Hydrogen production through alcohol steam reforming on Cu/ZnO-based catalysts

Barbara Lorenzuta, Tiziano Montinia, Loredana De Rogatisa,1, Patrizia Cantonb, Alvise Benedettib, Paolo Fornasiernoa,b

a Department of Chemistry, ICCOM-CNR Trieste Research Unit and INSTM, Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
b Department of Physical Chemistry, Università Ca’ Foscari Venezia, Via Torino 155, 30170 Venice, Italy

Abstract

Hydrogen production by steam reforming of methanol and ethanol is studied over a series of Cu/ZnO/Al2O3 catalysts prepared by different coprecipitation procedures and modified with the introduction of Ni and Co. The catalysts are characterized using N2 physisorption, X-ray diffraction (XRD), temperature programmed reduction (TPR) techniques, N2O decomposition, high resolution transmission electron microscopy (HR-TEM) and thermogravimetric analysis (TGA). Despite the influence of the preparation method on the texture and structure of Cu/ZnO/Al2O3 catalysts, their catalytic behavior appears not significantly affected. While Cu/ZnO/Al2O3 shows poor H2 selectivity in the ethanol steam reforming reaction, the presence of a second metal (Ni or Co) significantly improves the reforming reaction. Although coke deposition remains a drawback for these systems, formation of an alloy between Ni and Cu appreciably reduces carbon deposition with respect to the Co/Cu-based system.

1. Introduction

Driven by the need of cleaner air and less dependence upon foreign oil, the interest in alternative fuels for energy production has increased rapidly in recent years. Due to the ever-growing world energy demand, diversification of energy sources is foreseen [1,2]. Among the different efforts being currently pursued to meet the global energy needs, using molecular hydrogen as an energy vector has become an attractive option in terms of sustainability and low environmental impact. Hydrogen can store energy and deliver it to where it is needed [3,4].

Different raw materials and reactions can be proposed for hydrogen production [3,5–7]. The selection of the hydrogen source for a particular application depends on technical, economic and political factors [8]. Commercially, methane steam reforming is the primary method to produce hydrogen. However, for mobile applications, it is preferable to have a hydrogen source in liquid form that can be used in steam reforming reactions under mild operative conditions.

Catalysts based on copper-zinc composite oxides are the most frequently studied systems in the methanol steam reforming (MSR) due to their high selectivity and activity [3,11–14] and as an outgrowth of their extensive use in methanol synthesis. It is generally accepted that copper dispersion plays a key role in the catalytic performance of these materials while the function of ZnO is to maintain the catalytically active copper in optimal dispersion and to improve the reducibility of CuO [15–17]. The addition of small amounts of Al2O3 further inhibits thermal sintering of copper particles and, therefore, imparts chemical and thermal stability to the catalyst [18,19]. Shen and Song [20] examined the effect of the preparation method on the catalytic behaviour of Cu/Zn/Al catalysts and found that it significantly affects the dispersion of copper particles and, thus, the catalyst performance in terms of methanol conversion. H2 yield and CO concentration. A correlation between the observed catalytic activity and the presence of highly dispersed Cu metal particles, obtained by an appropriate synthetic procedure, was also proposed by Shishido et al. [21] and Li et al. [22]. A very high catalytic activity for methanol steam reforming at low temperature was reported by Zhang et al. [23] on Cu/ZnO/Al2O3 catalyst synthesized by a gel-coprecipitation approach with respect to the catalyst [18,19].

Corresponding author. Tel.: +39 040 5583973; fax: +39 040 5583903.
E-mail address: pfornasiero@units.it (P. Fornasiero).

1 Present address: Institute of Chemistry of Organometallic Compounds, ICCOM-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.
to the catalysts prepared by a conventional coprecipitation technique. This superior catalytic performance was attributed not only to the generation of highly dispersed copper and zinc components but also to the creation of catalytically active copper species with a much stronger Cu-Zn interaction. Similarly, Zhang et al. [24] attributed the better performance of a Cu/ZnO/Al2O3 catalyst obtained from a CuO/ZnO/Al2O3 sample, prepared by conventional carbonate coprecipitation method and aged under microwave irradiation, to the creation of highly strained copper nanocrystals in the active catalyst. Kurr et al. [11] found that among various Cu/ZnO/Al2O3 catalysts, prepared by hydroxycarbonate coprecipitation procedure, the catalytic activity and thermal stability under methanol steam reforming conditions are influenced not only by the copper specific surface area but also by defects in the bulk structure.

Only few reports on the addition of a second metal to Cu-based catalysts employed in the steam reforming of methanol can be found in the literature. Liao and Yang [25] reported that Ni–Cu alloys supported on carbon nanotubes (CNT) show better activity than the single metals, with the best performances with a Ni/Cu molar composition of 20/80. No indications on CH4 formation are reported. Gadhe and Gupta [26] studied the steam reforming of methanol under supercritical conditions catalyzed by the reactor wall made by Inconel (a Ni–Cr–Fe alloy). The CH4 formation can be reduced by alloying the internal wall of the reactor with Cu.

Despite the intense research activity on methanol steam reforming over Cu/ZnO-based catalysts, only few works can be found in the literature about the application of these catalysts for the ethanol steam reforming (ESR) process [27–30]. Ethanol requires higher reforming temperatures than methanol, due to the need to cleave the C–C bond. At high temperature Cu-based catalysts undergo a relatively fast deactivation mainly due to metal sintering.

A significant enhancement in ethanol reforming activity was documented in literature over bimetallic catalysts supported on ZnO-based oxides. Homs et al., for instance, studied bimetallic Co–Ni and Co–Cu samples containing 0.7 wt.% sodium promoter [29]. In the 250–450 °C temperature range, a remarkable improvement in H2 yield and stability was observed upon addition of Ni to a Co/ZnO sample. The same positive effect instead, was not detected with the introduction of Cu in the catalyst formulation.

Galetti et al. [27] described a quaternary mixed oxide Cu/Co/Zn/Al, which exhibited high activity and stability in the temperature range 400–600 °C producing mainly H2, CO2, CO and minor amount of CH4. The catalytic behavior was correlated to the structure of the catalyst composed by a spinel matrix (i.e. ZnAl2O4) with a high dispersion of oxidized Cu and Co species.

