renewable or atomic energy source (Fig. 1) [1].

Methanol synthesis via CO hydrogenation has been industrialized for about 50 years using CuZnOAl₂O₃ catalyst, which also seems like the best catalyst for methanol synthesis for CO₂ hydrogenation. However, methanol selectivity on CuZnOAl₂O₃ from CO hydrogenation is near 99%, while that from CO₂ hydrogenation is less than 60% caused by reverse water gas shift reaction (RWGS). The even more severe problem is the rapid deactivation caused by produced water, which accelerates the sintering of Cu active component during the CO₂ hydrogenation. Therefore, new catalyst is needed to develop to realize the process of CO₂ hydrogenation to methanol with high selectivity of methanol.

Much progress has been made in the development of supported metal catalysts for CO₂ hydrogenation, such as Cu/ZnO/ZrO₂ [2], Pd/ZnO [3], “georgeite” Cu [4], Cu(Au)/CeO_x/TiO₂ [5,6], Ni-Ga [7] and MnO_x/Co₃O₄ [8] cata-

lysts. However, the selectivity towards methanol is lower than 60% under their reported conditions.

Recently, Prof Can Li's Group at Dalian Institute of Chemical Physics presents a binary metal oxide, ZnO-ZrO₂ solid solution catalyst [9], which can achieve methanol selectivity up to 86%–91% with CO₂ single-pass conversion over 10% under the reaction conditions of 5.0 MPa, 24000 mL/(g h), H₂/CO₂ = 3/1–4/1, 320–315 °C (Fig. 2A).

In their experiments, ZnO phase was not observed in XRD when adding ZnO (5–33%) into ZrO₂, but leads to the phase change of ZrO₂ from monoclinic to tetragonal. The (011) of ZrO₂ shifts to a higher angle when Zn concentration is increased, indicating that ZnO-ZrO₂ is in a solid solution state with Zn incorporated into the ZrO₂ lattice matrix when ZnO contents in the range below 50% (Fig. 2B–D). Their CO₂-TPD experiments show that most of the CO₂ adsorbed by 13%ZnO-ZrO₂ is on Zr sites, however, H₂-D₂ experiments suggest that there is a strong synergetic effect in the H₂ activation between the two sites, Zn and Zr. The solid solution structure affords dual active sites for H₂ activation by Zn sites and CO₂ activation by its neighboring Zr sites respectively, and are responsible for the excellent catalytic performance. The ZnO-ZrO₂ catalyst was also evaluated for CO + H₂. Besides methanol as the major product, some additional products including DME and methane were detected. The space time yield (STY) of methanol on the 13%ZnO-ZrO₂ catalyst from CO₂ hydrogenation is 2.5 times of that from CO hydrogenation at their optimized temperatures for methanol production. These facts indicate that the ZnO-ZrO₂ solid solution catalyst is especially active for CO₂ hydrogenation to methanol.

There is a current debate about the mechanism of CO₂ hydrogenation [10,11]. Wang et al. [9] propose a mechanism of the direct hydrogenation of CO₂ likely via a formate intermediate, rather than consecutive RWGS and CO hydrogenation on ZnO-ZrO₂ solid solution catalyst. HCOO* and H₃CO* species were observed and identified by *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Their further isotopic experiments demonstrate that the surface HCOO* and H₃CO* species can be hydrogenated to methanol (Fig. 2E–F).

Fig. 1. Carbon capture and utilization (CCU) using H₂ from renewable energy.

Fig. 2. (A) The catalytic performance at the reaction temperatures from 200 to 380 °C with $\text{H}_2/\text{CO}_2 = 3/1$ and $4/1$. (B) HRTEM and (C) Aberration-corrected STEM-HAADF images and element distribution of 13%ZnO-ZrO₂. (D) XRD patterns of ZnO-ZrO₂. (E) *In-situ* DRIFT spectra of surface species from $\text{CO}_2 + \text{H}_2$ and subsequently switched to D_2 . (F) DRIFT-MS of $\text{CO}_2 + \text{H}_2$ and subsequently switched to D_2 .

Furthermore, their DFT calculation results suggest that CO_2 hydrogenation to methanol on the surface of ZnO-ZrO₂ is through the formate pathway, which is in line with the results of experiment.

An important work in heterogeneous catalysis is to bridge the gap between model and applied catalysts especially relative to DFT calculation. In Wang et al.'s work [9], the DFT modeling is based on their structure characterization, the intermediates considered in the pathway of DFT is based on the IR spectrum. The work of Wang et al. gives us an encouraging example. However, CO_2 hydrogenation to methanol is carried out under high pressure, while IR test and DFT calculation are preceded under atmosphere. In addition, the concentration varying regular of HCOO^* and H_3CO^* species is not in line with the methanol varying regular. Further study should be done to confirm whether there are other intermediates for CO_2 hydrogenation to methanol. If we continue to do research in heterogeneous catalysis with a holistic approach involving model materials for structural definition, theoretical modeling for micro kinetic function, and real catalysis data for the integration of high performance data, there is a good chance that this and other problems will be solved in the near future.

