

CO₂ hydrogenation to methanol using Cu/CeO₂ catalysts prepared by a one-step solution combustion method: Influence of copper content.

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Abstract

Cu/CeO₂ catalysts with three copper contents (5, 15 and 30 wt.%) were synthesized by a one step solution combustion method and characterized by XRD, BET, RTP and CO₂-TPD techniques. The catalytic activity of these materials was evaluated in the reaction of CO₂ hydrogenation to methanol. The 30% Cu/CeO₂ catalyst presented the highest CO₂ conversion, while the 15% Cu/CeO₂ catalyst was the most selective to methanol, what can be associated with the relative amounts of metallic and basic active sites.

Keywords: CO₂ hydrogenation, methanol, Cu/CeO₂ catalyst.

1. Introduction

Nowadays, the CO₂ hydrogenation is an important catalytic reaction due to its potential to transform a major atmospheric pollutant into chemicals, such as methanol, that can be used as fuel or precursor in the synthesis of many other important compounds [1]. Recent studies reported that the Cu/CeO₂ presents a promising catalytic performance comparable to the commercial Cu/ZnO used for this class of reactions [2].

In the synthesis of some materials, especially for high metal loadings, it is difficult to obtain well-dispersed phases between the metallic and oxide domains. Then, an alternative route, such as the one-pot method, that involves high dispersion and interaction between copper and the other elements, can be interesting for the reactions that require bifunctional catalysts [3]. In this context, the combustion synthesis presents advantages like simplicity, energy and time-effectiveness and low cost in the synthesis of nanomaterials [4].

The purpose of this study is to evaluate the influence of copper content in Cu/CeO₂ catalysts in the CO₂ hydrogenation reaction to methanol production.

2. Experimental

Cu/CeO₂ catalysts were synthesized by one-pot urea-nitrate solution combustion method with three different copper contents (5, 15 and 30 wt.%). In a typical procedure, appropriate molar quantities of cerium nitrate (Ce(NO₃)₃.6H₂O), copper nitrate (Cu(NO₃)₂.3H₂O) and urea (CO(NH₂)₂) were dissolved in 20 mL of distilled water. The urea/nitrate molar ratio was adjusted according to the principle of propellant chemistry and the solution was transferred to a crucible and pre-heated at 673K in a muffle furnace. After around seven minutes the mixture ignited spontaneously with evolution of a large quantity of gases, resulting in a foamy, voluminous powder. The obtained powder was calcined at 573K for one hour with a heating rate of 5 K.min⁻¹ in order to remove the carbonaceous residues.

The physicochemical properties of catalysts were investigated by XRD, BET, TPR and CO₂-TPD techniques. CO₂ hydrogenation reactions were carried out using a stainless steel reactor, which contained 0.6 g of catalyst diluted with 0.3 g of SiC. All catalysts were reduced in H₂ flow (30 mL.min⁻¹) at 573 K for 1 h and the reaction was conducted at 523K and 3MPa with a mixture of CO₂ and H₂ (molar ratio 1:3 and GHSV = 4 L.h⁻¹.g⁻¹).

3. Results and discussion

Figure 1 shows that all catalysts presented crystalline structures corresponding to CeO₂ (JCPDS 34-394) and CuO (JCPDS 48-1548) phases, but it was not possible to calculate the crystallite size of CuO in the

5%Cu/CeO₂ sample due to the low content of copper. In the other two catalysts, the increase in the copper content increased in the crystallite size. The specific surface areas of the catalysts area shown in Table 1.

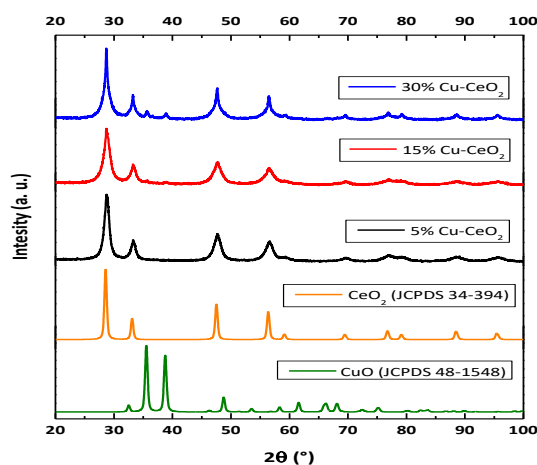


Figure 1. XRD patterns

The products obtained by CO₂ hydrogenation were methanol, CO and little amounts of methane. Two competing reactions can occur during CO₂ hydrogenation over metallic sites: methanol synthesis and reverse water-gas-shift. Methanation may also occurs since that is thermodynamically favored. It was observed that the increase in copper content lead to an increase in the CO₂ conversion, what is in agreement with the results reported in literature. The selectivity to methanol is strongly influenced by the basic sites of the catalysts (where CO₂ will adsorb), that can explain the higher selectivity observed by the 15%Cu/CeO₂ catalyst which presented the highest basicity by CO₂-TPD analyze. It is important to emphasize that although the basicity of 5% and 30%Cu/CeO₂ is similar, the lower quantity of copper in 5%Cu/CeO₂ (important for the adsorption and dissociation of H₂) can explain the much lower selectivity to methanol, once this is a bifunctional catalytic process requiring both sites in appropriated relationship.

Table 1. Textural and structural properties and catalytic performance of the Cu/CeO₂ catalysts.

Catalysts	<i>S_{BET}</i> (m ² /g)	Crystallite size CuO (nm)*	CO ₂ -TPD (mmol g ⁻¹)**	X(CO ₂) %	Methanol Selectivity
5%Cu/CeO ₂	34	---	1293	4.9	7.2
15%Cu/CeO ₂	23	12.7	1419	10.2	15.1
30%Cu/CeO ₂	24	16.6	1303	15.0	11.7

*Determined using Scherrer equation from full width at half maxima of CuO (111) XRD peak; ** at 250°C

4. Conclusions

CO₂ conversion is associated with the metallic content, considering that the higher conversion was obtained by the 30%Cu/CeO₂ catalyst. The production of methanol, however, requires basic sites associated with metallic sites in a bifunctional process, then the biggest basicity and appropriated content of metallic sites of the 15% Cu/CeO₂ catalyst resulted in the highest selectivity to methanol production.

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