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Performance of Cu-Zn-Al-Zr catalyst prepared by ultrasonic spray precipitation technique in the synthesis of methanol via CO_2 hydrogenation

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ABSTRACT

The effects of the newly improvised catalyst preparation technique, namely ultrasonic spray precipitation (USP), on the physicochemical properties as well as the catalytic performance of Cu-Zn-Al-Zr catalyst in CO_2 hydrogenation reaction were studied. Spraying technique is advantageous in generating micro-droplets of catalyst precursors by providing high surface area contact during precipitation, while the incorporation of an ultrasonic irradiation can physically alter the surface morphology of the catalyst. In this study, Cu-Zn-Al-Zr catalysts were prepared using both USP and conventional precipitation (CP) techniques for comparison purposes. Structural analysis showed that USP technique dictated the formation of finer Cu crystallites with better particle uniformity. Meanwhile, TPR results revealed a good interaction between different elements in the catalyst with the formation of single form of oxide species. In terms of reactivity, USP-prepared catalyst outperformed CP catalyst for CO_2 conversion by 20.9% and also improved methanol selectivity and yield by 2.7 and 27%, respectively, while reducing noticeably the unwanted CO. It is believed that the improved surface basicity of USP catalyst, which has a great influence on reaction pathways of intermediate species, contributed significantly to the enhanced catalytic performance, and hence justifying the superiority of this new preparation technique over the conventional ones.

1. Introduction

Exploration and research on clean technologies as well as renewable energy sources are becoming more important due to the rising environmental-related awareness among modern human society. CO_2 mitigation and sequestration is one of the areas that attracted immense amount of attention in the recent years in an effort to reduce the impact of carbon emission on global warming. Catalytic hydrogenation is considered as a promising technology to consume and convert this greenhouse gas into valuable chemicals or clean fuels [1–3]. Numerous researches have been carried out in the area of catalyst development particularly in the formulation and elemental composition aspects. Transition metals in multi-metallic formulation are widely accepted as active constituents to catalyse the hydrogenation reactions. Preparation method of these type of catalysts are equally important because phase composition of precursors and final catalyst microstructure, and thus the eventual catalytic performance, rely extremely on it [4]. However, only limited number of research works have so far been dedicated on exploring the aspect of catalyst preparation technique.

In the case of multi-component catalysts, the drop-wise titration of a mixed metal nitrates with precipitating agent is the widely used method of precipitation due to its effectiveness [5]. However, there are some weaknesses associated with this method that allow room for improvement. Based on the fact that solid precipitate formation is extremely dependent on polymerization within the contact area between two liquids, it is difficult to maintain a regular microscopic boundary due to the poor aggregation force or the disorganised agglomeration effect [6]. Additionally, vigorous stirring effect during drop wise titration randomises the nucleation, resulting in the formation of non-uniform size particles with poor porosity [7]. It is believed that random nucleation could also inhibit active metal dispersion, particularly in the case involving multi-elemental precursors.

Thermodynamically, generation rate as well as growth rate of the crystal nucleation, which are also related to the super-saturation state of the solution, are the two major factors that determine the particle characteristics of the dried precipitate [8]. Hence, in order to warrant the formation of uniform and ultrafine particles, a large number of crystal nucleus should be generated and grown simultaneously. This can only be achieved by providing a micro-droplet precursor to be reacted with precipitant. Suppose a single spherical droplet of 1 ml

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precursor has a surface area of only 4.84 cm^2, and the cumulative surface of multiple micro-droplets ($d \approx 2.48$ μm) within the similar volume could reach an approximately 2.42×10^4 cm^2. The dramatically increased contact area leads to more effective molecule collisions and eventually promotes better nucleation rates. Moreover, some researchers have attempted an ultrasonically assisted crystallisation (sonocrystallisation) that allows the exact control over nucleation generation and growth rates [9]. Naturally existing barriers for nucleation are easily overcomed due to the ultrasonic forces, and the surface morphology of catalyst powder is expected to change significantly.

In the present study, an improvised technique namely Ultrasonic Spray Precipitation (USP) was employed. In this technique, mixed metal precursor solution was introduced into the precipitating agent by spraying action under ultrasonic irradiation rather than conventional drop-wise titration. Critical catalyst microstructural properties such as crystallite size, particle size distribution, surface area, as well as the accessible active sites that determine the activity, selectivity and yield are among the improvements expected by adopting this method. The physicochemical properties of prepared catalysts were characterised by Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area method, Particle Size Distribution (PSD), Powder X-ray diffraction (XRD), N_2O dissociative adsorption, Temperature Programmed Reduction of H_2 (H_2-TPR), Temperature Programmed Desorption of H_2 (H_2-TPD) and CO_2-TPD analyses. The catalytic performance in CO_2 hydrogenation reaction were tested using a fixed-bed reactor. In order to justify the improvement of this technique, a comparison with catalyst prepared by conventional method (CP) was also made.

