

Structure-Activity Relationship of Gold Catalysts on Alumina Supported Cu-Ce Oxides for CO and Volatile Organic Compound Oxidation

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Abstract—The catalytic oxidation of CO and volatile organic compounds (VOCs) is considered as one of the most efficient ways to reduce harmful emissions from various chemical industries. The effectiveness of gold-based catalysts for many reactions of environmental significance was proven during the past three decades. The aim of this work was to combine the favorable features of Au and Cu-Ce mixed oxides in the design of new catalytic materials of improved efficiency and economic viability for removal of air pollutants in waste gases from formaldehyde production. Supported oxides of copper and cerium with Cu: Ce molar ratio 2:1 and 1:5 were prepared by wet impregnation of γ -alumina. Gold (2 wt.%) catalysts were synthesized by a deposition-precipitation method. Catalysts characterization was carried out by texture measurements, powder X-ray diffraction, temperature programmed reduction and electron paramagnetic resonance spectroscopy. The catalytic activity in the oxidation of CO, CH₃OH and (CH₃)₂O was measured using continuous flow equipment with fixed bed reactor. Both Cu-Ce/alumina samples demonstrated similar catalytic behavior. The addition of gold caused significant enhancement of CO and methanol oxidation activity (100 % degree of CO and CH₃OH conversion at about 60 and 140 °C, respectively). The composition of Cu-Ce mixed oxides affected the performance of gold-based samples considerably. Gold catalyst on Cu-Ce/ γ -Al₂O₃ 1:5 exhibited higher activity for CO and CH₃OH oxidation in comparison with Au on Cu-Ce/ γ -Al₂O₃ 2:1. The better performance of Au/Cu-Ce 1:5 was related to the availability of highly dispersed gold particles and copper oxide clusters in close contact with ceria.

Keywords—CO and VOCs oxidation, copper oxide, ceria, gold catalysts.

I. INTRODUCTION

NOWADAYS, reducing air pollution is a key issue. Growing emissions of CO and VOCs and urgent need to remedy the present environmental conditions stimulate increased research interest in the development of novel catalytic materials with improved efficiency in the removal of these air pollutants [1]-[3]. Generally, two types catalysts are

used for total VOC oxidation: supported noble metals (Pt, Pd, Rh) and transition metal oxide-based materials. Noble metals demonstrate higher activity and stability and they could be regenerated, but their high cost could be considered as disadvantage [4]. Gold, long regarded as a poorly active catalyst, gains significant attention in recent years due to the high activity in numerous environmental catalytic processes of finely dispersed gold nanoparticles [5], [6]. The activity of gold-based catalysts depends not only on the size of the supported gold particles but also on their interaction with the support. Due to their lower price, transition metal oxide catalysts are intensively studied as a suitable alternative for replacing noble metal catalysts [7], [8], although they are less active than noble metals at low temperatures. Among transition metal oxides, copper-based catalysts have shown a very good performance in CO and VOCs oxidation. However, many studies revealed that mixed oxides, in particular, CuO-CeO₂ exhibited higher CO and VOCs oxidation activity than the single metal oxides [9]-[13]. The suitability of CeO₂ for oxidation catalysis is already well documented in the literature [14]. It is related to its oxygen storage-release capacity and the ability to change the oxidation state of cerium between +3 and +4 depending on the reaction conditions easily. Additionally, ceria is able to maintain a high dispersion of supported noble or transition metals.

In a recent study, we investigated the modification of alumina supported mixed Cu-Mn oxides by cerium and the effect on the activity and selectivity of the catalysts in total oxidation of CO, methanol, and dimethyl ether (DME) [15]. The catalytic measurements of Cu-Mn-Ce/ γ -Al₂O₃ samples with molar ratio Cu/(Mn+Ce) 2:1 and 1:5, in which Mn is replaced by Ce in the whole concentration range from 0 to 100% demonstrated a clear tendency of increased CO oxidation activity by increasing the cerium content. The samples composed of alumina supported mixed oxides of Cu and Ce exhibited more than twice higher degree of CO conversion than that of alumina supported Cu-Mn mixed oxides, indicating that the synergism between copper and cerium is more advantageous than in the case of Cu and Mn.