The ZnO-ZrO₂ catalyst reported by Wang et al. shows no deactivation in CO_2 hydrogenation and no deterioration in methanol selectivity for over 500 h on stream at least. The further thermal stability test shows that no deactivation is observed after annealing the catalyst at 400 °C for 24 h. Furthermore, the catalyst shows the resistance to sulfur-containing molecules. The sulfur-containing molecules are always present in CO_2 sources from flue gas produced from coal or biomass burning. So the high stability of the catalyst toward the sul-

fur-containing molecules directly decreases the purification cost of the feed gas and results in a superior performance of solid solution catalyst comparing to supported metal catalysts.

The work is of interest to both industry and academia. The high selectivity and stability of the ZnO-ZrO₂ catalyst show potential application in carbon capture and utilization (CCU). The dual active sites nature of the solid solution catalyst offers a new opportunity in fine-tuning catalytic activity and selectivity of a wide range of catalysis.

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Received 30 October 2017

Accepted 2 November 2017

Published 5 November 2017

DOI: 10.1016/S1872-2067(17)62966-8

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1781–1783 doi: 10.1016/S1872-2067(17)62966-8

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ZnO-ZrO₂ solid solution catalyze CO₂ hydrogenation to methanol with 10% CO₂ conversion and 90% methanol selectivity by utilizing renewable energy resources.

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ZnO-ZrO₂固溶体催化剂上CO₂高选择性加氢制甲醇

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摘要: CO₂引起的气候变化已引起全世界的关注, 但同时CO₂也是一种可持续的碳资源. 将CO₂转化为高附加值的燃料或化学品不仅可以解决CO₂的问题, 还可变废为宝得到有用的化学品. CO₂加氢制甲醇是实现这一过程的理想选择之一, 因为甲醇不仅是很好的燃料, 还可转化得到烯烃、芳烃等高附加值化学品, 需要强调的是整个过程所需的氢气是利用太阳能等可再生能源通过光催化、光电催化或电解水制氢得到.

使用煤或天然气经合成气用CuZnOAl₂O₃催化剂合成甲醇已工业化50年左右, 甲醇选择性可达99%, 但该催化剂应用于CO₂加氢制甲醇时, 较强的逆水煤气变换副反应致使甲醇选择性只有60%左右, 另外, 反应生成的水会加速Cu基催化剂的失活. 因此, 开发新型高选择性催化体系显得尤为必要, 世界上很多科学家展开了新型催化剂的研发, 如Cu/ZnO/ZrO₂, Pd/ZnO, “georgeite”Cu, Cu(Au)/CeO_x/TiO₂, Ni-Ga, MnO_x/Co₃O₄催化剂等, 但这几类催化剂体系上甲醇选择性都不超过60%, CO₂加氢制甲醇选择性低的问题一直没有解决.

近期, 中国科学院大连化学物理研究所李灿院士课题组开发了一种不同于传统金属催化剂的双金属固溶体氧化物催化剂ZnO-ZrO₂, 在近似工业条件下(5.0 MPa, 24000 mL/(g h), H₂/CO₂ = 3/1~4/1, 320~315 °C), 当CO₂单程转化率超过10%时, 甲醇选择性仍保持在90%左右, 是目前同类研究中综合水平最好的结果. 研究表明, 该催化剂的固溶体结构特征提供了双活性中心反应位点, Zn和Zr, 其中H₂和CO₂分别在Zn位和原子相邻的Zr位上活化, 在CO₂加氢过程中表现出了协同作用, 从而可高选择性地生成甲醇. 原位红外-质谱同位素实验及DFT理论计算结果表明, 表面HCOO*和H₃CO*是反应主要的活性中间物种. 该催化剂反应连续运行500 h无失活现象, 还具有极好的耐烧结稳定性和一定的抗硫能力, 表现出了良好的工业应用前景. 传统甲醇合成Cu基催化剂要求原料气含硫低于0.5 ppm, 而该催化剂的抗硫能力无疑可使原料气净化成本大大降低, 在工业应用方面表现出潜在的优势.

关键词: 二氧化碳; 二氧化碳加氢; 甲醇合成; 固溶体; 氧化锌-氧化锆

收稿日期: 2017-10-30. 接受日期: 2017-11-02. 出版日期: 2017-11-05.

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