

The effect of palladium and CeO₂ on the catalytic and physicochemical properties of copper catalysts in methanol synthesis

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Received: 29 July 2014 / Accepted: 13 September 2014 / Published online: 20 September 2014
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Abstract This paper deals with the study of the bimetallic Pd–Cu and monometallic Cu, Pd catalyst used in the methanol synthesis reaction. To reveal the influence of the catalyst properties on methanol production, various characterization techniques were used, such as Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, TPR-H₂ and TPD-NH₃. The catalytic activity was studied in CO hydrogenation under elevated pressure (4.8 MPa) in a fixed bed high-pressure reactor. The activity results confirmed the promotion effect of palladium and CeO₂ on the catalytic activity of copper catalysts. The highest activity and selectivity of Pd–Cu/ZnAl₂O₄–5 % CeO₂ is explained by the Pd–Cu alloy formation during activation process. The presence of adsorption species attributed to b-HCO₃–Ce, b-HCOO–Ce and b-HCOO–Ce species on the surface of CeO₂ promoted catalysts was confirmed by FTIR method.

Keywords Methanol synthesis · Bimetallic catalysts · Pd–Cu · Ternary systems · Copper catalyst · Palladium catalysts

Introduction

Methanol synthesis is one of the basic chemical processes in the world, because it is the substrate for many chemicals e.g., formaldehyde, chloromethane, amines, acetic acid, methyl methacrylate. The increased interest in issues of methanol production methods may be due to the possibility of its use as a fuel (e.g., fuel cells) to produce

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electricity and its processing into high-octane methyl *tert*-butyl ether and dimethyl terephthalate [1–4].

In the twenties of the previous century in Germany, there was a growing interest in high-pressure processes (so-called “hydrerungs verfahren” processes), which contributed to the development of technological processes, including: ammonia synthesis “Haber - Bosch” synthesis, “hydrogen - desulfurization” process, Fischer–Tropsch synthesis and methanol synthesis from synthesis gas.

In 1922, M. Pier produced methanol in BASF’s laboratory. The process required high pressure (250–350 atm) and high temperature (320–450 °C), due to the operating conditions of the process it was named “high-pressure methanol synthesis”. It was a process widely used for over 45 years, in which production of methanol [5, 6] was carried out from synthesis gas obtained by gasification of coal or brown coal, using relatively resistant to poisoning ZnO/Cr₂O₃ catalyst.

Unfavorable conditions of the “high-pressure methanol synthesis” process led to a search for new, more efficient and selective catalysts for enabling operation of the methanol synthesis in a much milder conditions. The research led to the development of a copper catalyst, which in the 1966 has been improved by the company ICI (Imperial Chemical Industries, nowadays Syntex) by introducing Zn. As it turned out, zinc is an ideal dispersing agent of copper on the catalyst surface [7–9]. Promotion of copper catalyst by zinc caused an increase of the catalytic activity, which allowed to conduct the methanol synthesis under milder conditions, i.e., at a lower pressure 35–55 atm and in the lower temperature range of 200–300 °C. The process was named “low pressure methanol synthesis”. Currently, this is used for the methanol synthesis process on an industrial scale [1, 3, 10].

Typical catalysts used in industrial low-pressure methanol synthesis are systems containing copper, zinc and aluminum oxides. The molar ratio of the catalyst components varies depending on the manufacturer, but the content of CuO is contained in the range 40–80 %, ZnO 10–30 %, Al₂O₃ from 5 to 10 %. There are also various types of promoters of both structural and textural (e.g., MgO), but a detailed description of promoters and their content is protected by the manufacturers [1].

Many researchers claimed that the oxygen vacancies in the metal oxide support play an important role in the catalysis. Li et al. [11] investigated the adsorption of CO on partially reduced CeO₂ by Fourier transform infrared spectroscopy (FTIS). CO adsorbed on the oxygen vacancy of pre-reduced CeO₂ is turned into formate species. A possible proposed mechanism is that the activated CO molecules on reduced surface sites interact with the nearby OH groups to form formate species via an unstable intermediate, formyl species [11]. Considering those studies it was expected that the oxygen vacancies of CeO₂ could provide effective active sites for CO adsorption during methanol synthesis.

In addition, CeO₂ has a high oxygen storage capacity and excellent redox properties [12–14]. However, these properties disappeared at high temperature due to its poor thermal stability [15].

Palladium supported CeO₂ catalysts have been reported to be effective for the hydrogenation of CO and CO₂ to methanol. Pd/CeO₂ also exhibits a more stable

reaction activity for methanol synthesis from syngas containing sulfur in comparison to Pd/Al₂O₃ catalyst [16].

Shen et al. [17] studied the Pd/CeO₂ supported catalyst in methanol synthesis reaction from CO and H₂ and claimed that this catalytic system exhibited high activity due to the strong interaction between palladium and ceria. The interaction caused a change in the electronic charge density at the Pd surface.

A possible way to improve the activity of copper-based catalysts is to create multifunctional catalysts containing intermetallic or alloy compound [18–21] on the catalysts surface. The formation of these alloy or intermetallic compounds had to be carried out directly during activation process of studied systems. These compounds are thought to be a key factor to achieve highly active and selective systems.

Another way to improve the activity of copper catalysts is the introduction of the textural promoter such as CeO₂ into the support structure, which may create structural defects to facilitate the mobility of lattice oxygen and change the redox properties.

Based on the above suggestion in this study, we prepared multifunctional systems and investigated the effect of palladium and CeO₂ on the catalytic activity and selectivity of Cu/ZnAl₂O₄ catalyst in the methanol synthesis reaction. Using X-ray diffraction (XRD), FTIR, temperature programmed reduction (TPR)-H₂, and NH₃-TPD, the chemical and physicochemical properties of the investigated catalysts were characterized and correlated with the activity results in CO hydrogenation.

