Journal of Catalysis 324 (2015) 41–49

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# The Cu–ZnO synergy in methanol synthesis from $CO_2$, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu + ZnO mechanical mixtures

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ARTICLE INFO

*Article history:*
Received 15 September 2014
Revised 19 January 2015
Accepted 22 January 2015
Available online 11 February 2015

*Keywords:*
$CO_2$ valorization
Methanol synthesis
Structure–activity relationships
Cu–ZnO synergy
Sphere contact quantification
Mathematical model
Copper
Zinc oxide
Kirkendall effect
Core–shell structures

ABSTRACT

Cu/ZnO-based catalysts are of industrial importance for the methanol synthesis. However, the selectivity is generally moderate since methanol formation is accompanied with similar amounts of CO. The understanding of how the active site is created is a key for understanding the central role of the Cu–ZnO synergy and for the rational design of active and selective catalysts. Model Cu + ZnO mechanical mixtures with variable composition as well as core–shell structures were employed as a tool for correlating physical to catalytic properties and identify the active site. The catalyst activity was correlated to the number of contact points between Cu and ZnO particles (that generates reactive oxygen vacancies) using a mathematical model for Cu and ZnO contact quantification based on the geometry of spherical particle agglomerates, which is applicable to mechanical mixtures. The structure–activity relationships highlighted in this work opens a way to the rational design of ideal structures of catalysts.

## 1. Introduction

Methanol has been commonly industrially produced from synthesis gas (syngas) [1] for years over $Cu/ZnO/Al_2O_3$ catalysts. Nowadays, efforts are made to replace CO of the syngas by $CO_2$ in the perspective of valorization of greenhouse gases [2]. When using $CO_2$ as the reactant, methanol production is accompanied with CO as a by-product [3], which can be further valorized to hydrocarbons through catalytic hydrogenation or Fischer–Tropsch synthesis. Although this approach is technologically feasible [4], there is still a lack of comprehension on the true nature of the active site for Cu/ZnO-based catalysts. Taken separately, Cu and ZnO have a low activity for MeOH formation [5], whereas their combination leads to an increase of activity of several orders of magnitude, effect known as the Cu–ZnO synergy [6–8]. Up to now, three major hypotheses describing a synergetic effect between Cu and ZnO are commonly admitted: (i) a morphologic effect (surface) [9,10], (ii) creation of an active site through formation of a Cu/Zn alloy, or a decoration of Cu with ZnO or oxygen vacancies [11–14] and (iii) an atomic hydrogen reservoir located on ZnO particles [6,15,16]. Despite all of these hypotheses were experimentally confirmed, there is still a doubt regarding the importance and the role of each of them. As pointed out by Behrens et al. [13], who studied the active site on commercial catalysts, it is difficult to mimic the active site in a model catalyst as well as in a theoretical approach.

The objective of this study was to understand the creation of the active sites and explain the Cu–ZnO synergy on the basis of structure–activity relationships. Here, we show the impact of catalyst composition on its activity and explain the origin of active sites through a theoretical approach to explain the synergy between Cu and ZnO for methanol synthesis by using mechanical mixtures of Cu and ZnO of different ratios as well as different core–shell structures. We present a new method to estimate the contacts between Cu and ZnO particles in the full range of composition

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http://dx.doi.org/10.1016/j.jcat.2015.01.021

based on the geometry of spherical particle agglomerates, which is applicable to mechanical mixtures. Experimental data are compared to theoretical calculations to validate the model.

## 2. Materials and methods

### 2.1. Catalysts synthesis

### 2.1.1. Synthesis of CuO and ZnO reference catalysts

The metal oxide (CuO or ZnO) reference materials were prepared by precipitation of nitrate salt of the corresponding metal (copper or zinc) from approximately 1 mol $L^{-1}$ solution by the dropwise addition of 4 mol $L^{-1}$ sodium carbonate at 70 °C until the pH reached 7.0 ± 0.5. The formed precipitates were washed with deionized water, dried overnight at 100 °C and further calcined in air at 350 °C for 4 h (heating rate 2 °C $min^{-1}$).

### 2.1.2. Synthesis of the Cu + ZnO mechanical mixture catalysts

The Cu + ZnO systems were prepared by mechanically mixing the CuO and ZnO reference materials with different weight ratios of Zn/(Zn + Cu) listed in Table 1, pressed (1 ton), crushed in a mortar (5 min) and sieved to particle size fractions (0.40–0.20 mm).

### 2.1.3. Synthesis of the Cu–ZnO coprecipitate catalyst

The Cu–ZnO catalyst was prepared by coprecipitation of a copper nitrate salt solution (0.3 mol $L^{-1}$) and a zinc nitrate salt solution (0.7 mol $L^{-1}$) by the dropwise addition of 4 mol $L^{-1}$ sodium carbonate at 70 °C until the pH reached 7.0 ± 0.5. The formed precipitate was washed with deionized water, dried overnight at 100 °C and further calcined in air at 350 °C for 4 h (heating rate 2 °C $min^{-1}$). After that, powdered catalysts were pressed (1 ton), crushed in a mortar (5 min) and sieved to particle size fractions (0.40–0.20 mm) used for testing measurements.

