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Effect of magnetic field on CO_2 conversion over Cu-ZnO/ZrO_2 catalyst in hydrogenation reaction

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ABSTRACT

Based on green and sustainable innovation with efficient utilization concepts for enhancement of catalyst performance and energy conservation, an external magnetic field has been applied in CO_2 hydrogenation reaction in order to improve catalytic activity and reduce the energy consumption. In this research, the performances of Cu-ZnO/ZrO_2 catalyst under magnetic field with different magnetic field intensities (0, 20.8, and 27.7 mT) and orientations (north-to-south (N-S) and south-to-north (S-N) directions) in CO_2 hydrogenation were investigated. Cu-ZnO/ZrO_2 catalysts operated under magnetic field gave higher CO_2 conversions, compared to that of without magnetic field at all reaction temperatures. The highest CO_2 conversions were obtained under the magnetic field condition at 20.8 mT in S-N direction which was 1.8–3.0 times higher than that of without magnetic field. Accordingly, the operating temperatures were significantly lower than those of without magnetic field at the same reaction rate. This outstanding performance could be attributed to the fact that the external magnetic field facilitated adsorption of CO_2 reactant gas molecules over the surface of magnetized catalysts. Accordingly, the challenge in application of magnetic field in CO_2 hydrogenation process help reduce CO_2 emission into the atmosphere compared to the convention reactor, and therefore led to the carbon-neutral CO_2 conversion process.

1. Introduction

An increase in global emissions of carbon dioxide (CO_2) over the last decades directly affected climate change and global warming [1,2]. Large amounts of CO_2 mainly come from the combustion of coal and fossil fuels in the industrial processes, and anthropogenic activities including electricity production, transportation, agriculture, and other man-made activities [3]. Several strategies of utilizing CO_2 as a raw material for syntheses of useful chemicals, fuels, alternative energy, and hydrocarbon feedstock can contribute to solve global warming and climate change problems [4,5].

With high demand of energy worldwide, the development of green and alternative energy has become an important issue for energy and environmental sustainability [2,6]. CO_2 hydrogenation is considered as one of the important reactions due to the fact that methanol, dimethyl ether (DME), and chemical feedstock for petrochemical industries can be produced under low reaction temperature (lower than 300 °C) through this reaction [7–9]. In particular, methanol is a clean alternative energy substitute to fossil fuel, reactant for biodiesel production, and chemical feedstock [10,11]. As is well known, Cu-ZnO/ZrO_2 catalyst is active and selective for the synthesis of methanol through CO_2 hydrogenation [3,10,12]. Cu based material is a promising catalyst for methanol synthesis due to its low cost, availability and good performance [9,12,13], while ZrO_2 helps facilitate Cu dispersion on the catalyst surface, leading to an enhancement of active Cu nanoparticles [2,12]. Moreover, ZnO can enhance the performance of Cu catalyst by increasing the active Cu surface in forms of Cu^+ and Cu^0 at the interaction surface of Cu and ZnO, which those Cu forms have been active for the methanol synthesis [13–15]. However, in order to cleaner produce the value-added hydrocarbon products from CO_2 efficiently, the production process with less energy consumption has attracted much interest.

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In terms of green and sustainable innovation with efficient utilization concepts, the external magnetic field is considered as a tool with great potential application in various processes such as fluidized bed reactors to control the movement and avoid agglomeration of magnetic particles, eliminate slugging and channeling, and also reduce the apparent activation energy through improving the gas-solid contact [16–18]. Moreover, the external magnetic field was also applied to liquid-phase 4-nitrophenol reduction [19] and Suzuki cross-coupling reaction [20] over supported palladium (Pd) nanoparticle catalysts. The better catalytic activities due to the alteration of surface spin configuration of Pd nanoparticles from paramagnetic-like to ferromagnetic-like configuration under external magnetic field were reported. However, these research areas related to the application of magnetic field especially in catalytic gas-solid reaction in a fixed bed reactor have not been clearly reported. Accordingly, in this present study we propose a green innovation of an application of external magnetic field to the conventional fixed-bed reactor to facilitate physisorption and chemisorption of the reactant gas molecules over the surface of magnetized catalysts. As a result, the catalyst activity and product selectivity during reaction have been promoted. These phenomena simultaneously lead to the increase of reaction rate and the decrease of reaction temperature, resulting in the lower energy consumption during the reaction.

Accordingly, the exploring green and sustainable innovations regarding the effect of magnetic field (intensities and orientations) on the catalytic performance in CO_2 hydrogenation were investigated in detail. The reaction over Cu-ZnO/ZrO_2 catalyst was operated under magnetic field and compared to that of without magnetic field at different reaction temperatures. Moreover, the outstanding reactivity in term of activation energy (E_a) has been evaluated and discussed. It was found that magnetic field could not only significantly enhance the activity of Cu-ZnO/ZrO_2 catalyst with an intrinsic magnetic property, but also reduce the operating temperature during the reaction. As a result, the magnetic field-assisted reactor exhibited less environmental impact than the conventional reactor by means of CO_2 emission, leading to the carbon-neutral CO_2 conversion process. These advantages will provide potential application in the future chemical and petrochemical processes through green fuel production.

