

# Low-temperature steam-reforming of ethanol over ZnO-supported Ni and Cu catalysts

## The effect of nickel and copper addition to ZnO-supported cobalt-based catalysts

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Available online 3 July 2006

### Abstract

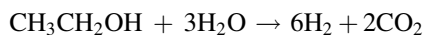
ZnO-supported Ni and Cu as well as bimetallic Co-Ni and Co-Cu catalysts containing ca. 0.7 wt% sodium promoter and prepared by the co-precipitation method were tested in the ethanol steam-reforming reaction at low temperature (523–723 K), using a bioethanol-like mixture diluted in Ar. Monometallic ZnO-supported Cu or Ni samples do not exhibit good catalytic performance in the steam-reforming of ethanol for hydrogen production. Copper catalyst mainly dehydrogenates ethanol to acetaldehyde, whereas nickel catalyst favours ethanol decomposition. However, the addition of Ni to ZnO-supported cobalt has a positive effect both on the production of hydrogen at low temperature (<573 K), and on catalyst stability. Evidence for alloy formation as well as mixed oxides at the microstructural level was found in the bimetallic systems after running the ethanol steam-reforming reaction by HRTEM–EELS.

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**Keywords:** Ethanol-reforming; Hydrogen; Bimetallic catalysts; Nickel catalysts; Copper catalysts

### 1. Introduction

The use of a renewable, non-toxic biomass-derived source, like bioethanol, to produce hydrogen is currently very attractive. In this domain, the search for a highly effective catalytic system for the selective steam-reforming process is of high research interest:



Besides noble metal-based systems, the reaction has been studied extensively over supported Ni [1–8], Cu [6], Ni–Cu [9,10] and Co [11–17]. From the data reported, not only the metal phase, but also the support used has been shown to influence the catalytic performance [18]. The steam-reforming of ethanol involves numerous steps and usually competes with

several parallel reactions that originate undesired products that result in lower hydrogen yields and create difficulties for practical applications. Undesired products like CO and CH<sub>4</sub> must be further processed in order to be removed, with additional energy cost. On the other hand, a major concern in the steam-reforming reaction of ethanol is the deactivation of catalysts, which mainly takes place via carbon deposition. Recently, we have shown that sodium addition to ZnO-supported cobalt catalysts promotes the steam-reforming of ethanol [15]. The promotion has been related to the increasing of H<sub>2</sub> yield and the stability of catalysts by suppressing the deposition of carbon. Taking into account these considerations and the well-documented state of the art of the reaction with Ni- and Cu-based systems, the present article reports our study of ZnO-supported Ni and Cu catalysts as well as the effect of Ni or Cu addition on the Na-promoted, Co-ZnO system. The catalysts were characterised by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) and tested in the steam-reforming reaction of bioethanol-like mixtures.

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Table 1  
Chemical analysis (wt%) and BET surface areas of catalysts

Catalyst	Co (%)	Ni (%)	Cu (%)	Na (%)	(m <sup>2</sup> g <sup>-1</sup> )
10Co1Ni(Na)-ZnO	9.40	0.95	–	0.64	41.4
10Co1Cu(Na)-ZnO	9.30	–	0.93	0.78	39.7
10Co(Na)-ZnO	10.7	–	–	0.78	36.2
10Ni/ZnO	–	10.9	–	–	47.9
10Cu/ZnO	–	–	10.4	–	46.8

## 2. Experimental methods

Bimetallic catalysts with a cobalt content of ca. 10 wt%, Ni or Cu content of ca. 1 wt%, and sodium content of ca. 0.7 wt% were prepared by the co-precipitation method. Precipitation was accomplished at 313 K by the addition of a Na<sub>2</sub>CO<sub>3</sub> solution to Zn(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solutions. After ageing at 313 K for 1.5 h, the suspensions were filtered and the filtrates washed with distilled water. The resulting solids were then dried at 363 K overnight and calcined in air at 673 K for 12 h. Samples were reduced under hydrogen at 673 K for 12 h and labelled as 10Co1M(Na)-ZnO (M = Ni, Cu). As reference, a sodium-promoted cobalt catalyst, 10Co(Na)-ZnO, was prepared similarly [15]. For comparative purposes, monometallic ZnO-supported Ni and Cu catalysts were prepared by impregnation from their respective nitrates on ZnO. The support was prepared by decomposition of 3ZnO·2ZnCO<sub>3</sub>·3H<sub>2</sub>O under Ar at 573 K. The salts were impregnated by the incipient wetness method from aqueous solutions. Samples were dried at 373 K for 6 h, calcined at 673 K for 6 h, and reduced under H<sub>2</sub> at 673 K. The resulting catalysts were labelled as 10M/ZnO (M = Ni, Cu). Table 1 compiles the chemical composition obtained by optical emission spectroscopy with inductively-coupled plasma (ICP-OES, Perkin-Elmer Optima apparatus) and BET surface area determined using a Micromeritics ASAP 9000 instrument of all samples. X-ray diffraction profiles were collected at a step width of 0.02° and by counting 10 s at each step