### 2.1.4. Synthesis of the CuZn@$ZnO_x$ and Cu@$ZnO_x$ core–shell catalysts

The CuZn@$ZnO_x$ and Cu@$ZnO_x$ core–shell systems were prepared by surface modification precipitation process [17]. 5 g of Cu (or CuZn brass) powder (Cu powder: Alpha Aesar (625 mesh) and CuZn brass powder: Alpha Aesar (325 mesh)) was added to an aqueous solution consisting of 0.11 g of citric acid and 120 mL distilled water in a flask under vigorous stirring at 40 °C. The mixed solution was stirred for 3 h, and the pH of the solution reached 4.5 ± 0.1. Then, 100 mL of zinc nitrate (0.16 mol $L^{-1}$) were dropped to the mixture under vigorous stirring. After 1 h, a 0.4 mol $L^{-1}$ ammonia solution was dropped until the pH reached 10.0 ± 0.1, and the solution was stirred for another hour. The formed precipitate was filtered and washed 3 times with water and twice with ethanol and finally dried overnight at 100 °C and calcined in air at 350 °C for 4 h with a ramp of 2 °C $min^{-1}$. After that, powdered catalysts were pressed (1 ton), crushed in a mortar (5 min) and sieved to particle size fractions (0.40–0.20 mm) used for testing measurements.

### 2.2. Characterization

### 2.2.1. In situ X-ray diffraction

*In situ* XRD-monitored reduction was performed in a Bruker-Nonius D8 Advance X-ray diffractometer equipped with an Anton-Paar XTK 16 reaction chamber. The powder catalyst was loaded in the chamber and heated with flowing 3%$H_2$/He to 350 °C (heating rate 5 °C $min^{-1}$, flow rate 30 mL $min^{-1}$) and kept at this temperature for 1 h in order to mimic the activation treatment performed *in situ* prior to the methanol synthesis catalytic tests. X-ray diffractograms were acquired before and after reduction at room temperature in the $2\theta$ range 20–80° (step size of 0.05°, scan speed 1 s $step^{-1}$) using Cu Kα radiation ($\lambda = 1.54$ Å). The crystallite sizes for the fresh and as-reduced catalysts were estimated by applying the Scherrer equation (Eq. (1)) to the (002), (101) and (111) diffraction lines of CuO, ZnO and Cu, respectively:

$$\text{size (Å)} = \frac{k\lambda}{\beta(2\theta)\cos\theta} \tag{1}$$

where $k$ is a constant (0.94), $\lambda$ is the X-ray wavelength and $\beta(2\theta)$ is the full width at half maximum in radians.

Metallic Cu surface area ($m^2$ per gram of fresh catalyst) was determined from Eq. (2) [18]:

$$S_{Cu} = \frac{6000X_{Cu}}{8.96\ \text{size}} \tag{2}$$

where $X_{Cu}$ is the mass fraction of Cu in fresh catalyst and size is the crystallite size of Cu in a reduced catalyst.

The lattice constants for the as-reduced catalysts were calculated, according to Bragg's law (Eq. (3)):

$$n\lambda = 2d\sin\theta \tag{3}$$

where $n$ is the order of diffraction ($n = 1$ in our case), $\lambda$ is the X-ray wavelength and $d$ is the spacing between planes of given Miller indices $h$, $k$ and $l$.

For the orientation (111), the lattice constant $a$ of Cu (cubic structure) was calculated by Eq. (4):

$$a = \frac{\sqrt{3}\lambda}{2\sin\theta} \tag{4}$$

for the orientation (100), the lattice constant $a$ of ZnO (hexagonal structure) was calculated with Eq. (5):

**Table 1**

Zn content in the catalyst (weight fraction), crystallites sizes (ZnO, CuO and Cu), molar content of Zn in the CuZn alloy by XRD analysis, metallic Cu surface area, Cu dispersion (*D*), $CO_2$ conversion ($XCO_2$) and TOF for Cu + ZnO mechanical mixtures.

| Cat | Zn/(Zn + Cu) | Crystallite sizes (nm) | | | | $x_{Zn}$ | $S_{Cu}$ ($m^2\ g^{-1}$) | $D^{a}$ (%) | $XCO_2$ (%) | $TOF_{MeOH}^{b}$ ($10^{-5}\ s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Fresh | | Reduced | | | | | | |
| | | ZnO | CuO | ZnO | Cu | | | | | |
| 1 | 0.00 | – | 36 | – | 43 | 0.00 | 13 | 3.03 | 0.0 | 0.58 |
| 2 | 0.10 | 17 | 37 | 18 | 43 | 0.00 | 11 | 3.03 | 0.2 | 20.1 |
| 3 | 0.30 | 16 | 36 | 18 | 43 | 0.02 | 9 | 3.03 | 0.6 | 93.2 |
| 4 | 0.50 | 16 | 35 | 18 | 44 | 0.03 | 6 | 2.96 | 0.7 | 165.6 |
| 5 | 0.62 | 17 | 35 | 18 | 43 | 0.05 | 5 | 3.03 | 0.9 | 277.4 |
| 6 | 0.70 | 16 | 36 | 18 | 43 | 0.05 | 4 | 3.03 | 0.7 | 267.9 |
| 7 | 0.90 | 16 | 34 | 18 | 42 | 0.07 | 1 | 3.10 | 0.3 | 381.2 |
| 8 | 1.00 | 16 | – | 18 | – | – | – | | 0.1 | – |

[a] Calculation of *D* was made by assuming a cubo-octahedron shape.

[b] For TOF calculation, see Supplementary informations.