Experimental section

Catalysts preparation

Copper catalysts were prepared by wet aqueous impregnation. In order to prepare the ZnAl₂O₄ support, the following molar ratio of Zn:Al = 0.5 zinc and aluminum nitrates were used. Aqueous solutions of 1 M zinc nitrate (Zn(NO₃)₂·6H₂O) and 1 M aluminum nitrate (Al(NO₃)₃·9H₂O) were mixed in appropriate quantity under vigorous stirring at 80 °C. A concentrated ammonia solution was then added by dropwise until the pH reached values of between 10 and 11, and then the mixtures were stirred for another 30 min. The resulting fine precipitates were washed two times in deionized water and then dried at 120 °C for 15 h and calcined for 4 h at 600 °C in air. Calcination at 600 °C was chosen because such high temperature is required for creation of spinel structure and for removal of the nitrate precursor from the catalytic systems.

Supports ZnAl₂O₄-1 % CeO₂ and ZnAl₂O₄-5 % CeO₂ were prepared by the impregnation method. An appropriate quantity of cerium nitrate was taken to obtain relevant content of CeO₂ and introduced on the carrier (ZnAl₂O₄) surface. The obtained material was further dried at 120 °C for 2 h and then calcined in air at 400 °C for 4 h.

Metal phase Cu and Pd was introduced on the previously prepared support surface (ZnAl₂O₄, ZnAl₂O₄-1 % CeO₂ and ZnAl₂O₄-5 % CeO₂) by wet impregnation using aqueous solutions of copper and palladium nitrates. The supported catalysts were then dried in air at 120 °C for 2 h and finally calcined for 4 h in air at

temperatures of 400 °C. Copper and palladium loadings were 20 and 2 wt%, respectively.

Catalysts characterization

Temperature programmed reduction (TPR-H₂)

The TPR-H₂ measurements were carried out in an automatic TPR system AMI-1 in the temperature range of 25–900 °C with a linear heating rate of 10 °C min⁻¹. Samples (weight about 0.1 g) were reduced in hydrogen stream (5 % H₂–95 % Ar) with a volumetric flow rate of 40 cm³ min⁻¹. Hydrogen consumption was monitored by a thermal conductivity detector.

XRD measurements

Room temperature powder XRD patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg–Brentano reflecting geometry. Copper Cu K_α radiation from a sealed tube was used. Data were collected in the range 5–90° 2θ with a step of 0.0167° and exposure per step of 27 s. Due to the fact that raw diffraction data contain some noise, the background during the analysis was subtracted using Sonneveld, E.J. and Visser algorithm. The data was then smoothed using cubic polynomial. All calculations were done using X'Pert HighScore Plus computer software.

Temperature programmed desorption of ammonia (TPD-NH₃)

The procedure of catalyst surface acidity measurement includes the purification of catalyst surface, adsorption of ammonia and TPD. Catalyst sample purification (about 0.15 g), removal of water from the system leading to surface dehydroxylation, was completed in pure argon stream with a volume velocity of 40 cm³ min⁻¹ at 400 °C for 2 h and after cooling sample to 100 °C argon stream was switched into a gaseous ammonia flowing 0.5 h through catalyst sample to entirely saturate its surface. After NH₃ adsorption, the excessive amount of weakly and physically adsorbed ammonia on the catalyst surface had been removed by flushing of the catalyst in pure argon stream with volume velocity of 40 cm³ min⁻¹. A TPD-NH₃ run was done in a temperature range of 100–500 °C with a linear heating rate of 27 °C min⁻¹ and a thermo-conductivity detector to obtain a TPD-NH₃ profile.

Catalytic activity test

Activity tests in the methanol synthesis reaction were carried out using the high pressure fixed bed reactor using a gas mixture of H₂ and CO with molar ratio 2:1. The process was carried out under elevated pressure (4.8 MPa) at 260 °C and products were analyzed by GC (gas chromatograph). Before the activity tests, all catalysts were pre-reduced for 2 h in a flow of 5 % H₂–95 % Ar mixture at 300 °C under atmospheric pressure. The steady-state activity measurements were taken

after at least 12 h on the stream. The analysis of the reaction products were carried out by an on-line GC equipped with a FID detector and 10 % Carbowax 1500 on Graphpac column. The CO and CO₂ concentrations were monitored by a GC chromatograph equipped with TCD detector (120 °C, 130 mA), and Carbosphere 60/80 (65 °C) column. CO conversion was calculated by the following equation:

$$\text{CO}_{\text{conv.}} = \left[\frac{(\text{CO in feed} - \text{CO in effluent})}{\text{CO in feed}} \times 100 \right].$$

The selectivities of the products were calculated as follows:

$$P_i \text{selectivity} = \left(\frac{P_i \text{yield}}{\sum P_i \text{yield}} \right) \times 100,$$

where P_i is the amount of substance of every organic product.

Diffuse reflectance FTIS

IR spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT (mercury cadmium telluride—MCT, HgCdTe) detector. Before analysis copper, palladium and palladium–copper catalysts supported on ZnAl₂O₄ and ZnAl₂O₄–5 % CeO₂ were reduced at 300 °C in gas reduction mixture 5 % H₂–95 % Ar for 1 h. After reduction, the catalysts were cooled down to 120 °C and then the reduction mixture was shifted to a mixture of approximately 1 vol.% CH₃OH in argon stream. A resolution of 4.0 cm⁻¹ was used throughout the investigations. 64 scans were taken to achieve a satisfactory signal to noise ratio. The background spectrum was collected at 120 °C after reduction. The adsorption process involved exposure of the reduced catalysts to 1 vol.% CH₃OH in argon stream flowing at 40 cm³ min⁻¹ for 30 min under atmospheric pressure. After the adsorption process, the cell was evacuated for 30 min at the same temperature in argon.

Result and discussion

The catalyst reducibility was evaluated by TPR. H₂-TPR results for the monometallic Cu and bimetallic Pd–Cu catalysts are shown in Figs. 1 and 2. Monometallic 20 % Cu/ZnAl₂O₄ supported catalysts exhibited two reduction peaks in the temperature range of 180–380 °C which are attributed to reduction of CuO and Cu₂O species [22–27]. TPR curves recorded for copper catalysts promoted by CeO₂ also showed two reduction stages, which were slightly shifted towards lower temperature. This indicates that the addition of CeO₂ into the copper catalyst improve the copper dispersion and facilitates the reduction of copper species.