The aim of present study was to combine the favorable features of supported gold nanoparticles and good redox properties of Cu-Ce mixed oxides in the design of new catalytic materials of improved efficiency and economic viability for an elimination of air pollutants in waste gases from formaldehyde production.

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II. EXPERIMENTAL

A. Catalysts Preparation

The catalyst samples were prepared by wet impregnation method. Commercial γ -alumina (fraction 0.6-1.0 mm) was preliminarily calcined within 2h at 450 °C. The impregnation with a mixed solution of copper and cerium nitrates with defined composition (Cu-Ce molar ratio 2:1 and 1:5) was carried out at 80 °C for 12h. The resulting materials were dried at 120 °C for 10h and calcined at 450 °C for 4h. The total amount of active phase was 20 wt.%. Deposition-precipitation method was used for modification of Cu-Ce/ γ -Al₂O₃ with 2 wt.% Au. The mixed metal oxide materials were suspended in water, and the deposition was carried out by simultaneous addition of an aqueous solution of H₂AuCl₄ and Na₂CO₃ at 60 °C and pH 7.0. The next steps included aging at 60 °C for 1h, filtering and washing until complete removal of Cl⁻ ions. Then, the solids were dried under vacuum at 80 °C and calcined in air at 400 °C for 2h.

B. Catalyst Characterization

• Texture Measurements

The texture characteristics were determined in a Quantachrome Instruments NOVA 1200e (USA) specific surface area and pore analyser by low-temperature (-195 °C) nitrogen adsorption.

• Powder X-ray Diffraction (XRD).

The phase composition was characterised by X-ray powder diffraction (XRD) using a PANalytical Empyrean equipped with a multichannel detector (Pixel 3D) using (Cu K α 45 kV-40 mA) radiation in the 20–115° 2 θ range, with a scan step of 0.01° for 20 s.

• Electron Paramagnetic Resonance Spectroscopy (EPR).

Electron paramagnetic resonance (EPR) spectra were recorded at JEOL JES-FA 100 EPR spectrometer operating in X-band with standard TE011 cylindrical resonator under the following conditions: modulation frequency 100 kHz, microwave power 1 mW, modulation amplitude 0.2 mT, sweep 500 mT, time constant 0.3 s and sweeping time 4 min. The samples were placed in quartz cuvettes and were fixed at the cavity centre.

• Temperature Programmed Reduction (TPR)

TPR measurements were conducted in a flow system under the following conditions: gas mixture hydrogen-argon (10 % H₂), temperature rises 15 °C/min, flow rate 24 ml/min and a sample amount of 0.05 g.

C. Catalytic Activity Measurements

The catalytic measurements were carried out on continuous flow equipment with a four-channel isothermal stainless steel reactor, containing 1.0 ml catalyst at atmospheric pressure and space velocity (GHSV) of 10000 h⁻¹. The flow of ambient air (40 – 50 % humidity) and CO (final concentration 1.5 %) was fed using mass flow controllers (GFC Mass Controller AABORG, Germany). Liquid methanol was dosed by Ismatec

micro-dosage pump, and additional air was added before reaching the preheater to final concentration of methanol 1.5%. DME (final concentration 0.8 - 1.0 %) was obtained by dehydration of methanol on γ -Al₂O₃ in tubular isothermal reactor. Gas mixtures at both input and output of the reactor were analysed with a gas chromatograph HP 5890 Series II, equipped with FID and TCD detectors, column Porapak Q (for CH₃OH, CO₂ and DME) and column MS-5A (for CO, O₂ and N₂). The catalysts' activity was evaluated on the basis of the degree of conversion of all compounds, in percentages.