Zhang et al. [31] presented a promising Ni(30 wt.%)/Cu(5 wt.%)/Al2O3–ZnO catalyst which showed complete conversion of ethanol in the temperature range 250–600 °C. Acetaldehyde was only observed below 350 °C, while for higher temperatures CO, CO2, CH4 and H2 were the only detected products. No ethylene was monitored in the investigated temperature range and the coking amount was very low.

The effect of Ni and Co introduction in a Cu/ZnO/Al2O3 commercial catalyst was also studied by Grzegorczyk et al. [32] The major differences were observed below 480 °C, where methane formation slightly decreased while H2 selectivity and yield increased. The effect was more significant for Co than Ni.

A dependence of the reforming activity upon the precursor used was discussed by Llorca et al. on Co/ZnO-based catalysts [33–35]. The sample prepared with CO2(CO)8 precursor showed the best performance at 350 °C producing only small amount of CH4 as by-product without CO formation. The results confirm the key role of metal dispersion of the active phase in determining the desired reforming activity.

In this work, hydrogen production by steam reforming of methanol and ethanol over Cu/ZnO/Al2O3 catalysts was examined. The influence of the synthesis method on the chemical and physical properties as well as the catalytic activity of Cu/ZnO/Al2O3 materials were investigated, in order to select a cheap and simple synthetic methodology for their preparation. Moreover, the effect of the introduction of a second metal (Co or Ni) in the catalyst formulation was also examined, with the aim at improving activity and stability in the ethanol steam reforming reaction. Temperature programmed reduction (TPR), BET surface area measurements and N2O decomposition were used to characterize the catalyst surfaces. X-ray diffraction (XRD) was used to study their bulk structure. Thermal analysis and HR-TEM were performed to study the morphology of selected used catalysts and of the carbon deposits on them.

2. Experimental

2.1. Catalyst preparation

Analytical grade reagents and solvents (Fluka) were used as received without further purification.

All the catalysts have the molar composition M/Zn/Al = 45/45/10 (M = Cu, Cu + Ni, Cu + Co). The three different methodologies adopted are summarized as follows:

2.1.1. Method A: Oxalate coprecipitation

A 1 M aqueous solution of oxalic acid (excess 20%) is added rapidly to an aqueous solution of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O and Al(NO3)3·9H2O (total metal concentration: 0.1 M) under vigorous stirring and aged at room temperature for 1 h. The precipitate is filtered and dried at 110 °C overnight. The solid is finally calcined in a muffle at 150 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, 300 °C for 1 h and 360 °C for 8.5 h (heating rate 3 °C min⁻¹). The complex calcination steps follow the optimized procedure reported in Ref. [23].

2.1.2. Method B: Oxalate gel-coprecipitation

This procedure is similar to the previous one, the only difference being the solvent, which is ethanol in this case. A 1 M ethanol solution of oxalic acid (excess 20%) is added rapidly to an ethanol solution of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O and Al(NO3)3·9H2O (total metal concentration: 0.1 M) under vigorous stirring and aged at room temperature for 1 h. The precipitate is filtered and dried at 110 °C overnight. The solid is finally calcined in a muffle at 150 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, 300 °C for 1 h and 360 °C for 8.5 h (heating rate 3 °C min⁻¹). The complex calcination steps follow the optimized procedure reported in Ref. [23].

2.1.3. Method C: Carbonate coprecipitation

A 1 M water/ethanol (1:1 v/v) solution of Na2CO3 (excess 20%) is added rapidly to a water/ethanol (1:1 v/v) solution of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O and Al(NO3)3·9H2O (total metal concentration: 0.1 M) under vigorous stirring. The precipitate is aged for 1.5 h at 40 °C and then recovered by filtration, followed by washing with bidistilled water. The solid product is dried at 90 °C overnight and then calcined at 400 °C for 12 h (heating rate 3 °C min⁻¹). The preparation was adapted from Ref. [23].

The effect of the preparation methodology was evaluated on Cu-based samples while the effect of the addition of a second metal (Ni or Co) was evaluated on samples prepared following the method C. Using the latter approach, two equimolar bimetallic Co–Cu and Ni–Cu samples were synthesized and designed as Co/Cu/ZnO/Al2O3 and Ni/Cu/ZnO/Al2O3, respectively. A molar ratio M/Cu/Zn/Al = 22.5/22.5/45/10 (with M = Co or Ni) was selected in order to keep constant the number of metal atoms.
2.2. Catalytic activity measurements

Before testing the catalytic activity in the MSR and ESR, the calcined materials were pretreated/cleaned under O2 (5%)/Ar at 300 °C for 1 h (40 mL min⁻¹, 10 °C min⁻¹) and activated by reduction in H2 (5%)/Ar at 360 °C for 2 h (40 mL min⁻¹, 5 °C min⁻¹) in order to obtain the active phase (metals in the reduced state).

Catalytic experiments were conducted in a U-shaped 4 mm ID quartz microreactor, loading an adequate amount of pelletized catalyst (~2 ton cm⁻², 250–300 μm), diluted in a 1:2 weight ratio with high purity α-Al2O3 (Grace Davison, calcined at 1300 °C for 24 h). CH3OH/H2O:1:1 or CH3CH2OH/H2O:1.5 mixtures were injected into an Ar flow with a Hamilton Gastight syringe using an INSTECH Model 2000 syringe pump in order to reach a concentration of the alcohol of 1% by volume. All the transfer lines between syringe, reactor and GC were heated to 120 °C.

