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Catalyst synthesis by continuous coprecipitation under micro-fluidic conditions: Application to the preparation of catalysts for methanol synthesis from CO_2/H_2

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ABSTRACT

A new method of synthesis based on micro-fluidic continuous coprecipitation has been used to prepare $CuO\text{-}ZnO\text{-}ZrO_2$ catalyst. The catalytic behavior was then investigated for CO_2 hydrogenation into methanol and compared with a $CuO\text{-}ZnO\text{-}ZrO_2$ catalyst prepared by classical coprecipitation and with the same amount of Cu^0 (30%). The novel synthesis method allows a better repeatability and homogeneity of the catalyst which leads to the best methanol productivity of 486 $g_{MeOH}\,kg_{cata}^{-1}\,h^{-1}$ at 280 °C under 50 bar and a GHSV of 10,000 h^{-1}.

1. Introduction

Numerous measures to reduce anthropogenic greenhouse gas emissions, especially CO_2, already exist such as its capture and storage. Another solution is to develop a method for converting CO_2 into valuable chemical compounds such as methanol, methane, formic acid or dimethylether [1–4]. The context of this work is to transform CO_2 emitted by industries into methanol by reduction with hydrogen produced by water electrolysis, using excess of electricity provided by decarbonized energies such as nuclear and renewable energies (Power to Liquid process). Beyond the valorization of CO_2, this process also allows to provide a management function for the electric grid. In fact, the production of hydrogen is correlated with the quantity of surplus electricity from the network.

Methanol is produced over 50 million tons per year [5] and is present in many industrial sectors. It is used as a raw material for the synthesis of formaldehyde, one of the most important organic molecules [6], for the synthesis of olefins [7,8] such as propylene and ethylene (biopolymer precursors). Methanol is also known as fuel [7,9–11] either for fuel cells [12,13] or mixed with gasoline, or indirectly as a raw material for the synthesis of diesel, gasoline, dimethylether, hydrocarbons.... Thus the synthesis of methanol allows getting stable and easily stored carbon energy, as an alternative to fossil fuels.

At first methanol was mostly produced by catalytic hydrogenation of CO [14] with a feed gas of CO/H_2 or $CO/CO_2/H_2$. In the 90s some studies comparing the reactivity of CO/H_2 and CO_2/H_2 have shown that hydrogenation of CO_2 is faster than that of CO [15–17]. The same studies show that even starting from $CO/CO_2/H_2$ mixtures, methanol is mainly produced from hydrogenation of CO_2. Thereafter, in the early 2000s the number of publications about CO_2 hydrogenation increased.

The conventional methanol synthesis catalysts were designed for $CO/CO_2/H_2$ and must be optimized and modified for the hydrogenation of CO_2 without CO addition. The literature review clearly shows that copper is the favored metal and highlights the importance of the presence of ZnO along with a good interface between Cu and ZnO [18,19] for this reaction which increases respectively

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the copper dispersion and the adsorption of CO_2. The beneficial effect of the support was also discussed for Cu/ZnO based catalysts. The addition of ZrO_2 leads to an increase of the copper dispersion and ZrO_2 is involved in the adsorption of CO_2 [20,21]. This higher metal dispersion is due to a large interfacial area of CuO and ZrO_2 favored by the formation of surface oxygen vacancies on the ZrO_2 support [22]. This high interfacial area was as well discussed to play a role in the improvement of the methanol formation due to microcrystalline copper particles which are stabilized by interaction with an amorphous zirconia support [23]. This is why it is important to have a right control of the synthesis parameters such as pH and temperature. These CuO-ZnO-ZrO_2 catalysts were synthesized by coprecipitation [24], a classical synthesis in discontinuous mode (batch) using a buffer solution of controlled pH [25] where nitrates are added in continuous and where the precipitating agent is used to regulate the pH throughout the reaction [26,27].

In this work we present the study of a new method of synthesis based on continuous coprecipitation to overcome the problems of repeatability and homogeneity of solutions and conditions during the conventional coprecipitation. It was inspired by the use of the micromixer [28,29] or microemulsion [30]. This continuous method is based on the formation of droplets formed by reagents brought about an immiscible fluid carrier [31]. These droplets are more precisely formed by the merger of two droplets, each containing one of the starting aqueous solutions [32,33]. Upon the merger of these solutions, coprecipitation occurs, allowing the same environment and the same conditions (pH and temperature) for each droplet during the coprecipitation, leading to better repeatability and homogeneity.

Here are presented the effects of the catalyst synthesis conditions on the characterization and the catalytic behavior of efficient CuO-ZnO-ZrO_2 catalysts in CO_2 hydrogenation into methanol.

2. Experimental

2.1. Catalyst preparation

Two CuO-ZnO-ZrO_2 catalysts were synthesized by two different coprecipitation methods: a coprecipitation at constant pH and a continuous coprecipitation. These catalysts contain 37.5% by weight of CuO (corresponding to 30% Cu^0), 41 wt% of ZnO and 21.5 wt% of ZrO_2. The notation is exemplified as follows: 30CuZnZ$_X$ refers to a catalyst containing 30 wt% of Cu^0 completed by zinc oxide and zirconia where X corresponds to the synthesis method (pH = coprecipitation at constant pH and M = micro-fluidic continuous coprecipitation).