III. RESULTS

• Texture Measurements

Some textural characteristics of the samples are listed in Table I. The decrease of the surface area, total pore volume (V_t), and average pore diameter (D_{aver}) was observed after impregnation of γ -alumina with mixed Cu-Ce solutions. This effect should be related to pore blocking due to deposition of copper and cerium oxide phases into the pores. Slight increase of specific surface area was registered after deposition of Au, in agreement with the observation of Gonzalez Castaño et al. [16]. The analysis of the adsorption-desorption isotherm and the corresponding pore size distribution indicated the presence of very well defined mesopores with narrow pore size distribution. These textural properties remained almost the same after addition of Au.

TABLE I
TEXTURE CHARACTERISTICS OF THE SAMPLES

Composition	S _{BET} m ² .g ⁻¹	V _t cm ³ .g ⁻¹	D _{aver} . nm
Al ₂ O ₃	219	0.40	7.4
Cu-Ce 2:1	156	0.29	7.3
Cu-Ce 1:5	165	0.29	7.0
Au/Cu-Ce 2:1	159	0.28	7.1
Au/Cu-Ce 1:5	176	0.28	6.5

• Powder X-Ray Diffraction (XRD).

The results of powder X-ray analysis of samples with molar ratio Cu-Ce 2:1 with and without gold are presented in Fig. 1. The reflections of CuO at 2 θ = 35.6, 38.8, 48.6 and 61.8 (marked with *) are clearly observed in the X-ray diffractogram of CuO/Al₂O₃ sample, reported for comparative purpose. The position of the peaks of CeO₂/Al₂O₃ at 2 θ = 28.6, 33.2, 47.7 and 56.6 (marked with o) corresponds to the face-centered cubic fluorite structure of ceria. The intensity of reflections of CuO and CeO₂ decreases significantly in the diffractogram of Cu-Ce 2:1 sample, indicating improved dispersion of both separate phases. This phenomenon could be attributed to the formation of small CuO crystallites in agreement with the well-known property of ceria to favour high dispersion of noble and transition metal particles. Additionally, diffraction peaks related to the presence of crystalline Au were not registered. The lack of such peaks is evidence for an availability of very small gold particles.

In Fig. 2, the XRD patterns of the catalysts with Cu/Ce molar ratio 1:5 are compared. The reflections are typical for

CeO₂ dominate in all diffractograms, but their intensity slightly decreases after deposition of gold. Reflections of CuO and metallic gold were not observed, evidencing high dispersion of these components.

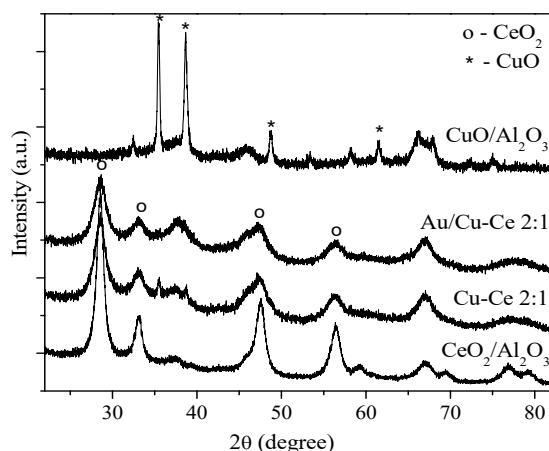


Fig. 1 XRD patterns of alumina supported Cu-Ce and Au/Cu-Ce catalysts with molar ratio 2:1