31 mg of pure catalyst and a gas flow rate of ~78 mL min⁻¹ were used in the case of MSR to ensure a GHSV value of ~150,000 mL g⁻¹ h⁻¹ and 12 mg of pure catalyst and a gas flow rate of ~30 mL min⁻¹ were used in the case of ESR to ensure a GHSV value of ~120,000 mL g⁻¹ h⁻¹. The gaseous mixture was first introduced in the reactor at 150 °C for 1 h, before ramping the furnace temperature to 700 °C at 1 °C min⁻¹. After 2 h at 700 °C, the furnace was cooled to 150 °C. The catalyst was subjected to two of these cycles. The gas phase composition was analyzed every 50 min and the catalyst temperature was recorded at the injection time. Catalytic activity results are reported by association of the gas phase analysis with the catalyst temperature. Repeated experiments indicated good reproducibility and the error bars in catalytic experiments were below 5%.

Stability tests were performed under steam reforming conditions. After being subjected to two consecutive run-up experiments, the catalyst temperature was set at 600 °C and the analysis of the gas phase composition was analyzed for at least 75 h.

Under the adopted experimental conditions, no mass or heat transfer limitations have been observed, thanks to the even low mass of catalyst loaded in the reactor.

On-line GC analysis was performed using a Hewlett Packard 5890 Series II gas chromatograph. A Molsieve 5A column, with Ar as carrier, was connected to a thermal conductivity detector (TCD) to analyze H2, O2, N2, CH4 and CO. A Select Permanent Gases/CO2 column (parallel PoraPLOT Q 50 m × 0.53 mm ID and Molsieve 5A 10 m × 0.32 mm ID columns), with He as carrier, was connected in series to a methanator and to a flame ionization detector (FID) to analyze the carbon-containing compounds.

The activity data (alcohol conversion and product yields) are presented reporting the ratio between the moles of each compound at the exit of the reactor (as determined by GC analysis) and the moles of alcohol in the feed as a function of the catalyst temperature. This presentation was selected in order to facilitate the comprehension of the reaction stoichiometry. Although for some samples a significant carbon deposition is observed during prolonged stability tests, the carbon balance in each GC analysis of the gaseous mixture is in line with the standard deviation of the analytical method (~2%).

2.3. Morphological and structural characterization

BET surface area measurements were conducted using a Micromeritics ASAP 2020 analyzer. N2 physisorption isotherms were collected at the liquid nitrogen temperature on 250 mg of sample, after evacuation at 300 °C overnight.

Powder X-ray diffraction patterns were collected on a Philips X’Pert instrument with Cu-Kα radiation. The Kα2 contribution was removed using the analysis software. Each XRD pattern was deconvoluted taking into account the overlapping of the patterns of the single phases. The mean crystallite size (CS) was evaluated applying the Scherrer’s equation to the main reflection of the XRD pattern of each identified phases.

Temperature Programmed Reduction (TPR) experiments were performed on 10 mg aliquots of the calcined materials. The samples were pre-treated at 350 °C for 1 h by pulsing 100 μL of O2 in an Ar flow every 75 s, then purged with Ar at 150 °C for 15 min and cooled to r.t. H2 (5%)/Ar was admitted into the reactor and the flow allowed to stabilize for 30 min before increasing the temperature to 900 °C at 10 °C min⁻¹. H2 consumption was monitored using a TCD.

N2O decomposition experiments were performed typically on 50–100 mg aliquots of calcined catalysts, cleaned under O2 (5%)/Ar at 300 °C for 1 h (40 mL min⁻¹, 10 °C min⁻¹) and activated by reduction in H2 (5%)/Ar at 360 °C for 2 h (40 mL min⁻¹, 5 °C min⁻¹) as before catalytic activity experiments. After degassing of adsorbed hydrogen at 360 °C, N2O decomposition was performed on the samples maintained at constant temperature pulsing pure N2O (100 μL) in an Ar flow (50 mL min⁻¹) every 5 min. The effluent was monitored using Hiden HPR 20 quadrupole mass spectrometer and pulses were continued until stable N2O peaks were obtained. The amount of oxygen adsorbed on the metal surface were calculated from the total N2O consumption. N2O decomposition experiments were performed at different temperatures depending from the composition of the metal phase as previously reported. In the case of Cu/ZnO/Al2O3, N2O pulses were introduced maintaining the samples at 60 °C and a N2O/CuₓO stoichiometry of 0.5 was used [36]. In the case of bimetallic systems, N2O decomposition was performed at 0 °C and a N2O/CuₓO stoichiometry of 0.25 was used, since metallic Co and Ni catalyze N2O decomposition and oxidation of metal in the bulk [37].

Temperature Programmed Oxidation (TPO) experiments were performed using a Hiden HPR 20 quadrupole mass spectrometer. Typically, 10 mg of the aged samples after ESR experiments were treated in O2 (15%)/Ar (60 mL min⁻¹) and heated to 900 °C at 10 °C min⁻¹.

The amounts of coke deposited on the aged catalysts after ESR experiments were evaluated by Thermo-Gravimetric Analysis (TGA) using Q500 TA Instruments. The weight changes of samples were measured against the temperature under flowing air (60 mL min⁻¹). Samples (ca. 18 mg) were pretreated for 1 h at 150 °C in N2 atmosphere to eliminate absorbed water and then heated at a constant rate (10 °C min⁻¹) up to 800 °C.

High Resolution Transmission Electron Microscopy (HR-TEM) images were collected on representative samples with a Jeol 3010 high resolution electron microscope (0.17 nm resolution at Scherzer defocus) operating at 300 kV using a Gatan slow-scan CCD camera (mod. 794). Energy dispersive Spectroscopy (EDS) analysis were performed using an Oxford-Isis detector with a spot size of ~25 nm. The samples were suspended in 2-propanol and a single drop was placed on a 200-mesh gold carbon-hole grid. Images were collected with different magnification, from 4× to 600×.

3. Results and discussion

3.1. Textural and structural characterization of calcined and activated sample

Three Cu/ZnO/Al2O3 catalysts, with a molar ratio of copper, zinc and aluminum 45:45:10, were prepared by different methods which will be referred to: (i) oxalate coprecipitation (method A) [23], (ii) oxalate gel-coprecipitation (method B) [23] and (iii) carbonate coprecipitation (method C – adapted from Ref. [23]). Briefly, methods A and B comprise the coprecipitation of the cations as oxalates. The two methods differ for the solvent used: water method A and ethanol method B. Finally, method C comprises...
the coprecipitation of the cations using sodium carbonate and a water/ethanol 1:1 by volume was selected as solvent.

