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Roles of nitrogen species on nitrogen-doped CNTs supported Cu-ZrO_2 system for carbon dioxide hydrogenation to methanol

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ABSTRACT

Cu-ZrO_2 catalysts supported on nitrogen-doped CNTs were tested for CO_2 hydrogenation to methanol in a fixed-bed plug flow reactor. The characterization results indicate that the presence of pyridinic nitrogen increases the copper oxide dispersion, promotes their reduction, decreases the Cu particle size and enhances H_2 adsorption capability; the activated CO_2 adsorption predominantly controls CO_2 conversion. In addition, pyridinic nitrogen contributes to the strong adsorption of CO_2, stimulating methanol formation, while pyrrolic nitrogen contributes to the medium adsorption of CO_2, mainly boosting CO formation. Thus, pyridinic nitrogen dominant CNTs supported catalyst (CZ/CNT-N) possesses more active sites compared with the other three catalysts, leading to maximum methanol yield (8.64%) and space time yield (102.21 mg g^{-1}_{cat} h^{-1}); pyrrolic nitrogen dominant CNTs supported catalyst (CZ/CNT-NH_2) obtains more highly active structure, giving the highest intrinsic activity (TOF values).

1. Introduction

CO_2, produced by carbon-rich fossil fuels (e.g., coal, oil, and natural gas) utilization, is one of the main “greenhouse gases”. In recent decades, the rapidly increasing amount of CO_2 emission caused huge negative impact on the environment and led to a series of environment problems, such as global warming, ocean acidification, climate change and so on [1]. Numerous efforts have been made to convert CO_2 to valuable industrial feed stocks instead of treating it as a waste [1–5]. Among them, CO_2 hydrogenation with its economy and effectiveness has been maintained as one of the most appropriate ways to achieve CO_2 chemical fixation, improve climate conditions and alleviate the depletion of fossil resources [1–5]. Methanol, as the main products, on one hand, is a bulk chemical produced in several million tons per year used as the basis for many important downstream products, such as formaldehyde, acetic acid, and plastics [1–5]. And on the other hand, methanol is considered as renewable energy storage medium, because it can be used as a direct fuel or converted into products with a high calorific value, such as dimethyl ether or hydrocarbons [3–5]. Thus, CO_2 hydrogenation to methanol has attracted more and more research interests [6–35].

For this catalytic hydrogenation (thermochemical) reaction, various catalytic systems have been studied. Among them, Cu-ZnO and Cu-ZrO_2 based catalyst systems have attracted great interests [8–20,24–33]. Currently, Cu-ZnO/Al_2O_3 catalyst is widely applied in CO_2 containing syngas hydrogenation to produce industrial methanol, under high pressures (5–10 MPa) and elevated temperatures (220–300 °C). Nevertheless, this Cu/ZnO/Al_2O_3 catalyst is not the same promising to methanol synthesis when the feed gas is changed from CO_2 containing syngas to CO_2/H_2. For CO_2 hydrogenation to methanol, large amount of water formation and CO formation by reverse water gas shift reaction (RWGS), were the key problems. Furthermore, CO_2 was supposed to be the main resources for methanol formation and CO only acts as scavenger of surface oxygen [32]. And therefore, a new, effective and robust catalyst system for CO_2 hydrogenation to methanol was in urgent need [7,14–23,34,35]. ZrO_2 is of special interest for its outstanding mechanical properties, good long term stability, high specific surface area and semiconducting properties[14–20,28–33]. Besides, Cu-ZrO_2 catalyst also has high selectivity to methanol. Therefore, Cu-ZrO_2 based catalysts were studied in the current article.

In comparison to synthesis gas for methanol production, when

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produced from CO_2 hydrogenation, an equivalent amount of H_2O is generated. Large amount of H_2O can both decrease methanol yield and accelerate the crystallization of Cu and ZrO_2, which usually led to the rapid decrease of catalytic activities [36,37]. Thus, the promising catalyst should possess high hydrothermal stability and then hydrophobic materials are most desirable. Carbon nanotubes (CNTs) with excellent hydrophobicity can resistant to high temperature water steam and also accelerate H_2O desorption from the surface soon after its formation. Moreover, CNTs have shown great potential in methanol synthesis [15,16,22,34], because of its hydrophobicity, large specific surface area, tunable porosity, distinct pore-confinement effects, unusual stability in acid and basic media even at high pressures and temperatures. In addition, our previous research demonstrated that the nitrogen-containing CNTs could further benefit to both CO_2 and H_2 adsorption [15]. However, the roles of nitrogen doping on the catalytic performance of CO_2 hydrogenation was not clear.

In fact, except for CO_2 hydrogenation, the catalytic performance of Fischer-Tropsch synthesis [38] and various organic reactions [39–41] as well as the electro-catalytic performance such as fuel cells [42], lithium-air battery [43] and hydrolysis of water [44–47], was also significantly improved by nitrogen doped (N-doped) carbon materials including CNTs, graphene, carbon nanofibers, etc. Although superior catalytic performance of N-doped carbon catalysts has been widely reported, there are wide disagreements on the nature of the catalyst active sites, and the relative importance of the pyridinic, graphitic, and pyrrolic nitrogen (pyrrolic-N) groups, including the role of defect sites [38]. Even for the extensively investigated electro-catalytic reactions, graphitic nitrogen (graphitic-N) [40], pyridinic nitrogen (pyridinic-N), graphitic- and pyridinic-N [45], pyridinic- and pyrrolic-N [39] or carbon atoms adjacent to nitrogen atoms [47] are all reported to be responsible for the considerably improved catalytic performance. This huge controversy can be ascribed to the mixing of graphitic-, pyridinic-, and pyrrolic-N species in the carbon materials, which is inevitable in the doping processes (e.g., by annealing under NH_3 atmosphere) [38–47]. Therefore, it turns out to be a very challenging but interesting task to reveal the roles of nitrogen species on the enhanced catalytic performance of CO_2 hydrogenation.