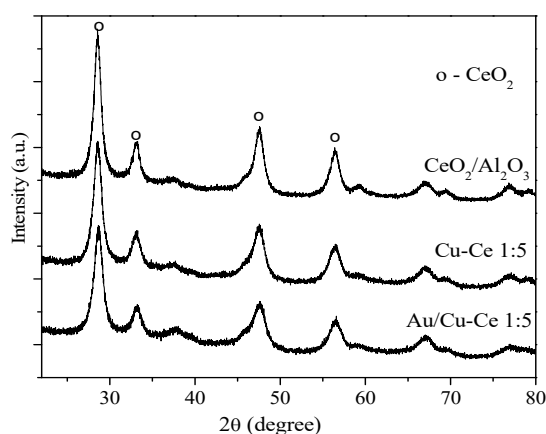


Fig. 2 XRD patterns of alumina supported Cu-Ce and Au/Cu-Ce catalysts with molar ratio 1:5

• Electron Paramagnetic Resonance Spectroscopy (EPR)

An EPR study was performed in order to characterize the oxidation state of copper and cerium in alumina supported Cu-Ce mixed oxides with Cu/Ce molar ratio of 2:1 and 1:5 and corresponding Au-containing catalysts. The EPR spectra of all studied samples collected at RT are shown in Fig. 3. The spectra of Cu-Ce/Al₂O₃ and Au/Cu-Ce/Al₂O₃ catalysts with spectral parameters $g_{\parallel} = 2.3286$ and $g_{\perp} = 2.0954$ are interpreted as arising from the distorted octahedrally coordinated Cu²⁺ ions. The hyperfine splitting indicates a presence of isolated Cu²⁺ ions ($I=3/2$) in all samples. EPR signal due to cerium ions was not recorded, evidencing that cerium exists as Ce⁴⁺ in agreement with XRD observations. The deposition of Au does not change the shape of the EPR spectra but causes differences in the intensity of the spectra.

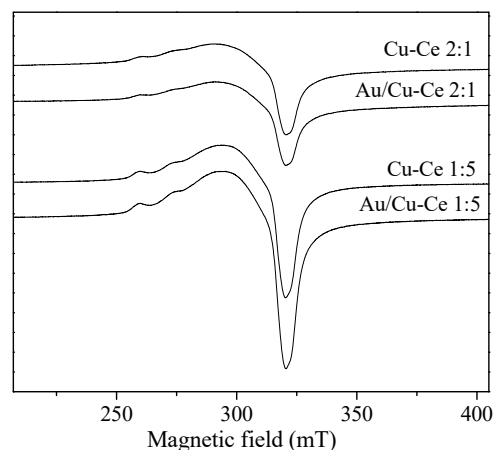


Fig. 3 EPR spectra of the studied samples

The EPR signal intensity is closely related to the number of paramagnetic centres. Quantitative EPR is very difficult to approach, but the EPR spectroscopy is a relative method in which determination of the absolute concentration of paramagnetic ions is not necessary. In Fig. 4, the changes in the EPR signal intensity of Cu-Ce/Al₂O₃ catalysts with different Cu-Ce molar ratio and respective Au supported samples are demonstrated. It can be seen that deposition of Au influenced the concentration of paramagnetic Cu²⁺ ions. In the case of Cu-Ce sample with molar ratio 2:1, the EPR signal intensity decreased slightly. This finding could be associated with the formation of diamagnetic copper ions (Cu⁺) or copper clusters with diamagnetic nature.

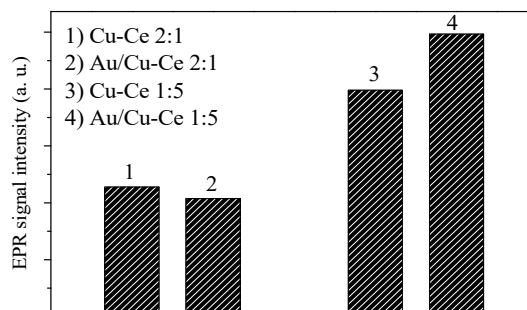


Fig. 4 Comparison of EPR signal intensity in the spectra of the studied samples

Contrarily, the signal intensity increased after Au deposition on Cu-Ce sample with molar ratio 1:5, evidencing abundance of active Cu²⁺ centers. Analysing the results of this EPR study, it can be concluded that the best dispersion of CuO was detected over Au/Cu-Ce 1:5 catalyst. The highest concentration of paramagnetic Cu²⁺ ions correlates well with the best CO oxidation activity of Au/Cu-Ce (1:5) (see below discussion of catalytic activity data).