All the samples present type IV N$_2$ physisorption isotherms with hysteresis loop typical of mesoporous materials. The $t$-plot analysis reveals that the microporous volume is always negligible, while the BJH analysis confirms the presence of a wide mesoporous network of pores with ink-bottle shape (Table 1).

Comparison of the samples with the same composition shows that the use of ethanol in the precipitation medium (methods B and C) results in a higher surface area with respect to water (method A). The material prepared using carbonate (method C) presents the highest surface area within the Cu/ZnO/Al$_2$O$_3$ samples, contrary to the reported results [23]. This could be related to the use of an ethanol/water mixture in our case. Therefore, the latter synthesis method was adopted to investigate the effect of catalyst doping with Co and Ni. A small increase of surface area was observed, while the mean pore diameter and the pore volume are significantly reduced.

The reducibility of the samples was examined by TPR (Fig. 1). As a general feature, both monometallic and bimetallic samples reveal a main reduction peak at low temperature, in the 200–300 °C temperature range. Moreover, some features attributable to possible artifacts due to sinterization of the samples can be recognized at temperatures higher than the calcination treatment. The reduction of CuO-species takes place at lower temperature than bulk CuO (maximum at 250 °C with a shoulder at 320 °C – data not reported). Cu/ZnO/Al$_2$O$_3$ samples show very similar reducibility both in term of reduction temperature and in total hydrogen consumption. The partial substitution of Cu with Co or Ni results in a modest shift to higher temperature of the main reduction peak and the appearance of additional features at higher temperatures: in the case of Co/Cu/ZnO/Al$_2$O$_3$-C the maximum is around 210 °C with a shoulder at 280 °C while a maximum at 225 °C with a broad peak centered around 370 °C are observed for Ni/Cu/ZnO/Al$_2$O$_3$-C. These results suggest that the introduction of Co or Ni in the formulation of the material has only a marginal effect on the reduction of Cu-species while the new reduction peaks could be associated with the reduction of CoO$_x$ or NiO$_x$-species. Co-based catalysts are usually not completed reduced below 500 °C [38,39] and consistently Co/ZnO/Al$_2$O$_3$ shows two well distinct reduction peaks, at 350 and 650 °C. Presence of Cu significantly shifts the high temperature peak to lower temperatures. Similar results have been obtained on materials with analogous composition prepared from layered double hydroxides [40,41] or by co-precipitation [42]. Based on the TPR results, a pre-reduction at 360 °C for 2 h was scheduled as activation pre-treatment before catalytic activity tests.

The composition and morphology of the calcined and reduced materials was evaluated using powder XRD (Fig. 2 and Table 2). As a general comment, no indications of Al-related phases (such as transitional Al$_2$O$_3$) were evidenced, mainly due to the relatively low Al content and the mild calcination treatment which prevents crystalization of the material. Similarly, no evidences of ZnAl$_2$O$_4$ formation were obtained.

The XRD pattern of calcined Cu/ZnO/Al$_2$O$_3$-A sample indicates the presence of well developed reflections of ZnO (31.8°, 34.4° and 36.2°) and CuO (35.5° and 38.7°). The mean crystallite size of ZnO and CuO are quite large (Table 2), in agreement with the low surface area of the material (Table 1) and its catalytic behavior similar to that of bulk CuO (see below). In the case of calcined Cu/ZnO/Al$_2$O$_3$-B and Cu/ZnO/Al$_2$O$_3$-C samples, broad XRD patterns are observed, with a partial overlapping of the reflection of ZnO and CuO. Similar crystallite sizes for the two phases were estimated (Table 2). The crystallite sizes are smaller than those of Cu/ZnO/Al$_2$O$_3$-A sample. The higher dispersion of the CuO crystallites justifies the lower reduction temperature observed during TPR experiments. After reduction at 360 °C for 2 h, all the samples present well developed reflections related to metallic Cu (43.3° and 50.4°) and ZnO. The crystallite size of the latter is almost unaffected by the reduction treatment. In the Cu/ZnO/Al$_2$O$_3$-B and Cu/ZnO/Al$_2$O$_3$-C samples, traces of CuO are detected (reflection at 38.7°), although the TPR characterization suggests that the reduction of Cu-species is complete at 360 °C. The amount of CuO is higher in the Cu/ZnO/Al$_2$O$_3$-C sample. Although the XRD patterns of reduced samples were acquired immediately after the pre-treatment, the presence of CuO can be attributable to an easy reoxidation of highly dispersed nanosized Cu particles during exposure to air.

The XRD pattern of Co/Cu/ZnO/Al$_2$O$_3$-C (recorded few times on different aliquots of sample) indicates very low crystallinity. The observed pattern could be related to the presence of a Co-based spinel phase, with Cu(II) distributed as a dopant of these structures. ZnCo$_2$O$_4$, Al$_2$O$_3$ and Co$_3$O$_4$ might be reasonable candidates as host phase with the spinel structure, since these materials present a very similar XRD patterns (same space group and similar cell parameters). After reduction, the spinel structure is decomposed and the onset of the reflections of highly dispersed ZnO is observed. A very broad reflection is present in the region of 2θ = 40–45°. The broadness of the reflection does not allow for a clear attribution to a metallic phase, suggesting that metal Co and Cu should be widely dispersed. Consistently, Gross et al. observed that these two metals do not form an alloy but that Cu segregates preferentially to the surface of the mixed metal [43].

In the case of Ni/Cu/ZnO/Al$_2$O$_3$-C material, the introduction of Ni(II) leads to the formation of a Ni–Cu mixed oxide (main reflection

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)$^a$</th>
<th>$d_{MAX}$ (nm)$^b$</th>
<th>CPV (mL g$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$-A</td>
<td>30</td>
<td>29</td>
<td>0.22</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$-B</td>
<td>89</td>
<td>14</td>
<td>0.32</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$-C</td>
<td>106</td>
<td>56</td>
<td>0.84</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al$_2$O$_3$-C</td>
<td>122</td>
<td>22</td>
<td>0.46</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al$_2$O$_3$-C</td>
<td>123</td>
<td>14</td>
<td>0.36</td>
</tr>
</tbody>
</table>

$^a$ Surface area from BET analysis.