with a Siemens D-500 instrument equipped with a Cu target and a graphite monochromator. Photoelectron spectra (XPS) were acquired with a Perkin-Elmer PHI-5500 spectrometer equipped with an Al X-ray exciting source and a hemispherical electron analyser. High-resolution transmission electron microscopy and electron energy loss spectroscopy was performed with a JEOL JEM 2010F instrument working at 200 kV and equipped with a field emission source. Catalytic studies of ethanol steam-reforming were performed at atmospheric pressure in a U-shaped quartz reactor (5 mm internal diameter). 0.1–0.2 g of catalyst were charged and diluted with inactive SiC, giving a catalyst bed volume of 0.6 ml. A constant mixture of C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O = 1:4 (v/v) (C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O ~ 1:13 molar basis, HPLC purity grade) was supplied by a Gilson 307 Piston Pump and vaporised at 453 K. The temperature of the catalyst was first raised under Ar to that of the first temperature tested, and then the Ar stream was mixed with the C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O mixture ((C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O):Ar = 1:5 molar basis). The GHSV was 5000 h<sup>-1</sup> in all cases. At the end of the catalytic tests, the flow of C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O was stopped and the catalysts were cooled under Ar stream and stored for characterisation. The analysis of the reactants and all the reaction products was carried out on-line by gas chromatography as described previously [12]. The detection limit of CO was ca. 20 ppm. Response factors for all products were obtained with appropriate standards before and after each catalytic test. The selectivity of the products was calculated on the basis of molar percentage of each product evolved (water excluded) with respect to the total moles of products formed.

## 3. Results and discussion

### 3.1. Monometallic catalysts

In this section, we evaluate the catalytic behaviour of monometallic ZnO-supported nickel and copper catalysts, and discuss their bulk structural characteristics from X-ray

Table 2  
Catalytic performance of 10M/ZnO (M = Cu, Ni) in the ethanol steam-reforming reaction

Catalyst	T (K)	t (h)	Conversion (%)	Activity <sup>a</sup> (mol C <sub>2</sub> H <sub>5</sub> OH/mol M h)	Selectivity <sup>b</sup> (%)								mol H <sub>2</sub> /mol EtOH <sup>c</sup>	mol CO <sub>2</sub> /mol EtOH <sup>c</sup>
					H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CHO	Me <sub>2</sub> CO		
10Cu/ZnO	573	2	<1	–	–	–	–	–	–	–	–	–	–	–
	623	4	3.0	0.17	52.4	–	0.3	–	3.1	–	44.2	–	0.03	0.00
	673	6	21.1	1.22	53.6	–	1.1	–	3.2	–	42.1	–	0.25	0.01
	673	26	18.5	1.07	52.1	–	1.5	0.1	2.4	0.1	43.3	0.5	0.20	0.01
	723	28	82.2	4.77	56.2	–	8.3	0.5	1.9	0.5	24.8	7.8	1.06	0.16
	723	48	84.1	4.88	58.6	–	9.0	1.2	0.9	0.4	23.0	7.0	1.23	0.19
10Ni/ZnO	573	2	77.3	4.27	47.6	15.9	6.3	15.3	0.1	–	14.7	–	1.09	0.14
	623	4	100	n.a.	54.2	–	25.0	20.7	0.2	–	–	–	2.35	1.09
	673	6	100	n.a.	55.6	–	25.0	19.4	–	–	–	–	2.50	1.12
	673	26	100	n.a.	65.1	–	25.0	9.9	–	–	–	–	3.73	1.43
	723	28	100	n.a.	64.5	1.2	24.0	10.2	–	–	–	–	3.64	1.35
	723	48	100	n.a.	66.5	1.3	23.8	8.4	–	–	–	–	3.96	1.42

C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O:Ar = 1:13:70 (molar ratio); GHSV = 5000 h<sup>-1</sup>; 0.1 g of catalyst.

<sup>a</sup> n.a., Non-applied.

<sup>b</sup> Molar percentage of products (water excluded).

<sup>c</sup> Corresponds to ethanol in the reactant mixture.

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