• Temperature Programmed Reduction (TPR)

The reduction behaviour of the samples was studied by TPR with hydrogen. The analysis of TPR profiles of alumina

supported Cu-Ce mixed oxides indicated a strong dependence of the reducibility on the composition of the samples (Fig. 5). A narrow peak with $T_{\max} = 228^\circ\text{C}$ was registered in the TPR profile of Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ with molar ratio Cu-Ce 2:1. In agreement with the literature data, this single step reduction process should be ascribed to the reduction of CuO to Cu⁰. As concerns reduction of ceria, it is known from the literature that its H₂-TRP profile consists of two major peaks, one at lower temperature (around 500 °C), related to the reduction of surface oxygen, and one at higher temperature (at about 800 °C), ascribed to the removal of bulk oxygen from the ceria structure [17]. The promotional effect of noble and some transition metals (Cu, Ni) on ceria surface reduction has been reported in many studies and it is related to a shift of first reduction peak to much lower temperature. The shoulder at higher temperature side in the profile of Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ (2:1) could be assigned to the reduction of oxygen in ceria surface layers. The addition of gold affected additionally mobility of ceria surface oxygen. A weak peak at 117 °C was an evidence for this influence.

The peaks intensity in the profile of Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ with molar ratio Cu-Ce 1:5 was significantly lower because of the different sample composition. A two-step reduction profile with maxima at 218 and 259 °C was observed. The first peak was attributed to the reduction of highly dispersed CuO particles, in agreement with EPR results. This peak was shifted to a lower temperature in comparison with the peak in the profile of the sample with molar ratio Cu-Ce 2:1, which may be due to the stronger promotional effect of CeO₂. The second peak included the reduction of some larger CuO particles and surface oxygen of ceria. A single peak at 228 °C was observed in the profile of Au/Cu-Ce (1:5) due to the enhanced surface ceria reduction in the presence of gold.

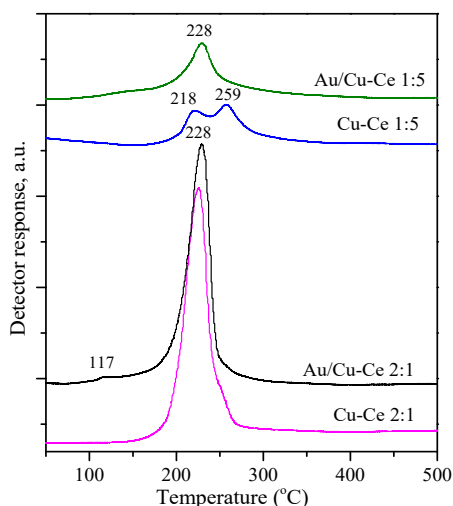


Fig. 5 TPR profiles of Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ with molar ratio Cu-Ce 2:1 and 1:5 and respective gold-containing samples

• Catalytic Activity Measurements

The catalytic activity in the reaction of CO, CH₃OH and DME oxidation over Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ samples with molar ratio

Cu-Ce 2:1 and 1:5 and corresponding gold-promoted catalysts, expressed as temperature dependence of the conversion degree, is presented in Figs. 6-8. The comparison of results about catalysts behaviour in CO oxidation (Fig. 6) showed that both Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ samples exhibited the same activity at the whole temperature range and total oxidation of CO was attained at 180 °C. Promotion by gold strongly affected catalysts behaviour. Very high degree of CO conversion was observed at room temperature: 89% and 70% over Au/Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ with ratio Cu-Ce 1:5 and 2:1, respectively. It should be pointed out that, at this temperature, the samples without gold were not able to oxidize CO. An increase of the activity of gold-containing catalysts was registered at increased reaction temperature, and complete CO conversion was reached at 80 °C. The remarkable improvement of the catalytic performance could be related to the ability of highly dispersed gold particles to adsorb and activate CO in combination with good redox properties of Cu-Ce mixed oxides.