$^b$ Diameter corresponding to the maximum of the pore distribution obtained using the BJH analysis.

$^c$ Cumulative pore volume.
Fig. 2. Powder XRD patterns of the calcined (A) and reduced in H2 (5%)/Ar flow at 360 °C for 2 h (B) for Cu/ZnO/Al2O3-A (a), Cu/ZnO/Al2O3-B (b), Cu/ZnO/Al2O3-C (c), Co/Cu/ZnO/Al2O3-C (d) and Ni/Cu/ZnO/Al2O3-C (e).

Table 2
Mean crystallite size (nm) determined by the Scherrer’s equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcined</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al2O3-A</td>
<td>16</td>
<td>41</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3-B</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3-C</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al2O3-C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al2O3-C</td>
<td>–</td>
<td>2</td>
</tr>
</tbody>
</table>

at 42.9°, with the cubic structure of NiO and a very small crystallite size. After reduction, a Ni–Cu alloy is formed, as revealed by the single reflection at 43.8°, between those of pure Ni and pure Cu (44.5° and 43.3°, respectively). A cell parameter of 0.357 nm can be calculated from the position of the main reflection of the alloy, in very good agreement with the theoretical value calculated on the basis of Vegard’s law. For an equimolar Ni/Cu metal phase, the presence of two alloys is expected on the basis of previous reports on Ni/Cu catalysts [44]. The presence of a single alloy could be related with the relatively low reduction temperature and/or with the formation of the mixed oxide in the calcined material, which prevents metal segregation after reduction. Notably, the reduction induces a deep crystallization of both ZnO and (Ni,Cu) particles (Table 2). N2O decomposition experiments were performed on pre-reduced samples in order to estimate the metal surface area adopting experimental conditions reported in the literature [36,37]. The obtained results are summarized in Table 3. All the samples demonstrates a quite low metal dispersion (<11%), as a result of the high metal loading present in the materials. Furthermore, the very low metal accessibility could be an indication that a partial metal encapsulation occurs as recently reported by Behrens et al. [45]. The larger contact area between Cu and ZnO was indicated as the origin of the high activity of those partially embedded catalysts [45]. The results obtained on Cu/ZnO/Al2O3 samples evidences that significant differences in the metal surface can be induced by the different preparation methods. In addition, all the samples prepared by carbonate-gel precipitation (method C) present similar exposed metal surface area (18–21 m2 g–1).

Table 3
Metal dispersion and surface area determined by N2O decomposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mₓ/Mₙ (%)</th>
<th>Metal surface area (m² g⁻¹)</th>
<th>Apparent particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al₂O₃-A</td>
<td>4.7</td>
<td>11.6</td>
<td>142</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-B</td>
<td>10.4</td>
<td>25.7</td>
<td>64</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-C</td>
<td>7.4</td>
<td>18.3</td>
<td>90</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al₂O₃-C</td>
<td>7.8</td>
<td>20.8</td>
<td>81</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al₂O₃-C</td>
<td>8.0</td>
<td>21.0</td>
<td>81</td>
</tr>
</tbody>
</table>

a Molar ratio between surface exposed metal atoms (Mₓ) and the total metal atoms (Mₓ+Mn).
b Metal surface area expressed as m² of metal exposed for each gram of catalyst.
c Calculated assuming a spherical shape of the particles.
d N2O decomposition performed at 60 °C as reported in Ref. [36].
e N2O decomposition performed at 0 °C as reported in Ref. [37].
ues of the particle sizes estimated for such low metal dispersions are one order of magnitude higher than the correspondent crystallite sizes. Taking into account that a single metal particle can be formed by various crystallites and considering the qualitative agreement between crystallite sizes and HR-TEM images, it is possible to suggest that an appreciable fraction of metal nanoparticles is partially embedded by the ZnO/Al2O3 support.

3.2. Catalytic activity: methanol steam reforming (MSR)

Fig. 4(a–c) shows the results of the steam reforming of methanol over Cu/ZnO/Al2O3 prepared according to the three different coprecipitation methods. On all the samples, methanol conversion starts above 150 °C. Below 300 °C, CO2 and H2 are detected as most abundant products. The formation of small quantities of CO is observed only above 300 °C, consistently with the fact that, increasing the temperature, CO2 and H2 are involved in the reverse WGS reaction. Notably, experiments performed without the catalyst (homogeneous reaction) or using only pure α-Al2O3 used to dilute the samples gave negligible methanol conversion in the temperature range involved in the MSR on the catalysts investigated in this study. The three synthetic procedures do not seem to significantly influence the catalytic performance of Cu/ZnO/Al2O3 samples, despite the fact that they lead to materials with different Cu metal dispersion and total surface area. Indeed, rather small changes in product distribution are observed. All the catalysts are able to convert 100% methanol already above 275 °C and reverse WGS reaction reaches the equilibrium in the same range of temperatures. The results obtained in this study on Cu/ZnO/Al2O3 are in good agreement with the proposed mechanisms of methanol steam reforming. Some early studies proposed that the steam reforming of methanol consists in the sequence of the methanol decomposition followed by WGS equilibrium, being CO the primary product that is easily converted into CO2 [46,47]:

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2
\]

Later studies demonstrated that the reaction follow a methyl formate reaction route, being CO2 and H2 the primary products [48,49]:

\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCHO} + \text{H}_2
\]

\[
\text{CH}_3\text{OCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH}
\]

Fig. 4. Methanol steam reforming results on Cu/ZnO/Al2O3-A (a), Cu/ZnO/Al2O3-B (b), Cu/ZnO/Al2O3-C (c), Co/Cu/ZnO/Al2O3-C (d) and Ni/Cu/ZnO/Al2O3-C (e). Comparison of CH3OH conversion on the investigated catalysts is reported in the last panel. Reaction conditions: CH3OH (1.0%) + H2O (1.0%) in Ar, GHSV = 150 000 mL g−1 h−1.
HCOOH $\rightarrow$ CO$_2$ + H$_2$

In this case, CO is a secondary product, being produced through the reverse WGS reaction.