The reduction behavior of Pd–Cu supported catalysts was also studied in this work. The comparison of the reduction measurements carried out for unpromoted copper 20 % Cu/ZnAl₂O₄ supported catalysts and for promoted by Pd and CeO₂ is shown in Fig. 2. The TPR-H₂ results performed for palladium catalysts showed that

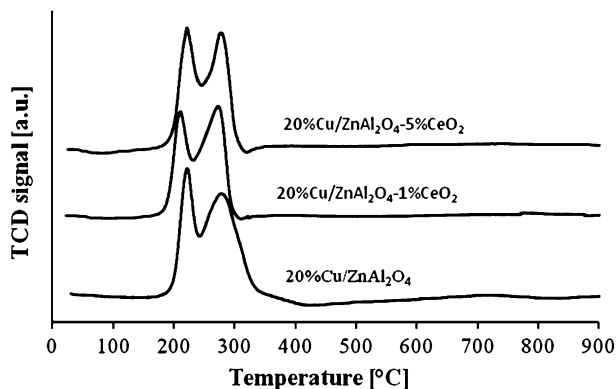


Fig. 1 TPR profile of Cu/ZnAl₂O₄ and copper promoted by CeO₂ catalysts after calcination in air for 4 h at 400 °C

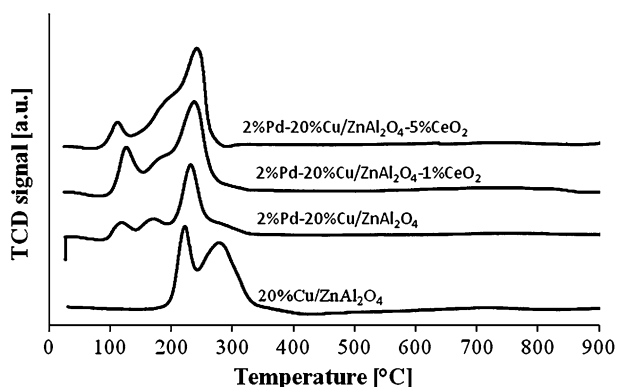


Fig. 2 TPR profile of copper and palladium–copper catalysts after calcination in air for 4 h at 400 °C

all Pd–Cu catalytic systems reduced in three stages. The first effect observed in the temperature range 80–140 °C for all palladium doped catalysts is connected with PdO reduction. The next two hydrogen consumption peaks are assigned to the reduction of CuO and Cu₂O copper species reduction according to the following scheme: CuO → Cu₂O → Cu [28].

In our previous work, we investigated the reduction behavior of palladium 2 % Pd/ZnAl₂O₄ catalyst. TPR-H₂ of this catalyst showed two hydrogen consumption peaks situated at about 30 and 80 °C. The first hydrogen consumption effect was attributed to the reduction of highly dispersed palladium oxide which is slowly reduced at room temperatures. The second reduction peak indicates the reduction of small palladium crystallites interacting with the surface of ZnAl₂O₄ [29].

Cubeiro and Fierro [30] also studied the reduction behavior of Pd/ZnO catalysts. They claimed that PdO is an easily reducible oxide, even at room temperature, they observed a low temperature reduction peak situated in the temperature range 30–150 °C, which was assigned to the reduction of PdO to metallic Pd.

The reduction behavior of Pd supported on mixtures of zinc oxide, zinc aluminate, and alumina, prepared from γ -alumina and zinc nitrate, were studied by Nilsson et al. [31]. The authors observed H_2 consumption peak with its maximum at around 90 °C for all studied palladium catalysts and this hydrogen consumption peak authors ascribed to the formation of metallic Pd and Zn by hydrogen spillover from Pd [31]. Additionally, the Pd catalyst supported on a mixture of ZnO and γ -alumina exhibited a peak at 450 °C. This reduction profile was assigned to the ZnO reduction. The authors have proposed this conclusion based on reduction studies performed for the reducibility of ZnO/ γ - Al_2O_3 bi-oxide. The TPR profile of ZnO/ γ - Al_2O_3 , prepared by impregnating alumina with zinc nitrate, exhibits a reduction peak located in this temperature region [31].

The Pd and Pd–Cu catalysts reducibility was evaluated by measuring the TPR by Wang and Lu [32]. The authors claimed that the Pd/ Al_2O_3 catalyst reduced in one reduction stage with the maximum of hydrogen consumption peak situated at a lower temperature of 125 °C. This effect was related to the reduction of PdO, which means that there was a weak interaction between Pd and the support. The TPR profiles recorded for bimetallic Pd–Cu/ γ - Al_2O_3 catalysts showed that the reduction peaks were shifted toward higher temperature, which suggested that the addition of Cu species enhanced the interaction between active Pd species and alumina, meanwhile the presence of Pd facilitated the reduction of copper oxides. This result is believed to arise from an interaction of palladium and copper oxides, which results in the formation of a Pd–Cu alloy.

Canner and Falconer [33] proposed that the enhanced reduction of copper species in the presence of Pd on the catalyst surface can be explained by hydrogen spillover from metal Pd to copper species.

Kugai et al. [34] studied the reduction behavior of monometallic Pd, Cu and bimetallic Pd–Cu catalysts supported on CeO_2 using TPR method. TPR measurements of those systems indicate that Pd catalysts reduced at 130 °C. In contrast, the monometallic Cu catalyst exhibited two reduction effects with the maximum of hydrogen consumption peaks positioned at around 135 and 160 °C. These peaks were attributed to the reduction in highly dispersed CuO cluster interacting with ceria and/or bulk copper species. In the case of copper catalysts containing 25 wt% of Cu, a new third effect situated at 180 °C appeared and this effect has been assigned to bulk CuO species reduction. The authors noticed that the third peak occurs at lower temperature and compared it to non-supported bulk CuO as suggested by Fierro et al. [35], which means that even bulk CuO species is under strong influence of ceria support. The reduction effects positioned at 135 and 160 °C were assigned to two types of dispersed CuO species closely interacting with ceria to different extents or dispersed CuO species and isolated Cu^{2+} ion directly interacting with ceria. In the case of Pd–Cu catalysts on the TPR curve, only a single peak was observed at around 135 °C. The interaction between Pd and Cu led to the metal species more reducible than Cu and less reducible than Pd. The broadness of the peak indicates a certain variation in Pd–Cu species, such as variation in the Cu/Pd ratio on the microscopic level or in alloy crystallite size, during reduction [34].