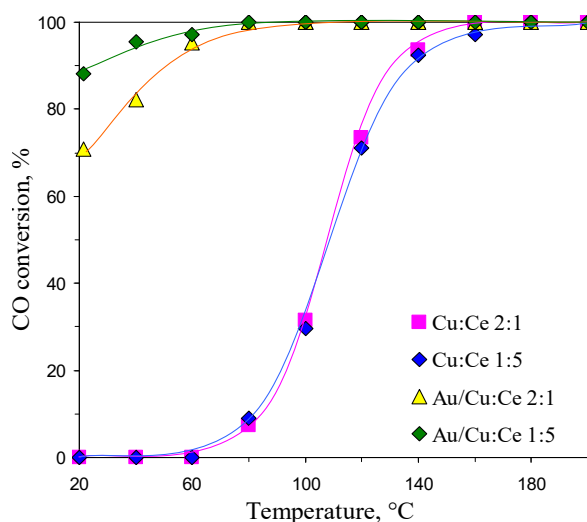


Fig. 6 Temperature dependence of CO conversion degree over the studied samples

In contrast to the results in CO oxidation, catalytic measurements of CH₃OH oxidation over Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ demonstrated the role of the composition on the activity of these samples (Fig. 7). The conversion curve of the sample with higher CuO content, i.e. those with Cu-Ce ratio 2:1, was shifted toward lower temperature. The almost complete degree of CH₃OH conversion, 95%, was achieved at 200 °C, while over the sample with Cu-Ce ratio 1:5 about 60 % of MeOH was oxidized. The addition of gold caused significant enhancement of the activity, and the light-off curves were shifted by more than 100 degrees to lower temperature. An opposite trend in the activity of gold-based catalysts in comparison with non-promoted samples was observed. The gold deposition played a more favorable role in the case of ceria-rich sample. Au/Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$ 1:5 exhibited higher activity in the low-temperature range. Over this sample, 98%

conversion was attained at 120 °C, which is almost twice higher than that over Au/Cu-Ce/ γ -Al₂O₃ 2:1. The explanation of this behavior could be based on the assumption for the role of Mars - Van Krevelen mechanism in VOCs total oxidation. According to this mechanism, surface oxygen from the oxide lattice participates in the oxidation of VOC molecule [3]. Considering the important property of ceria in providing active oxygen species, it is reasonable to assume the availability of higher amount mobile oxygen in the case of ceria-rich samples. The beneficial effect of gold on enhanced oxygen mobility should be again underlined, in agreement with TPR results.

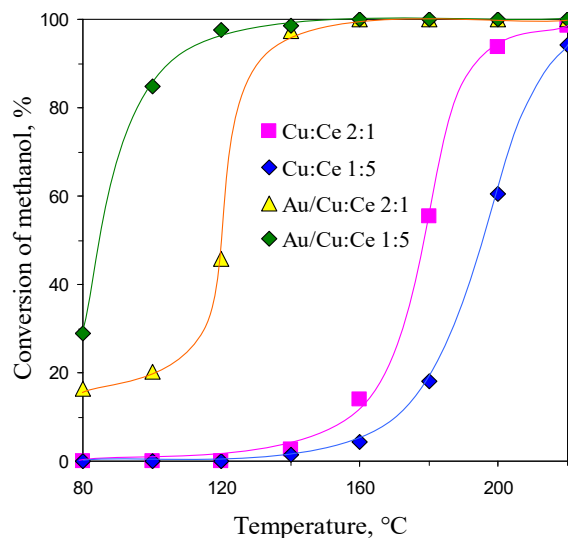


Fig. 7 Temperature dependence of CH₃OH conversion degree over the studied samples