The comparison with the catalytic performances of commercial catalysts was not possible in our case due to the lack of agreement by industrial companies. Although the different experimental conditions presented in the literature, the performances of our materials are only slightly lower with respect to industrial catalysts such as Synetix 33-5 [50], BASF K3-110 [51] or Süd-Chemie G-66 MR [52]. Notably, the composition and morphological characteristics of BASF K3-110, as reported by Peppley et al. [51], are very similar to that of our Cu/ZnO/Al$_2$O$_3$ catalysts.

Literature data indicate that methanol conversion on Cu/ZnO/Al$_2$O$_3$ materials greatly depends on the status of copper, such as the dispersion, metal surface area and particle size [23,53–57].

In this work, the three coprecipitation procedures lead to three catalysts, Cu/ZnO/Al$_2$O$_3$-A, B and C, with different surface area as well as different copper dispersion as indicated by TPR, XRD and N$_2$O decomposition measurements. The catalytic activity does not seem to be greatly influenced by these properties. Notably, as indicated by XRD data (Table 2), the reduction leads to an increase in Cu and ZnO crystallite sizes. The effect is more pronounced for the Cu/ZnO/Al$_2$O$_3$-A sample with the lowest surface area and lowest metal dispersion. However, the intrinsic limitations of the XRD technique, which is rather insensitive to small crystallites and/or amorphous fractions of a material, must be kept in due consideration: the contribution of such catalyst portions to the overall activity might well be substantial [58]. Therefore, to explain activity observations, other aspects have to be taken into account, such as the adsorption properties of the support. It was reported that the adsorption capacity of the oxides used as support affects catalytic performances, because spillover effects can play a key role in reaction mechanisms for these systems. In fact, hydrogen species were shown to be mobile over both Cu and ZnO phases of these catalysts and can be stored on the surface [59], whereas oxygen species move from ZnO to Cu, most likely in the form of hydroxides [60]. It was also proposed by Peppley et al. [51,61] a mechanism scheme for methanol steam reforming on Cu/ZnO/Al$_2$O$_3$ catalyst according to which the active sites for the methanol decomposition and for the direct methanol steam reaction and WGS are different. Moreover, hydrogen adsorption does not seem to compete for the active sites on which the oxygen-containing species adsorb. On the basis
of these considerations, it is clear that several factors act simultaneously and in opposite directions with regard to the catalytic activity. Recently, Behrens et al. nicely demonstrated that enhanced activity in methanol synthesis can be obtained by partially embedding Cu into ZnO/Al2O3 oxide [45]. The lack of substantial differences in the performance of the different materials might thus be due to various concomitant effects.

The catalytic activity changes with the introduction of a second metal component (Co or Ni) as displayed in Fig. 4(d and e). In particular, although the activity in methanol decomposition remains high, CO is observed among the products already at low temperatures (<300 °C). The CO yield reaches a maximum around 270 °C, after which it decreases while CO2 formation increases. These results suggest that in the case of bimetallic catalysts the methanol decomposition/WGSR pathway could be preferred highlighting that the introduction of the second metal (Co or Ni) decreases the activity of the catalysts for WGSR. Moreover, CH4 is also detected, as a product of CO and CO2 hydrogenation.

3.3. Catalytic activity: ethanol steam reforming (ESR)

Fig. 5(a–c) presents typical activity profiles for Cu/ZnO/Al2O3 (−A, −B, −C) catalysts for the ethanol steam reforming reaction. The contribution of the homogeneous reaction (performed with an empty reactor) is negligible while black experiments performed using only α-Al2O3 used to dilute the catalysts evidences only the formation of ethylene at high temperature (above 600 °C) with a maximum ethanol conversion of ~12%. The behavior of the Cu/ZnO/Al2O3 catalysts is very similar at low temperature while differences can be observed above 400 °C. On all samples, ethanol conversion starts above 150 °C producing essentially acetaldehyde and H2, which are the main products up to 400–450 °C. Increasing the temperature, on Cu/ZnO/Al2O3-A the acetaldehyde yield decreases while CH3COCH3 and CO2 start to be formed up to 600 °C. Small amounts of CH4 are also monitored. Above this temperature, the only detected products are CH3CHO and H2O. On Cu/ZnO/Al2O3-B, the formation of CH3COCH3, CO2 and CH4 is shifted towards higher temperatures (>450 °C) and they remain the main products together with H2 up to 650 °C, after which their yields decrease while acetaldehyde is again observed. The performance of Cu/ZnO/Al2O3-C is very similar to Cu/ZnO/Al2O3-B. Noteworthy, CO formation is not observed to any significant extent. The dehydration of ethanol to ethylene is well known to proceed on the strong acidic sites of oxide supports, such as Al2O3 [44,62,63].
Table 4
Mean Crystallite sizes of the phases observed in the XRD patterns of the aged samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO</th>
<th>ZnAl₂O₄</th>
<th>Graphite</th>
<th>Cu</th>
<th>Co</th>
<th>NiCu alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al₂O₃-C</td>
<td>44</td>
<td>12</td>
<td>–</td>
<td>26</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al₂O₃-C</td>
<td>88</td>
<td>13</td>
<td>6</td>
<td>32</td>
<td>25</td>
<td>–</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al₂O₃-C</td>
<td>55</td>
<td>13</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>23</td>
</tr>
</tbody>
</table>

the case of Cu/ZnO/Al₂O₃, the absence of ethylene production can be related to the small amount of alumina with respect to the Cu and Zn content of the samples and/or to the partial coverage of the alumina surface by copper and ZnO (basic oxide), with consequent reduction of the number of the acidic sites. However, the activity of Cu/ZnO-based materials in the reforming of ethylene cannot be completely excluded.