The phase composition studies of unpromoted and promoted by Pd and CeO_2 Cu/ $ZnAl_2O_4$ supported catalysts after calcination and reduction were carried out to

elucidate the interaction between the active component and support. Fig. 3 displays XRD patterns of copper catalysts supported on ZnAl_2O_4 -1 % CeO_2 after calcination in air atmosphere at 400, 700 and 900 °C for 4 h. The diffraction peaks of the oxide phase in the case of copper catalyst calcined at 400 °C are attributed to ZnAl_2O_4 , ZnO , $\gamma\text{-Al}_2\text{O}_3$ and CuO phases [22, 23].

The increase of the calcination temperature caused the increase of the crystallinity degree for studied system. In addition, the appearance of CeO_2 phase in the case of copper catalysts being after calcination at 900 °C was confirmed.

The phase composition studies of $\text{CuO}\cdot\text{ZnO}\cdot\text{ZnAl}_2\text{O}_4$ multi metal oxide was investigated using XRD patterns by Abdus Subhana et al. [36]. The authors observed sharp diffraction peaks attributed to crystalline copper oxide (CuO), zinc oxide (ZnO) and ZnAl_2O_4 [37].

In Fig. 4, the phase composition studies of copper catalysts calcined at 400, 700 and 900 °C promoted by 5 % CeO_2 are given. On the XRD curves recorded for this system, we can easily observe the same oxidic phases as in the case of copper catalysts promoted by 1 % CeO_2 .

The phase composition studies of 2 % Pd-20 % $\text{Cu}/\text{ZnAl}_2\text{O}_4$ catalyst calcined at various temperatures (400, 700 and 900 °C) confirmed the presence of the following oxidic phases: ZnAl_2O_4 , ZnO , PdO, $\gamma\text{-Al}_2\text{O}_3$ and CuO (see Fig. 5). The appearance PdO and CuO phases in the investigated catalytic systems confirmed the reduction behavior of copper palladium doped catalyst. In the next step of our XRD investigation, we carried out the diffraction measurements for copper palladium catalysts promoted by 5 % CeO_2 , the results of these studies are shown on Fig. 6.

On the diffractograms recorded for this system, the same oxidic phases were observed as in the case of unpromoted palladium-copper catalysts. The only

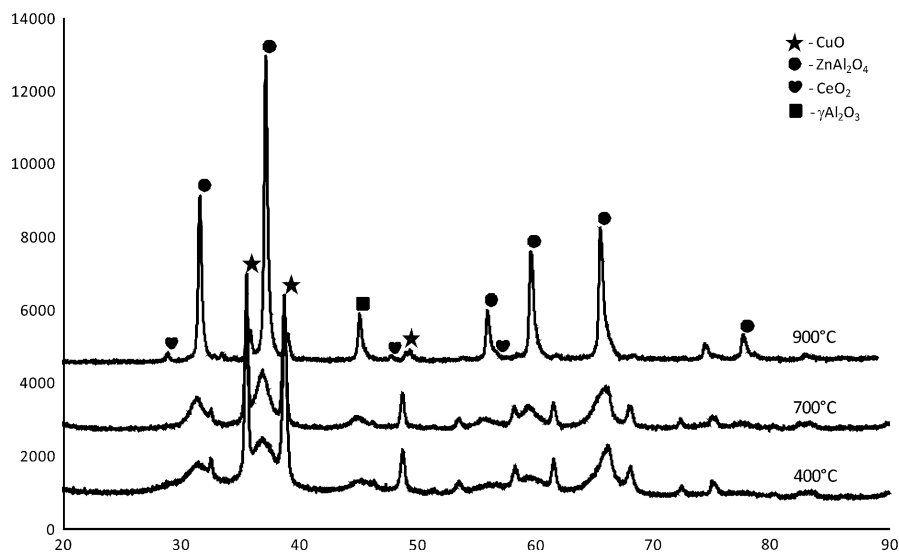


Fig. 3 XRD patterns for 20 % $\text{Cu}/\text{ZnAl}_2\text{O}_4$ -1 % CeO_2 after calcination in air atmosphere at 400, 700 and 900 °C for 4 h

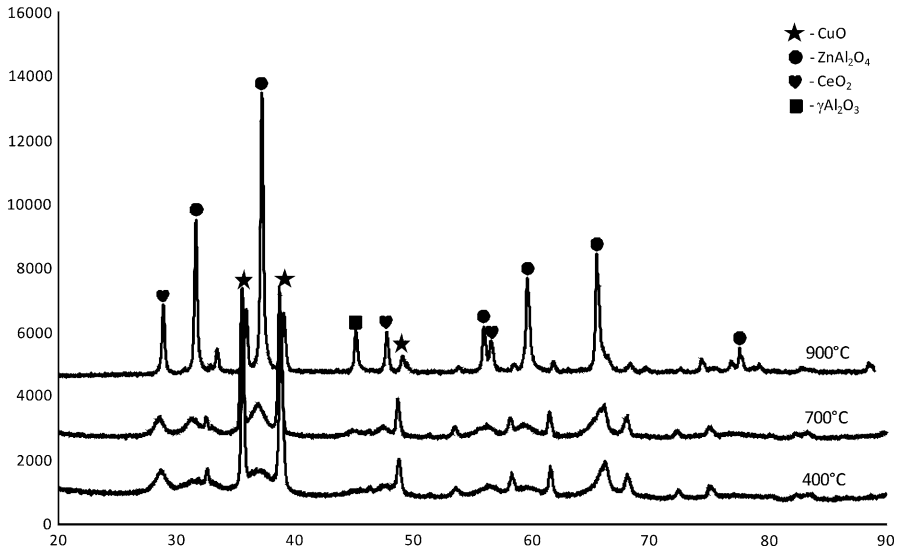


Fig. 4 XRD patterns for 20 % Cu/ZnAl₂O₄-5 % CeO₂ after calcination in air atmosphere mixture at 400, 700 and 900 °C for 4 h