2. Experimental

2.1. Catalyst preparation

Cu-ZnO/ZrO_2 catalyst with Cu:Zn:Zr molar ratio of 1.3:1.2:1 was synthesized through reverse co-precipitation method. Note that the effect of metal oxide composition on the catalytic activity and methanol selectivity in CO_2 hydrogenation has been primarily investigated, and it was found that Cu:Zn:Zr molar ratio of 1.3:1.2:1 exhibited the highest CO_2 conversion and methanol yield. Therefore, this composition was applied throughout this study. Consequently, 100 ml of mixture containing $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $ZrOCl_2{\cdot}8H_2O$ was slowly dropped into $NaHCO_3$ solution (0.1 M, 500 ml) under stirring at room temperature. After that the pH of mixture was adjusted to pH 7 by adding 0.1 M of $NaHCO_3$ solution at room temperature and the mixture was then stirred at 80 °C for 2 h. The obtained solid was filtered, washed with distilled water and with ethanol, consecutively. The solid product was dried at 100 °C overnight and calcined in air at 500 °C for 2 h.

2.2. Catalyst characterization

The textural properties of catalyst including specific surface area, pore volume, and pore diameter were analyzed by nitrogen sorption technique measured at −196 °C using a Quantachrome Autosorb-1C instrument. Prior to each sorption measurement, the sample was degassed at 200 °C for 12 h.

The catalyst morphology was observed by using scanning electron microscopy (SEM: JEOL, JSM-7600F) operated at 15 keV with Pt-coated on the samples. The elements on catalysts (Cu, Zn and Zr) were mapped with energy dispersive X-ray spectroscopy (EDS: OXFORD, X-Max^N). The surface structure of Cu-ZnO/ZrO_2 catalyst was observed by using transmission electron microscopy (TEM: JEOL JEM-2010) with an acceleration voltage of 200 kV.

The amounts of Cu, Zn, and Zr metals on catalysts were analyzed by using inductively coupled plasma-optical emission spectrometry (ICP-OES: Agilent technologies 715). The crystallographic structure of catalysts was examined by using X-ray diffraction spectroscopy (XRD: Bruker, D8 Advance) operated with monochromated Cu Kα radiation (40 kV and 40 mA) at 2θ range of 20–60°.

The magnetic properties of unreduced and reduced catalysts were analyzed by using vibrating sample magnetometer (VSM) under applied magnetic field of 10 kOe at room temperature (Lakeshore model 7404).

The reduction temperature of catalysts was examined by using H_2-temperature programmed reduction (H_2-TPR) technique. This measurement was operated in a continuous-flow Inconel tube reactor. In this series of experiments, H_2/Ar gas mixture (9.6% H_2, Ar balance) was introduced into the catalyst bed at total flow rate of 30 ml/min at room temperature, and the temperature was increased to 900 °C with heating rate of 5 °C/min.

The CO_2 desorption behavior of catalysts under magnetic field was measured by using CO_2 temperature programmed desorption (CO_2-TPD) technique. This measurement was carried out in a continuous-flow tube reactor with and without magnetic field. Prior to each measurement, the catalyst was reduced at 480 °C for 3 h in pure H_2 gas, followed by flushing with Ar gas for 1 h, and then the reactor was cooled down to room temperature. Afterwards, CO_2/Ar gas mixture was introduced into the catalyst bed at 50 °C for 1 h, after that the catalyst was flushed with pure Ar gas. In CO_2 desorption process, the catalyst was heated with a heating rate of 5 °C/min to 500 °C under Ar flow, and the desorbed CO_2 was monitored by using Shimadzu gas chromatograph (GC-2014) equipped with a thermal conductivity detector (TCD).

2.3. Investigation of external magnetic field affecting the catalyst performance

Effects of external magnetic field on the performance of Cu-ZnO/ZrO_2 catalyst in CO_2 hydrogenation reaction were investigated compared to that of without magnetic field. The permanent magnet rings (Bunting Magnetics Co., Ltd.: O.D., 1″; I.D., 0.75″; thickness, 0.5″; grade 5) were placed around a stainless steel reactor (SUS-316, O.D. 3/8″) located horizontally in a center of a tubular furnace equipped with K-type thermocouple positioning in the center of the catalyst bed. Fig. 1a and b show the schemes of magnetic field-assisted fixed bed reactor and magnetic line of force in the direction of north-to-south for four pairs of magnets, respectively. The magnetic field intensity, in the range of 20.8–27.7 mT measured at the center of catalyst bed, was controlled by varying the number of magnet pairs, where the intensities were 20.8 and 27.7 mT when two and four pairs of magnets were applied, respectively. For magnetic field orientations in this series of study, north-south (N-S) direction was the orientation parallel to the flow of reactant gases in north-to-south direction, whereas south-north (S-N) direction was the orientation counter flow to the flow of reactant gases in north-to-south direction.