The product distribution described above differs from the few data presented in literature on similar Cu/ZnO/Al₂O₃ systems. Cavallaro and Freni [64] investigated the steam reforming of ethanol over CuO/ZnO/Al₂O₃ prepared by coprecipitation procedure and found that the catalyst exhibited good activity with CO, CO₂ and H₂ as the main products above 360 °C. The formation of oxygenated by-products, like acetaldehyde, acetic acid and ethyl acetate, was found to be favored only at low temperatures (<330 °C). Notably, acetone formation, which is observed in the present work for temperatures higher than 400–450 °C, was not described by the Cavallaro and Freni [64]. Elliott and Pennella [65] reported that alcohols with n carbon atoms can be converted over Cu/ZnO/Al₂O₃ catalysts into esters with 2n carbon atoms or ketones with 2n or 2n−1 carbon atoms, depending on the reaction conditions. The presence of CO in the gas phase moves the selectivity to the formation of ketones with 2n−1 carbon atoms. Nishiguchi et al. [66] reported that ethanol can be converted into H₂ and acetone passing ethanol/water mixture over Cu/CoO₂–MgO catalysts at 350 °C, with high yield in acetone. The formation of acetone was also observed during steam reforming of ethanol over Rh@CeₓZr₁−ₓO₂–Al₂O₃ catalysts [67]. In all the cases, the formation of acetone is related to a complex network of reactions involving dehydrogenation of ethanol, aldol condensation of acetaldehyde, oxidation to adsorbed carboxylic acid and finally dehydrogenation and decarboxylation of the adsorbed intermediate.

Significant improvements of the catalytic activity are observed introducing a second metal into the formulation of Cu/ZnO/Al₂O₃ catalysts. On Co/Cu/ZnO/Al₂O₃-C (Fig. 6a), ethanol conversion starts immediately. Up to 250 °C, the main products are acetaldehyde and hydrogen. Above this temperature, CO and CH₄ are formed while acetaldehyde yield decreases. The yield of hydrogen grows con-

![Fig. 10. TEM investigation on the aged Co/Cu/ZnO/Al₂O₃-C sample. (a) Graphitic carbon deposits; (b) SAED patterns; (c) HR-TEM image evidencing Cu and Co particles, with the corresponding EDS analysis.](image-url)
continuously as the temperature increases. \( \text{CO}_2 \) is also observed for temperatures higher than 350 °C. On Ni/Cu/ZnO/Al\(_2\)O\(_3\)-C (Fig. 6b), ethanol conversion becomes significant above 200 °C. The product distribution is similar to Co/Cu/ZnO/Al\(_2\)O\(_3\)-C with some differences. The formation of CH\(_4\) is inhibited, due to the ability of Ni to promote the steam reforming of methane [68] and CO is detected only above 300 °C. In the case of the addition of Co, the bimetallic system possesses a better catalytic activity also with respect to the corresponding Co/ZnO/Al\(_2\)O\(_3\)-C sample (Fig. 6c). In fact, ethanol conversion on Co/ZnO/Al\(_2\)O\(_3\) starts only above 300 °C and large amounts of acetone are produced between 400 and 600 °C. On the other hand, the catalytic behavior of Ni/ZnO/Al\(_2\)O\(_3\)-C (Fig. 6d) is quite similar to that of Ni/Cu/ZnO/Al\(_2\)O\(_3\)-C, with the difference that ethanol conversion starts above 300 °C and acetaldehyde is observed only in marginal amounts.

The stability of catalytic activity under isothermal conditions was tested at 600 °C (Fig. 7) since, at this temperature, \( \text{H}_2 \) production reaches a maximum while CH\(_4\) formation is negligible on the samples with the best reforming activity (Co/Cu/ZnO/Al\(_2\)O\(_3\) and Ni/Cu/ZnO/Al\(_2\)O\(_3\)). All the samples present an initial activity comparable to that observed at 600 °C during the run-up experiments. Cu/ZnO/Al\(_2\)O\(_3\) converts ethanol into a mixture of CH\(_4\), CO\(_2\), and H\(_2\), being not able to promote the steam reforming of CH\(_4\) (Fig. 7a). The initial activity is maintained for 20h. After this time, a slow deactivation occurs, resulting in the un-complete ethanol conversion, in the decrease of H\(_2\), CO\(_2\), and CH\(_4\) production and in the increase of acetaldehyde production. On the other hand, the addition of a second metal (Co or Ni) strongly increases the stability of the catalytic activity. In fact, no significant alteration of the initial activity is observed during the investigated period. XRD data suggest that a significant increase of crystallite sizes occurs for all the samples (Fig. 8), as a result of the thermal treatment at high temperature. Table 4 summarizes the mean crystallite sizes of the different phases revealed by XRD diffraction. The presence of ZnAl\(_2\)O\(_4\) is evidenced in the oxide supports, together with ZnO. In the case of Co/Cu/ZnO/Al\(_2\)O\(_3\)-C, two distinct metal phases are observed. On the contrary, the alloy formed by Ni and Cu during the initial reduction pre-treatment remains unperturbed for Ni/Cu/ZnO/Al\(_2\)O\(_3\)-C sample (cell parameter of the alloy: 0.3579 nm). The reflection near 26.6° observed in XRD spectra of both Co/Cu/ZnO/Al\(_2\)O\(_3\)-C and Ni/Cu/ZnO/Al\(_2\)O\(_3\)-C can be attributed to graphite, indicating that the deposition of large amounts of graphitic coke occurs.