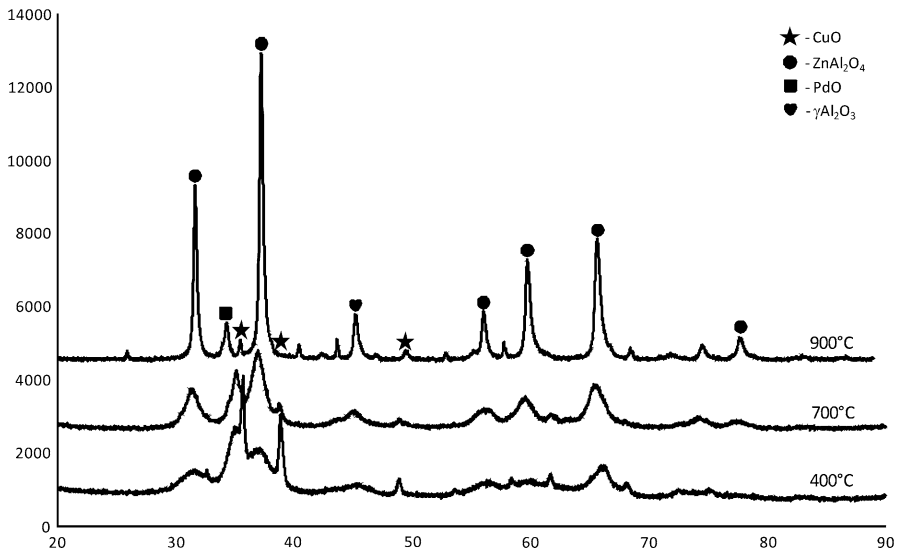


Fig. 5 XRD patterns for 2 % Pd-20 % Cu/ZnAl₂O₄ after calcination in air atmosphere at 400, 700 and 900 °C for 4 h

difference observed in this case was the appearance of additional CeO₂ phase, which was visible on the XRD curves starts from 400 °C. To understand this better and to elucidate the reduction results obtained for palladium–copper promoted by cerium oxide, we performed the analogical diffraction measurements for copper and

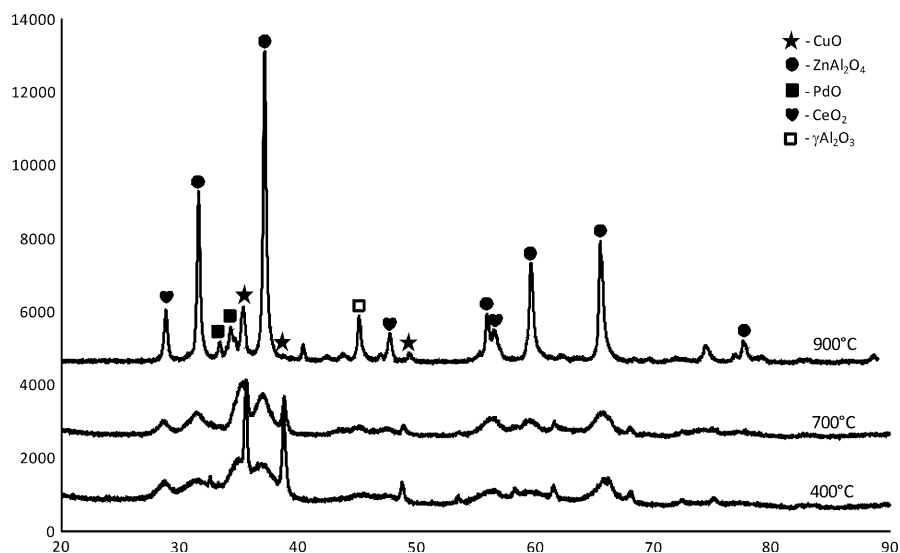


Fig. 6 XRD patterns for 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ after calcination in air atmosphere at 400, 700 and 900 °C for 4 h

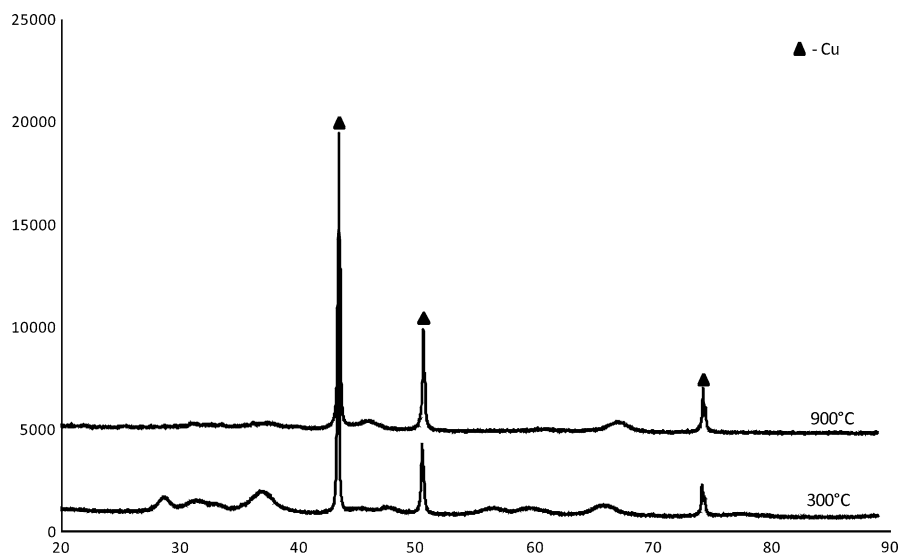


Fig. 7 XRD patterns for 20 % Cu/ZnAl₂O₄–5 % CeO₂ after reduction in 5 % H₂–95 % Ar atmosphere at 300 and 900 °C for 2 h

bimetallic Pd–Cu catalysts being after reduction at 300 and 900 °C. The phase composition studies performed for those systems are presented on Figs. 7 and 8. The XRD analysis of 20 % Cu/ZnAl₂O₄–5 % CeO₂ copper catalyst reduced in H₂ atmosphere are given in Fig. 7. Only ZnAl₂O₄ and metallic copper phases were visible on the diffraction patterns. The increase of the reduction temperature caused