Until very recently, Guo et al. [47] confirmed the active sites of oxygen reduction reaction (ORR) in fuel cells over N-doped carbons through developing pyridinic and graphitic N-dominated HOPG (highly oriented pyrolytic graphite) model catalyst. Meantime, the powder catalysts, varying amounts of N-doped graphene dominant with various percentages of pyridinic-N, were prepared to investigate the active sites of ORR reaction in order to avoid the gap between the model catalyst and powder catalyst. The obtained linear relationships between the ORR activities and the concentration of pyridinic-N were in consistent with the model catalysts. Their research is encouraging which indicates that there is probability to disclose the roles of nitrogen species on the catalytic performance with powder catalysts.

In order to find a new, effective and robust catalyst system for CO_2 hydrogenation to methanol, the catalysts with high hydrothermal stability should be developed, methanol and CO formation mechanisms and the corresponding active sites should be clearly revealed. Thus, hydrophobic CNTs with nitrogen doping from zero to 2.98 wt%, pyridinic-N increase from 28.7 to 46.2% accompanying with pyrolic-N content decrease from 33.4 to 23.8%, were designed to prepare robust Cu-ZrO_2/CNTs catalysts for CO_2 hydrogenation. The catalysts were extensively characterized and the roles of nitrogen species, especially pyridinic- and pyrolic-N, on catalyst dispersion, reactant activation and catalytic performance were revealed. And the active sites of methanol and CO formation were proposed.

2. Experimental

2.1. Materials and catalyst preparation

Two different kinds of multi-walled carbon nanotubes (CNTs): amino doped (0.84 wt%) CNTs with inner diameters 8–15 nm and outer diameters 10–30 nm and nitrogen doped CNTs (2.98 wt%), are labeled as CNTs-NH_2 and CNTs-N, respectively. Both of them are supplied by Chengdu Institute of Organic Chemistry and used directly without further purification. CNTs-NH_2 calcinated in 10 vol%NH_3/Ar and pure Ar at 700 °C for 5 h were marked as CNTs-NH_2-NH_3-700 and CNTs-NH_2-Ar-700, respectively.

Deposition-precipitation method was applied to load Cu-ZrO_2 on the as prepared CNTs with the mass ratio of 10/40/50 for Cu/ZrO_2/CNTs. The catalysts were prepared through the following steps: the calculated amounts of $Cu(NO_3)_2{\cdot}3H_2O$ and $ZrO(NO_3)_2$ (AR grade, Shanghai Aladdin) were dissolved in de-ionized water, then the mixed metal precursor aqueous solution as well as 0.2 mol L^{-1} NaOH (AR grade, Shanghai Aladdin) aqueous solution was added into the glass container with a predetermined amount of CNTs suspension in water drop by drop. During this process, the suspension should keep vigorous stirring at 70 °C to maintain pH around 7.0–7.5. Then, the obtained precipitation was treated in the same way as published in our previous work [15]. The catalysts supported on nitrogen-doped CNTs supports were named as CZ/CNTs-NH_2-Ar-700, CZ/CNTs-NH_2, CZ/CNTs-NH_2-NH_3-700 and CZ/CNTs-N, respectively.

2.2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS) characterization was carried out on an ESCALAB 250 spectrometer (Thermo Fisher Scientific) using Mg Kα radiation (1253.6 eV) with the energy resolution of 0.1 eV. C1s with the binding energy of 284.6 eV was applied as reference to position the other peaks. The fitting of XPS spectra were conducted on XPS PEAK 4.1 software.

X-ray diffraction (XRD) was conducted on a D8 Advance X-ray diffractometer (Bruker) with Cu Kα radiation ($\lambda = 0.15418$ nm, 40 kV, 40 mA) in the 2θ range of 10–90°. And the XRD results were obtained by comparing with JCPDS cards.

The reduction properties and adsorption capacity of H_2 and CO_2 were characterized by temperature-programmed reduction in H_2 (H_2-TPR), temperature-programmed H_2 desorption (H_2-TPD) and temperature-programmed CO_2 desorption (CO_2-TPD), respectively. All of these processes were carried out on a Micromeritics AutoChem II2920, equipped with a TCD detector. For H_2-TPR, the calcined catalysts (100 mg) was pretreated in Ar at 300 °C for 30 min and then cooled to 50 °C. Then, the sample was flushed by a 10 vol% H_2/Ar mixture until the baseline is stable. Finally, the sample was heated from 50 to 800 °C at a heating rate of 5 °C min^{-1}. The total amount of hydrogen consumption was calculated through the TCD detector signals. For H_2-TPD, the calcined samples were firstly reduced in 5 vol% H_2/Ar at 240 °C for 6 h, then cooled in Ar to 60 °C and saturated with 10 vol% H_2/Ar, followed by flushing with Ar (30 mL min^{-1}) to remove the physically adsorbed molecules. Afterward, H_2 desorption in Ar flow was started with temperature ramping from 60 to 800 °C. CO_2-TPD test was similar to that of H_2-TPD, except that the catalyst was saturated by 20 vol% CO_2/Ar and TPD experiment was conducted in He flow.

2.3. Catalyst evaluation

The catalysts were evaluated under pressurized condition in a fixed-bed reactor. 500 mg catalyst was set in the middle of the reactor. Before the reaction, the calcinated catalysts were reduced in 5 vol% H_2/Ar at