The constant pH coprecipitation [34,35] was realized in a buffer solution at pH 6–6.5 heated at 60–65 °C. A solution (1 M) of Cu nitrate, Zn nitrate and ZrO nitrate was added drop by drop in parallel with a solution of Na_2CO_3 (1.6 M), used as precipitating agent and pH control leading to a 1.13 molar ratio of carbonate/metal cations. The precipitate was aged for 3.5 h in the mother liquor, and then filtered, washed with water and dried for 5 days at 100 °C.

The micro-fluidic continuous coprecipitation was realized in a micro-fluidic system (Scheme 1) [36] by a continuous formation of little droplets, of diameter around 1 mm, made by the solution of nitrates (1 M) and the precipitating agent (1.6 M Na_2CO_3) in a constant flux ($0.9\,mL\,min^{-1}$) of silicon oil. The aqueous solutions are delivered to a constant total flow of $40\,\mu L\,min^{-1}$ with a 1.13 molar ratio of carbonate/metal cations. The precipitate was aged for one night in the mother liquor, and then the aqueous phase is separated, filtered, washed with water and dried for 2 days at 100 °C.

The resulting powders were then calcined in air at 400 °C for 4 h with a heating ramp of $2\,°C\,min^{-1}$ to give fresh catalysts.

2.2. Catalyst characterization

The catalyst apparent density was determined using a cylindrical glass tube of internal diameter of 1.5 cm, on fresh catalyst initially sieved to particle size fraction between 100 and 125 μm.

Specific surface areas measurements were performed by nitrogen adsorption–desorption at −196 °C using the Brunauer-Emmet-Teller (BET) method on a Micromeritics ASAP 2420 apparatus. Samples were previously outgassed at 250 °C for 3 h to remove the adsorbed moisture.

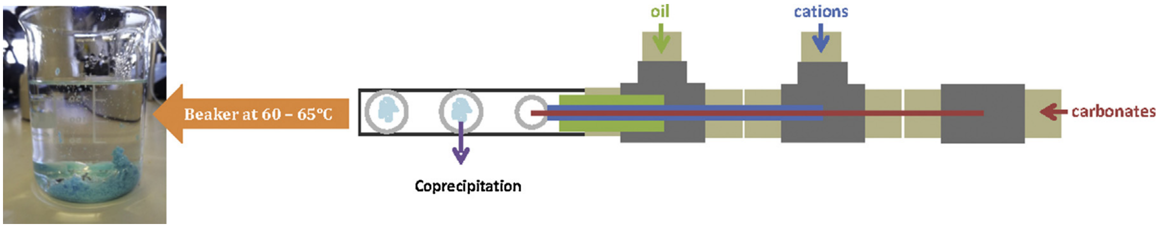
The crystalline structure of the catalysts was determined by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer equipped with a LYNXEYE detector and a Ni filter for Cu Kα radiations over a 2θ range of 10–95° and a step of 0.016° every 0.5 s. The crystallite size was calculated using the Debye-Scherrer equation [37].

Reducibility studies were performed by temperature programmed reduction (TPR) on a Micromeritics AutoChem II 2920 with 400 mg of fresh catalyst and a total gas flow rate of $50\,mL\,min^{-1}$ of 10% H_2 in Ar with a heating ramp of $1\,°C\,min^{-1}$ until 300 °C.

Metal surface area was determined by N_2O reactive frontal chromatography [38,39] on a Micromeritics AutoChem II 2920 in $50\,mL\,min^{-1}$ of 2% N_2O in Ar. Approximately 400 mg of fresh catalyst were first reduced at 300 °C for 12 h under a flow of $50\,mL\,min^{-1}$ of 10% H_2 in Ar and then cooled to 50 °C after a Ar purge. The copper surface area was calculated by quantifying the amount of consumed N_2O and assuming 1.46×10^{19} copper atoms per square meter [40].

The morphology after calcination was studied using conventional transmission electron microscopy (TEM) as well as scanning transmission electron microscopy (STEM) or electron tomography. All the investigations were performed on a JEOL 2100F TEM/STEM microscope, operating at 200 kV and equipped with a probe corrector and a GIF Tridiem energy filter. For S/STEM analyses, after sonication of the catalysts powder in ethanol, a droplet of the solution was dropped on a holy carbon silver TEM grid.

For the electron tomography analysis, a high tilt sample holder from GATAN Company was used in order to acquire the tilt image series. The angles range from +65 to −65 degrees, with projections taken every 2° according to Saxton scheme. 84 TEM images were recorded per tilt series with a cooled GATAN ULTRASCAN 1000 CCD



Scheme 1. Schematization of micro-fluidic continuous coprecipitation.