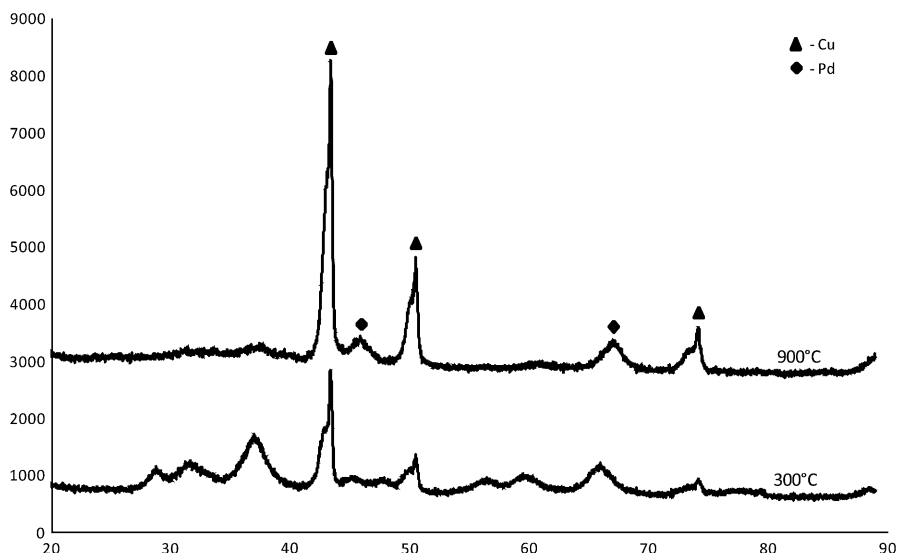


Fig. 8 XRD patterns for 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ after reduction in 5 % H₂–95 % Ar atmosphere at 300 and 900 °C for 2 h

only the growth of the degree of crystallinity of investigated system. We did not observe any alloying process between the individual components of this system. In contrast, the analogous measurements carried out for palladium–copper catalysts 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ (see Fig. 8) confirmed the alloy formation between Pd and Cu and the presence of spinel structure ZnAl₂O₄ phases. The confirmation of the alloy formation between those two components was the shift of the reflections coming from metallic copper and palladium in comparison to the same reflections observed in the case of monometallic copper supported catalysts. The shift and broadening of the observed reflections attributed to the metallic copper confirmed the Pd–Cu alloy formation for the Pd–Cu catalyst after reduction at 300 and 900 °C for 2 h in 5 % H₂–95 % Ar atmosphere.

The morphology of the Pd–Cu/CeO₂ catalysts using SEM–EDS techniques was investigated by Kugai et al. [38]. All studied bimetallic supported catalysts were reduced in H₂ flow at 260 °C and exposed to oxygen-enhanced water–gas shift condition “ex situ” for about 2 h. The SEM–EDS analysis showed that Pd–Cu alloy was dispersed on CeO₂, whose composition was not elucidated. Additionally, the same authors [34] performed EXAFS studies of ceria-supported bimetallic Pd–Cu catalyst, and they confirmed that Cu forms alloy with Pd upon reduction and claimed that Pd helps to keep Cu in reduced state during the reaction.

It is worth noticing that the alloying process that occurs between Pd and Cu was observed at 300 °C, which means that the high activity and selectivity to methanol production of palladium promoted catalysts in the methanol synthesis reaction can be explained by the alloy formation during activation process (reduction at 300 °C) of this system before the activity tests.

PdCu bimetallic catalysts supported on alumina prepared by different synthesis routes were investigated in trichloroethylene (TCE) hydrodechlorination to ethylene by Meshesha et al. [39]. The bimetallic supported catalysts were studied to elucidate the relationship between structure, interaction between active phase component and catalytic properties in the hydrodechlorination of TCE in gas phase. The authors confirmed that the alloy phase formation between Pd and Cu leads to high activity and selectivity of palladium–copper supported catalysts in studied reaction.

The CO hydrogenation to methanol was also studied in this work. The results of activity tests carried out for mono- and bimetallic Pd–Cu supported on spinel structure catalysts promoted by CeO₂ in methanol synthesis expressed as CO conversion and in g CH₃OH kg_{cat.}⁻¹ h⁻¹ are shown in Table 1. Additionally, the selectivities of studied catalysts to methanol production and other organic products are also given in the same table. The activity results clearly showed that methanol and methane were the only organic products formed during the reaction. The highest methanol formation (238 g CH₃OH kg_{cat.}⁻¹ h⁻¹) and carbon monoxide conversion (24.5 %) was observed in the 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ system. Lower values of CO conversion and yield of methanol production were exhibited by copper catalysts promoted by CeO₂. The lowest activity was shown for the monometallic Cu/ZnAl₂O₄ catalyst. The improvement of the catalytic activity observed for CeO₂ and/or Pd modified systems can be explained by the presence of alloy compound PdCu formed during the activation process and by increasing the mobility of lattice oxygen and by the redox properties after CeO₂ addition. The mobile oxygen coming from CeO₂ oxide can oxidize the metallic copper phase and contribute to the formation of Cu⁺ ions on the catalyst surface increasing thereby the number of active centers in the studied reaction. The occurrence of PdCu alloy on the catalyst surface increases the CO adsorption, which leads directly to an increase in carbon monoxide conversion. Based on the results of this work, we could assume that the role of Pd in the promotion effect is the promotion of hydrogen activation due to the hydrogen spillover effect and increase the adsorption of CO during the reaction.