2. Materials and methods

2.1. Preparation of catalysts

Multi-metallic catalyst used in this study (denoted as CZAZ) was a modified formulation based on the similar elemental composition to that of commercially available catalyst for methanol synthesis, comprising of Cu, Zn and Al with an addition of Zr (to improve activity and stability of the catalyst) at 4:3:1:2 ratio. The catalyst was synthesised using both CP and USP method. For every sample, the pre-calculated amount of each metal nitrate salt that gives a final mass of 7.5 g of dried catalyst was mixed and dissolved in 100 ml solution. In CP method, the metal precursor solution was dropwise titrated into precipitating agent of Na_2CO_3 under vigorous stirring. However, different approach was employed in USP method using customised apparatus setup (Fig. 1). The introduction of metal precursors into Na_2CO_3 was by means of spraying action. Pneumatic spraying tool (0.3 mm nozzle) dispersed the metal precursor solution into micro – size droplets. A controlled pneumatic supply ensured an appropriate impact momentum of the sprayed droplets as well as constant precursor delivery. The mixing chamber was submerged in a thermostatic bath with ultrasonic generator (37 kHz) that provided heat and ultrasonic energy in assisting the mixing and precipitation process. In order to investigate the individual contribution of spraying and sonication effect, another two catalyst samples were prepared using each technique independently, and the resulting catalyst was denoted as SP and UCP, respectively. During precipitation in all methods, temperature and pH were maintained at 333 K and 7.0, respectively. The precipitate was aged for 3 h and then filtered and washed multiple times with deionised water before being dried overnight at 388 K. Subsequently, it was crushed, sieved (45–63 μm), and calcined in air at 623 K for 4 h. Synthesised catalysts were denoted as USP, UCP, SP and CP (Fig. 2).

2.2. Characterization of catalysts

2.2.1. Surface morphology and physical properties

Surface morphology of the catalysts was observed using FEI Quanta FEG 650 FE-SEM at an accelerating voltage of 15 kV and a working distance of 6.3–9.2 mm. The FE-SEM was equipped with Large Field Detector (LFD) and Everhart-Thornley Detector (ETD). The structural analysis was performed using Micromeritics ASAP 2020 based on multipoint nitrogen adsorption-desorption principle. Prior to the analysis, sample was degassed at 423 K for 3 h. The bulk surface area was calculated using the BET method. XRD patterns were recorded using a Bruker D8 Advance diffractometer, with CuKα radiation at 1.5406 nm and in the range of $10^\circ < 2\theta < 70^\circ$, using both calcined and reduced catalysts. In the reduction step, a purified H_2 flowing at 80 ml/min was used as a reducing agent, and the reactor was heated from 323 K to 573 K at 10 K/min and held at 573 K for 5 h.

The PSD was analysed using NanoPlus (Particulate Systems). Catalyst powder was dispersed in isopropyl medium by which the particulate characteristics were measured and calculated by laser scattering method.

The measurement of Cu surface area and dispersion were carried out using the method described by Yuan et al. [10], namely N_2O dissociative adsorption, using Micromeritics Autochem II 2920 instrument. The catalyst sample (50 mg) was firstly pre-treated with pure He flow (50 ml/min) at 393 K for 10 min before it was reduced in 10%

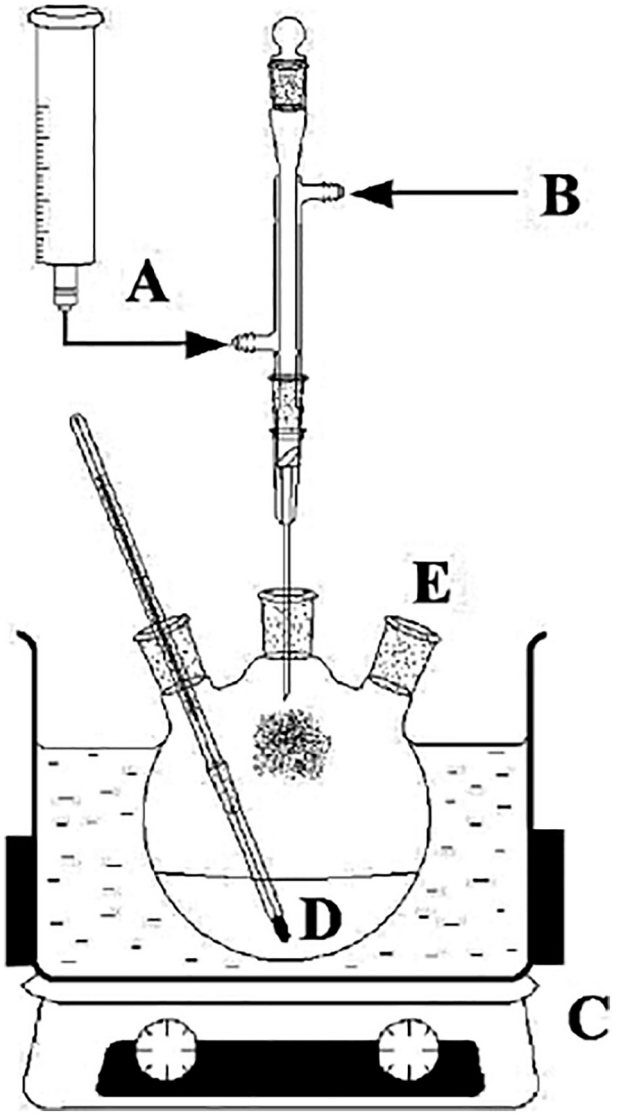

Fig. 1. Ultrasonic spray precipitation (USP) apparatus set-up. (A) metal precursors feed (B) pneumatic supply (C) thermostatic bath with ultrasonic generator (D) precipitation agent (E) pH probe opening.