The conversion of DME as a function of temperature is presented in Fig. 8. The composition of Cu-Ce/ γ -Al₂O₃ affected catalytic behavior; however, the activity order is opposite to the one found in the case of methanol oxidation. Complete DME oxidation over ceria-rich sample took place at 340 °C, while the temperature required for complete DME conversion over CuO-rich sample was shifted by 40 °C to a higher temperature. In contrast to our expectations, modification by gold has completely different effect on the behavior of gold-based catalysts. Higher activity was observed in the case of Au/Cu-Ce/ γ -Al₂O₃ 2:1, while deposition of gold has unfavorable effect on the activity of ceria-rich sample. This result implies that the catalytic sites, which are responsible for the activity in CO and methanol oxidation, are not operative under conditions of DME oxidation. On the basis of isotopic measurements and Density Functional Theory calculations, Ishikawa et al. have described the mechanism of DME oxidation on supported Pt clusters [18]. The results have indicated that kinetically relevant step was C-H bond activation in chemisorbed DME, accompanied with formation of methoxy methyl and hydroxyl surface intermediates. This step occurs on site pairs consisting of chemisorbed oxygen atoms and surface vacancy sites in close vicinity. The

calculation of DME turnover rates has revealed that the activity depends on the concentration of reactants (DME and O₂) and products (CO₂ and H₂O), as well as on platinum cluster size because all these factors control the density of active sites required to abstract H atoms from adsorbed DME molecules. Additionally, the authors have found that, over acidic supports such as γ -alumina, DME oxidation follows bifunctional pathways involving interaction between DME and H₂O produced in oxidation step and formation of CH₃OH, which reacts with O₂ much faster than DME [19]. All these results allow explaining improved DME oxidation over gold-promoted Cu-Ce/ γ -Al₂O₃ with ratio 2:1. However, at this stage, we do not have any plausible explanation for the behavior of Au/Cu-Ce/ γ -Al₂O₃ with ratio 1:5.

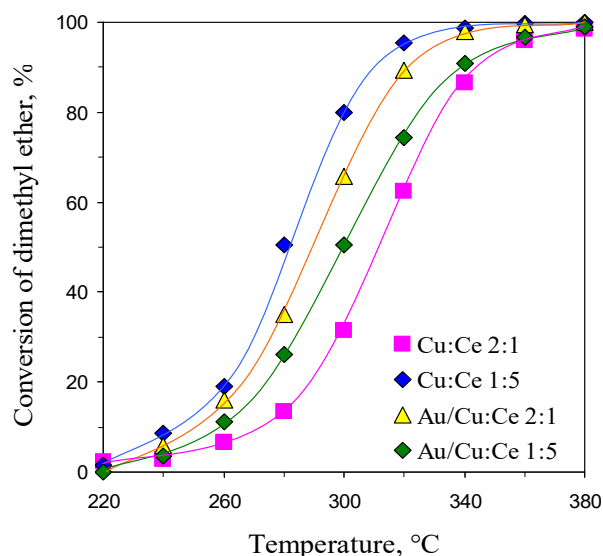


Fig. 8 Temperature dependence of DME conversion degree over the studied samples

IV. CONCLUSION

The effect of alumina supported mixed Cu-Ce oxide composition and promotion by gold on catalytic oxidation of CO, CH₃OH and DME was investigated. The results indicated that combination of nanosized gold particles and Cu-Ce mixed oxides with good redox properties, dispersed on high surface area γ -alumina is an attractive approach for the preparation of cost-effective and active catalytic materials for abatement of air pollutants in waste gases from formaldehyde production. Future efforts will be focused on clarifying the effect of gold deposition on catalytic performance for DME oxidation.

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