In order to explain the differences between the activity results observed for 20 % Cu/ZnAl₂O₄, 20 % Cu/ZnAl₂O₄–5 % CeO₂ and 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ catalysts, the surface adsorbed species formed during methanol adsorption were investigated by FTIR technique. Fig. 9 displays the IR spectra taken after the exposure

Table 1 The reaction results for methanol synthesis from CO/H₂ over promoted and unpromoted 20 % Cu/ZnAl₂O₄ catalysts

Catalysts	CO conversion (%)	Yield (g CH ₃ OH kg _{cat.} ⁻¹ h ⁻¹)	Selectivity to organic products		
			CO ₂ (%)	CH ₄ (%)	CH ₃ OH (%)
20 % Cu/ZnAl ₂ O ₄	10.9	49	41	3	56
20 % Cu/ZnAl ₂ O ₄ –5 % CeO ₂	14.5	170	8.2	1.8	90
2 % Pd–20 % Cu/ZnAl ₂ O ₄ –5 % CeO ₂	24.5	238	7.8	2.2	90

Reaction conditions weight of catalyst = 2 g, H₂/CO ratio in the feed = 2, temperature = 260 °C, total pressure = 4.8 MPa

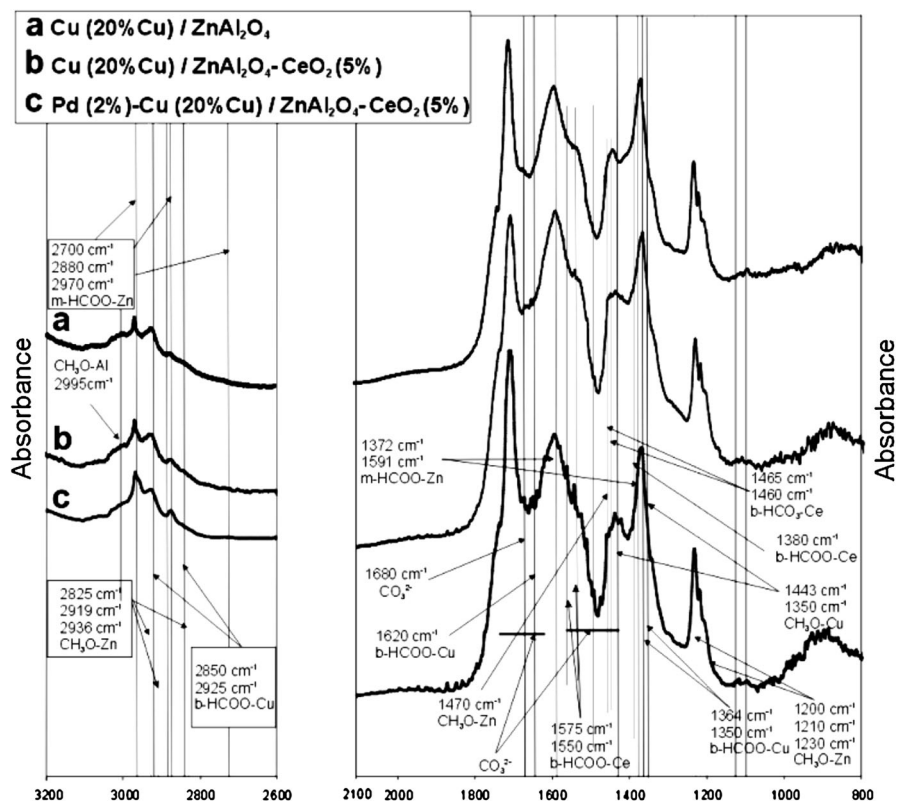


Fig. 9 Infrared spectra of adsorbed species taken after reduction at 300 °C in the 5 % H₂–95 % Ar mixture and exposure of the following catalytic systems: (a) 20 % Cu/ZnAl₂O₄, (b) 20 % Cu/ZnAl₂O₄–5 % CeO₂, and (c) 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ to a 1 vol.% methanol–argon mixture at 120 °C

of investigated catalysts to a 1 vol.% CH₃OH in argon stream at 120 °C under atmospheric pressure. The IR spectra collected for 20 % Cu/ZnAl₂O₄ catalyst (Fig. 9a) showed that copper formate (HCOO–Cu: 2925, 2850, 1620, 1364, and 1350 cm⁻¹), zinc formate (HCOO–Zn: 2970, 2880, 2700, 1591, 1372, and 1365 cm⁻¹), carbonate (CO₃²⁻: 1680, 1620, 1570–1440, and 1220 cm⁻¹), zinc methoxide (CH₃O–Zn: 2936, 2919, 2825, 1470, 1230–1200 and 1060 cm⁻¹), copper methoxide (CH₃O–Cu: 1,443 and 1,350 cm⁻¹), and aluminum methoxide (CH₃O–Al: 2995, 1020–1100 cm⁻¹) species were adsorbed on its surface [22, 23].

Analogous measurements were performed for promoted systems. The FTIR results confirmed the presence of the same adsorbed surface species after exposure of 1 vol.% CH₃OH in argon mixture (see Fig. 9b and c). The observed difference in the FTIR spectrum in the case of promoted systems was the appearance of additional bands attributed to following species: 1,380 cm⁻¹: b-HCO₃–Ce, 1,460 cm⁻¹ and 1,465 cm⁻¹: b-HCOO–Ce and 1,550, 1,575 cm⁻¹: b-HCOO–Ce. The occurrence of these surface species on the catalyst surface after methanol exposure confirms the promotion effect of CeO₂ on CO hydrogenation towards methanol formation. These adsorption centers are involved in methanol synthesis reaction and contribute to

increase the catalytic activity of copper promoted catalysts. It is worth to notice, that palladium promoted systems exhibited also the more intensive bands recorded for adsorbed species over copper species after methanol exposure in comparison to 20 % Cu/ZnAl₂O₄ catalyst. The higher intensity of the adsorption bands can be explained by the fact that palladium addition into copper catalyst facilitate the reduction of copper species and change the electronic properties of metallic copper. Additionally, it leads to active center formation on the catalyst surface, on which the CO or/and CO₂ are reduced to main product methanol. Additionally, it is well known in literature data that the formate species formed on the copper or support surface plays pivotal role in the methanol synthesis reaction. The formate species formed on the support surface or on the perimeter between metal (copper) or alloy (PdCu) and support would play important role in the methanol synthesis as those formed on supported copper catalysts in our case.

TPD-NH₃ is a conventional method for characterizing acidity in catalytic systems. The acidity of all investigated catalysts was evaluated by the TPD-NH₃ method and ammonia desorption profiles for copper and palladium doped copper supported catalysts are shown in Figs. 10 and 11.

The total amount of desorbed ammonia expressed as $\mu\text{mol NH}_3 \text{ g}_{\text{cat}}^{-1}$ and distribution of acid centers for all studied systems in the temperature range 100–600 °C are given in Table 2. It can be easily observed from Figs. 10 and 11, and Table 2 that all catalytic systems exhibited three different acid centers.

