Molecular Catalysis 446 (2018) 98–105

Contents lists available at ScienceDirect

Molecular Catalysis

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

Cu-ZnO catalysts for CO_2 hydrogenation to methanol: Morphology change induced by ZnO lixiviation and its impact on the active phase formation

Céline Tisseraud, Clément Comminges*, Aurélien Habrioux, Stéphane Pronier, Yannick Pouilloux, Anthony Le Valant*

Université de Poitiers, UFR SFA, IC2MP, UMR-CNRS 7285, Bât B27, 4 rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex 9, France

ARTICLE INFO

Article history:
Received 12 September 2017
Received in revised form
20 December 2017
Accepted 24 December 2017

Keywords:
Copper
Zinc oxide
Chemical memory
Morphology change
Methanol synthesis

ABSTRACT

Synthesis of Cu-ZnO catalysts for the direct hydrogenation of CO_2 to methanol requires catalyst precursors able to display a strong Cu-Zn interaction. Copper and zinc mixed hydroxynitrates are good candidates to fulfill this specification. The synthesis of such a phase was achieved by a wet impregnation of copper nitrate on ZnO. Solvent evaporation and catalyst drying at moderate temperatures allowed retaining the metals hydroxynitrate structure, leading to a memory effect for the reduced catalysts. Depending on the Cu content in the reaction mixture, a ZnO lixiviation gradually occurs, what induces an important change in the morphology of the reduced catalyst. Catalyst activity is proportional to the amount of Zn migrated in the active phase, the latter consisting most probably of an oxygen deficient mixed oxide comprising both Cu and Zn. The most active catalyst is obtained when ZnO is fully lixiviated during the catalyst precursor synthesis, giving a core-shell structure after reduction.

1. Introduction

Methanol synthesis from CO_2 (Eq. (1)) is a reaction of paramount importance in the perspective of a methanol economy [1]. This exothermal reaction is favored at low temperature and high pressure. To be economically viable, this process requires the use of efficient and stable catalysts consisting of earth abundant transition metals, involving a simple, economic and sustainable synthesis.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (1)$$

In particular, the Cu-ZnO system is a good candidate to fulfill these specifications. The activity of these catalysts relies on the Cu-ZnO synergy that leads to the creation of active sites for this hydrogenation reaction. The associated mechanism for the creation of active sites has been long discussed and can be summarized as follows. Initial contacts between CuO and ZnO crystallites prior to catalyst reduction [2] are at the origin of the creation of an heterojunction [3] which makes the ZnO more reducible [4] and favors the formation of an oxygen deficient layer of ZnO_x [5]. Then, a cross migration of Cu and Zn according to the Kirkendall effect [6] engenders a surface Zn enrichment what correlates to the catalyst activity [7–9]. In a macroscopic point of view, the catalyst morphology is crucial. An efficient catalyst needs a maximization of the Cu-ZnO interface [10] what can be achieved by designing core-shell structures [9]. To date, several active phase precursors were described. Generally, catalysts are synthesized trough the co-precipitation of Cu^{2+} and Zn^{2+} salts with a carbonate precipitating agent. This leads to different hydroxycarbonate precursors such as zincian malachite [11,12], georgite [13], rosacite and aurichalcite [14]. The strategy is to take the benefit of a memory effect (chemical memory) of the carbonate salt after the catalyst reduction. However, other precursor than carbonate salts can also be used. For instance, copper and zinc mixed hydroxynitrates [15,16] are potentially ideal candidates to favor the critical Cu-Zn initial interface. These hydroxynitrates are layered hydroxide salts (LHS) whose structure derives from the Brucite like structure [17]. This layered packing of 2D assemblies is well suited for the obtaining of large specific surface areas. This type of precursor has been studied for the hydrogenation of crotonaldehyde to crotyl alcohol, where a similar memory effect has been observed [18]. This study showed that a calcination step before catalyst reduction partially destroys the interaction between Cu^{II} and Zn^{II}. The extent of the Cu^0-Zn^{II} interaction after reduction is governed by the basicity of the support which favors the formation of hydroxy-compound during further impregnation with copper

---

* Corresponding authors.
E-mail addresses: clement.comminges@univ-poitiers.fr (C. Comminges), anthony.le.valant@univ-poitiers.fr (A. Le Valant).

https://doi.org/10.1016/j.mcat.2017.12.036
2468-8231/© 2017 Published by Elsevier B.V.

or copper-zinc nitrate [19]. A recent example on the use of copper-zinc mixed hydroxynitrates for the methanol synthesis from syngas on SiO_2 supported catalysts showed catalytic performances close to the industrial catalyst Cu-ZnO/Al_2O_3 [20]. In this example, the hydroxynitrate precursor is decomposed under an NO atmosphere. In this work, we report on the use of copper-zinc hydroxynitrates with ZnO as the basic oxide support for the obtaining of the catalyst precursor for the methanol synthesis from CO_2.

2. Experimental section

2.1. Catalyst synthesis

The different catalysts were prepared by a wet impregnation of an aqueous solution containing the copper nitrate salt solution and a commercial ZnO powder (Sigma-Aldrich) under stirring for 5 h at room temperature. The amount of copper nitrate was adjusted to obtain the desired amount of Cu in the catalyst. The resulting solution containing the impregnated support was evaporated at 70 °C and dried at 100 °C for 15 h. The catalyst was finally pressed (7 t), crushed in a mortar (5 min), and sieved to particle size fractions (0.40–0.20 mm) used for testing measurements.