The species evolved during carbon removal were analyzed during Temperature Programmed Oxidation experiments (Fig. 9a–c). The amount of carbon deposited on catalysts was estimated separately by TGA (Fig. 9d) while, on the whole, TGA experiments show a slight initial increase of the weight, followed by a decrease related to carbon species removal. The initial weight increase could be related with the oxidation of the metal phases to the corresponding oxides. Assuming the formation of CuO, Co\(_3\)O\(_4\), and NiO as metal oxide phases (similarly to the phases observed in the calcined samples), the exact weight loss due to carbon removal can be calculated. The results showed that coke deposition is strongly reduced on Ni/Cu with respect to the Co/Cu system. Indeed, on Co/Cu/ZnO/Al\(_2\)O\(_3\) sample the amount of carbon was 0.5765 gC/gcat while 0.3804 and 0.0974 gC/gcat was calculated for

![Fig. 11. TEM investigation on the aged Ni/Cu/ZnO/Al\(_2\)O\(_3\)-C sample. (a) Carbon whiskers; (b) SAED patterns evidencing NiCu alloy formation; (c) HR-TEM image evidencing NiCu alloy and ZnO particles, with the corresponding EDS analysis obtained in different position on the HR-TEM image.](image-url)
Ni/Cu/ZnO/Al_2O_3 and Cu/ZnO/Al_2O_3, respectively. Notably, during two run-up experiments (24 h each) and the 75 h stability test, each aged sample was subjected to 123 h under reaction stream and, during this period, a total amount of ~181 g of carbon passes over 1 g of catalyst. The small coking tendency of Cu/ZnO/Al_2O_3 sample is consistent with its poor reforming activity at 600 °C as displayed in Figs. 5 and 7. As indicated by XRD data, the alloy formation between Co and Cu does not take place. Large amounts of coke are deposited on the Co/Cu/ZnO/Al_2O_3-C sample due to the high coke tendency demonstrated by Co [69], which is not mitigated by the presence of Cu. On the other hand, lower coke deposition is observed for the Ni/Cu system with respect to that of the Co/Cu system. This can be correlated to the Ni/Cu alloy formation. The Cu atoms in the alloy can occupy preferentially either flat terrace sites, or edge and kink Ni sites which are mainly responsible for carbon formation [70]. Notably, the higher CO_2 evolution temperature observed during TPO experiments on aged Ni/Cu/ZnO/Al_2O_3-C is an indication of the presence of a larger graphitic carbonaceous deposits with respect to the aged Co/Cu/ZnO/Al_2O_3-C. This in agreement with the higher dehydrogenation activity and lower CO hydrogenation activity demonstrated by Ni/Cu-based catalyst with respect to the Co/Cu-based one.

TEM investigations were performed on the aged Co/Cu/ZnO/Al_2O_3-C and Ni/Cu/ZnO/Al_2O_3-C samples in order to better characterize the morphology of the catalysts and of the carbon deposits. Fig. 10 shows representative results obtained on the aged Co/Cu/ZnO/Al_2O_3-C sample. In general, low magnification images show the presence of very large amounts of carbon deposits, which fully cover the surface of the catalyst and makes confusing the low magnification images. Only high resolution images allow to understand the morphology of the aged sample. Fig. 10a shows the carbon deposits formed by highly graphic materials, in agreement with XRD results (Fig. 7 and Table 4). Due to the large amount of carbon deposits and to their nanocrystalline form, the exact identification of metal and ZnO nanoparticles was quite hard. Anyway, distinct Co and Cu nanoparticles were detected analyzing lattice spacing and by identification of spots in the SAED analysis. A representative HR-TEM image is presented in Fig. 10c, where Co and Cu nanoparticles were observed (the presence of the two metals were confirmed by EDS analysis). The dimensions of Co, Cu and ZnO nanoparticles are in agreement with the mean crystallite dimensions calculated from XRD reflections broadening (Table 4).

Fig. 11 presents representative results from the TEM characterization of the Ni/Cu/ZnO/Al_2O_3 catalyst. Low magnification images evidence the growth of carbonaceous deposits as carbon whiskers (Fig. 11a), with a graphitic nature as revealed by lattice spacings observed in high magnification images (not shown). SAED confirms the formation of a Ni–Cu alloy, since a single diffraction circle is observed (Fig. 11b). Fig. 11c shows a representative HR-TEM image presenting a Ni–Cu alloy nanoparticles supported on a ZnO particle. The nature of the particles is confirmed by EDS analysis, as reported. Also in this case, a good agreement between the dimension of the particles and the mean crystallite size calculated from XRD is obtained.

4. Conclusion

Active and cheap catalysts, comprising base metals (Cu, Co and Ni) as active phase and ZnO as promoter, can be prepared following simple ways, demonstrating good performances in the hydrogen production through the steam reforming of alcohols.

The optimization of the preparation methodology leads to high surface area materials, although the metal dispersion remains quite low due to the high metal loading. N_2O decomposition experiments, XRD analysis and HR-TEM images suggest that metal nanoparticles could be at least partially embedded into the ZnO/Al_2O_3 support.

Despite different morphological properties, methanol steam reforming reaction on Cu/ZnO/Al_2O_3 is in our case marginally affected, as a combination of structural factors. The addition of Ni or Co has a detrimental effect on the selectivity of methanol steam reforming, due to the significant activity in CO/CO_2 hydrogenation to methane. Moreover, the introduction of Ni or Co negatively affects the WGSR equilibrium, resulting in lower H_2 and CO_2 yields. Cu/ZnO/Al_2O_3 is active for the dehydrogenation of ethanol, producing quantitatively acetaldehyde and H_2 at moderate temperature (350 °C). The reforming activity at higher temperature remains very poor since Cu is not able to activate the C–C bond. Nevertheless, this result suggests the possibility to convert ethanol into acetaldehyde at moderate temperature with the aim to produce important chemicals (such as acetic acid and its derivatives) from a renewable source.

Ni forms an alloy with cubic structure with Cu while Co does not, forming distinct and separated phases, as revealed by XRD and HR-TEM. The introduction of Ni and/or Co in the formulation of the active phase enhances the ethanol steam reforming activity. In both the cases, above 600 °C ethanol is fully converted into a mixture of H_2, CO and CO_2 with minor traces of CH_4. Steady-state experiments at 600 °C indicate that coke deposition occurs significantly on Co/Cu/ZnO/Al_2O_3. HR-TEM evidences that the surface of Co/Cu/ZnO/Al_2O_3 is almost fully covered by graphitic coke, which strongly complicates the investigation. In the aged Ni/Cu/ZnO/Al_2O_3, the presence of carbon whiskers is evidenced. Formation of a Ni–Cu alloy significantly reduces deactivation phenomenon on the sample.

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References