Weak, medium and strong acid sites are visible on TPD curves. The mutual relationship between three various kind of acidic centers is given in Table 2. The obtained results reveal that the total surface acidity of prepared systems increases with increasing of Ce content in the catalytic systems. The same trend was observed after palladium promotion of copper supported catalyst. The difference was only observed in the case of 2 % Pd–20 % Cu/ZnAl₂O₄ catalyst for which a slight decrease of total acidity was observed compared with the monometallic copper catalyst. The highest total amount of desorbed NH₃ exhibited 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ catalyst ($228 \text{ NH}_3 \mu\text{mol g}_{\text{cat}}^{-1}$).

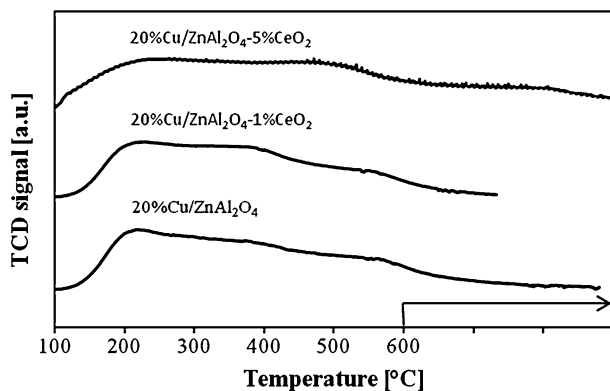


Fig. 10 TPD-NH₃ profiles for 20 % Cu/ZnAl₂O₄, 20 % Cu/ZnAl₂O₄–1 % CeO₂ and 20 % Cu/ZnAl₂O₄–5 % CeO₂ catalysts calcined in air atmosphere for 4 h at 400 °C

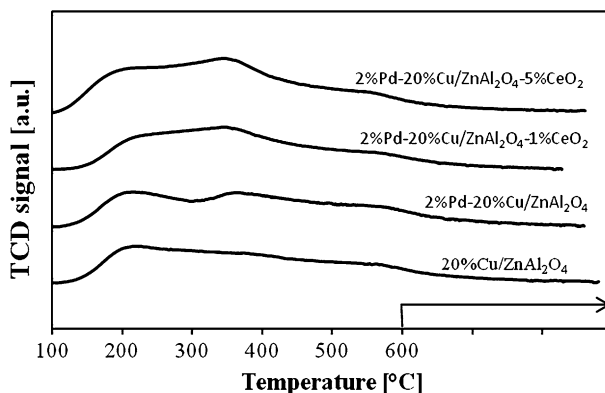


Fig. 11 TPD-NH₃ profiles for 20 % Cu/ZnAl₂O₄, 2 % Pd–20 % Cu/ZnAl₂O₄, 2 % Pd–20 % Cu/ZnAl₂O₄–1 % CeO₂ and 2 % Pd–20 % Cu/ZnAl₂O₄–5 % CeO₂ catalysts calcined in air atmosphere for 4 h at 400 °C

Table 2 The influence of Pd and CeO₂ on distribution of acid centers for copper catalysts calcined at 400 °C in air atmosphere

Catalysts	Weak centers ($\mu\text{mol g}_{\text{cat}}^{-1}$) 100–300 °C	Medium centers ($\mu\text{mol g}_{\text{cat}}^{-1}$) 300–450 °C	Strong centers ($\mu\text{mol g}_{\text{cat}}^{-1}$) 450–600 °C	Total amount of desorbed NH ₃ ($\mu\text{mol g}_{\text{cat}}^{-1}$)
20 % Cu/ZnAl ₂ O ₄	45	57	57	159
20 % Cu/ZnAl ₂ O ₄ –1 % CeO ₂	71	61	42	174
20 % Cu/ZnAl ₂ O ₄ –5 % CeO ₂	49	53	93	195
2 % Pd–20 % Cu/ZnAl ₂ O ₄	63	36	53	152
2 % Pd–20 % Cu/ZnAl ₂ O ₄ –1 % CeO ₂	60	72	50	181
2 % Pd–20 % Cu/ZnAl ₂ O ₄ –5 % CeO ₂	44	132	52	228

It is worth noticing that the palladium–copper catalysts showed also the lowest content of weak acid centers (see Table 2). In addition, a correlation can be found between the activity and acidity of all catalysts. The highest activity and selectivity in methanol synthesis reaction was observed for catalyst exhibited the highest total acidity. The 20 % Cu/ZnAl₂O₄, catalyst which showed the lowest value of total acidity, was the least active and selective to methanol formation. Additionally, the acidity result explain the differences in the activity observed for all systems in methanol synthesis.

Conclusion

In this study, we prepared unpromoted and promoted by CeO₂ monometallic copper and bimetallic Pd–Cu supported catalysts by a wet aqueous impregnation method and tested in CO hydrogenation reaction. The physicochemical and catalytic

properties of prepared catalytic systems were studied using various techniques TPR, XRD, TPD-NH₃ and FTIR. The following conclusions can be drawn from the present investigations dealing with the mono- and bimetallic catalysts. The catalytic activity of mono and bimetallic catalysts depends on the surface acidity and its chemical composition.

Activity results obtained for the investigated catalysts in the methanol synthesis reaction confirmed the promotion effect of Pd and CeO₂ on catalytic activity and selectivity. The improvement in activity observed for copper catalysts after CeO₂ addition is associated with the increasing of oxygen mobility on CeO₂ doped surface catalysts which can oxidize the metallic Cu and form Cu⁺ ions on the catalyst surface and by the acidity of promoted catalyst.

Another factor that plays an important role during the reaction is the presence of oxygen vacancies, which can adsorb the CO or CO₂ species on the catalyst surface, which then may migrate to the adjacent H–Cu site to be reduced into methanol.

In the case of a copper–palladium doped catalyst, the increased activity and selectivity is explained by the Pd–Cu alloy formation. The resulting alloy changes the electronic properties of metallic copper on which the CO or/and CO₂ are reduced to main product methanol. In addition, Pd promotes hydrogen activation due to the hydrogen spillover effect and increases the adsorption of CO during the reaction.

Acknowledgments Partially financed from Grant number 0680/B/H03/2011/40 is gratefully acknowledged.

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