2.2. ICP

Inductively coupled plasma (ICP) optical emission spectroscopy was used for the determination of the metal content in each sample synthesized. The measurements were performed with a Perkin Elmer Optima 2000DV spectrometer. The sample was previously dissolved in an acidic mixture of HNO_3 and HCl.

2.3. XRD

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 a first X-ray diffractogram was acquired at room temperature for the as prepared catalyst. Then, the catalyst was heated with flowing 3% H_2/He up 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 after reduction at room temperature in the 2θ range $20°–80°$ (step size of 0.05°, scan speed 1 s $step^{-1}$) using Cu-Kα radiation (λ = 1.54 Å). Rietveld refinements were performed on reduced catalysts using HighScore Plus software. More details can be found in supporting information S1.

2.4. TEM-EDX

Transmission Electron Microscopy (TEM) was performed with a Jeol 2100 UHR microscope at 20 kV, which was equipped with an energy dispersive X-ray (EDX). Reduced catalysts (with 30 mL min^{-1} of H_2 at 350 °C during 1 h, heating rate 5 °C min^{-1}) were ground in a mortar, the powder was suspended in ethanol under sonication for 5 min and loaded on holey carbon film Au grid (300 mesh).

2.5. Catalytic tests

Methanol synthesis catalytic tests were performed in a continuous fixed-bed stainless steel reactor (L = 400 mm, $Ø_{int}$ = 12.5 mm). Before the CO_2 hydrogenation reaction, the catalyst (0.50 g, 0.40–0.20 mm sieve fraction) was reduced *in situ* at 350 °C. Then, the reaction was carried out at 250 °C and 30 bar of the reactant gas mixture ((H_2:CO_2 = 3:1, vol., GHSV = 18 000 h^{-1}). Under these experimental conditions, CO_2 conversion is ≤ 2%. Reaction products were analyzed with an Agilent 7890A gas chromatograph (GC) connected online. Detection limits are 0.65% and 0.44% for methanol and CO, respectively. Quantification limits are 2.16% and 1.47% for methanol and CO, respectively. CO_2 conversion is calculated from the CO + methanol carbon mass balance. According to the detection limits for CO, no CO signal detected means methanol selectivity comprised between 95% and 100%. Methanol rate is calculated from the average of 4 consecutive GC injections. Typically, the relative standard deviation is comprised between 0.5% and 3%. More experimental details can be found elsewhere [6].

Table 1
Chemical composition of the reduced catalysts determined by ICP along with pH of the $Cu(NO_3)_2$ precursor solution.

Cat.	Metal content (wt.%)		pH
	Cu	Zn	
1	–	77	–
2	1	76	4.30
3	5	73	3.48
4	10	69	3.09
5	19	62	2.07
6	38	48	1.16

3. Results and discussion

A series of five impregnated catalysts whose Cu content is ranging from 1 to 38% (as determined from ICP measurements) was prepared. The wet impregnation method consists in mixing a copper nitrate aqueous solution with a commercial ZnO powder. The increasing amount of copper nitrate results in the decrease of the reaction mixture pH (Table 1) due to the dissociation of the acidic $[Cu(H_2O)_6]^{2+}$ complex, as shown in Eq. (2).

$$[Cu(H_2O)_6]^{2+}_{(aq)} \leftrightharpoons [Cu(H_2O)_5(OH)]^{+}_{(aq)} + H^{+}_{(aq)} \qquad (2)$$

Fig. 1 show the XRD patterns of the as prepared catalysts after solvent evaporation at 70 °C and drying at 100 °C. It has to be noticed that no additional calcination step was carried out in order to retain any possible memory effect of the catalyst precursor [18]. Significant differences in terms of crystallographic structure along the series are observed (JCPDS files can be found in supporting information Table S1). Copper is identified to crystallize in the form of a copper hydroxynitrate ($Cu_2(NO_3)(OH)_3$) whereas zinc can be found in its oxide form (ZnO) as well as in nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hydroxynitrate form ($Zn_5(NO_3)_2(OH)_8{\cdot}2H_2O$). The ZnO signal vanishes when the copper content in the catalyst is ranging between 19 and 38%. This is explained by a lixiviation of ZnO induced by the low pH of the reaction mixture and is further activated during the solvent evaporation step at 70 °C. The consequence of the gradual ZnO lixiviation is that copper salt is both impregnated on the remaining oxide support and dispersed in a mixture of zinc nitrate and hydroxynitrate. Although separate hydroxynitrate phases for Zn and Cu were indexed, it cannot be ruled out that a mixed hydroxynitrate of general formula $Cu_{2-x}Zn_x(NO_3)(OH)_3$ is formed. Indeed, this kind of mixed hydroxynitrate has the same type of structure as $Cu_2(NO_3)(OH)_3$ [18].

Fig. 2 shows the X-ray diffraction patterns of reduced catalysts. All diffraction lines can be indexed either to the face centered cubic crystalline phase of Cu or hexagonal ZnO crystalline phase. No additional peaks have been observed indicating the high purity of reduced samples. Rietveld refinement was performed for each reduced sample so as to obtain information regarding the crystalline structure, the crystallite sizes, as well as microstrains affecting different phases composing each catalyst. The methodology used is detailed in supporting information S1. In each case