



# Preparation and Characterization of Au Supported $MO_x-Al_2O_3$ (M = Mn, Cu) Powders for Low-Temperature CO Oxidation

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## Abstract

$MO_x-Al_2O_3$  (M = Mn, Cu) powders were synthesized by the spray pyrolysis process and then used as a support for Au/(Mn,Cu)  $O_x-Al_2O_3$  catalysts preparation via the deposition-precipitation method. Gold catalysts on oxide supports were tested for oxidation of CO. The samples were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and via determination of specific surface area by the BET method. The SEM results showed that all catalysts have a small-dimension circular shape of particles. Catalysts obtained with the spray-pyrolysis method were found to have great specific surface areas. Gold catalyst containing copper oxide on alumina is shown to be more active than manganese oxide on the same support.

**Keywords:** Spray pyrolysis, Catalyst,  $MO_x-Al_2O_3$ , Au, Powder

## WYTWARZANIE I CHARAKTERYSTYKA PROSZKÓW $MO_x-Al_2O_3$ (M = Mn, Cu) JAKO NOŚNIKA Au DLA NISKOTEMPERATUROWEGO UTLENIANIA CO

Wykorzystując proces pirolizy rozpyłowej zsyntezowano proszki  $MO_x-Al_2O_3$  (M = Mn, Cu), a następnie wykorzystano jako nośnik do otrzymania katalizatora Au/(Mn,Cu) $O_x-Al_2O_3$  metodą strącania-osadzania. Katalizatory ze złotem osadzonym na nośniku tlenkowym badano w przypadku utleniania CO. Próbki charakteryzowano za pomocą dyfrakcji promieniowania X (XRD), skaningowej mikroskopii elektronowej (SEM) wraz z rentgenowską spektroskopią z dyspersją energii (EDS) i drogą oznaczenia powierzchni właściwej metodą BET. Wyniki SEM ujawniły, że wszystkie katalizatory mają okrągły kształt drobnych cząstek. Katalizatory otrzymane metodą pirolizy rozpyłowej miały bardzo dużą powierzchnię właściwą. Katalizator ze złotem osadzonym na podłożu z tlenków miedzi i glinu okazał się bardziej aktywny w porównaniu do katalizatora wykorzystującego tlenek magnezu jako dodatek do tlenku glinu.

**Słowa kluczowe:** piroliza rozpyłowa, katalizator,  $MO_x-Al_2O_3$ , Au, proszek

## 1. Introduction

Supported metal oxide catalysts have a wide range of application, especially in industrial reactions, such as CO oxidation or  $H_2$  purification. The high cost of noble metals has increased the interest in their substitution. A good catalyst operating in lower temperatures than standard systems has been searched. The work on supported catalysts with gold nanoparticles by Haruta *et al.* [1], brings about a rise of a gold application in different branches of industry, especially in the energy industry. Theoretical and experimental studies have been conducted to study unique properties of gold but various properties of supported gold are still unclear. Gold as a catalysts in a highly dispersed form is applied in chemical reactions, for example in the preferential oxidation of CO (PROX) [2, 3] and the selective CO hydrogenation [4]. Gold supported catalysts are used in the following fields of application: fuel cell systems (PROX and WGS reactions), speciality bulk chemical synthesis (production of vinyl acetate monomer or olefins), pollution and emission control systems (exhaust gas cleaning, water purification, respirators for protection from CO poisoning, mercury removal).

Manganese oxide, depending on the preparation conditions, has a different composition: MnO,  $MnO_2$ ,  $Mn_2O_3$ , and  $Mn_3O_4$ . The properties and potential applications depend on crystal structure, morphology, surface area and particles size. Gold nanoparticles supported on various manganese oxides have been intensively investigated. All oxides have been prepared by the deposition-precipitation with urea method and ordered according to the decrease catalytic reactivity in the low-temperature oxidation of CO. The catalytic reactivity followed the range of  $Au/Mn_2O_3 > Au/MnO_2 > Au/Mn_3O_4$  [5]. Manganese oxide has a practical application as catalysts in oxidation CO [2], methane [6, 7] and hydrocarbons [8] and as the materials for electrodes [5].

The catalysts containing copper oxide are well known to be active in different catalytic reactions, *i.e.*, oxidation of carbon monoxide [3], hydrocarbons [8, 9] and ammonia [10]. A number of gold catalysts, consisting of various transition metal (Co, Mn, Cu, Fe, Ce) oxides, have been studied for the total oxidation of methane, ethane and propane. The catalytic activity of each oxide was confronted with their performance for oxidation of CO at ambient temperature. The presence of

gold in the catalysts enhances the reducibility of the support, increasing their reactivity. The authors have not observed any correlation between the activity for alkane combustion and CO oxidation. It has confirmed different active sites for these reactions [8].

The noble metal catalysts are relatively expensive and more sensitive to poisons in comparison to base metal catalysts or gold supported catalysts. A commercial hopcalite, which is a mixture of CuO and MnO<sub>2</sub>, according to McCabe and Michell, exhibits comparable to Pt/Al<sub>2</sub>O<sub>3</sub> activity in ethanol and acetaldehyde combustion [11]. Hopcalite is the commercial catalysts used in the personnel protection devices to oxidize a range of environmentally harmful gases. Mixed oxides of manganese and copper with different wt% of copper were found to be catalysts in combustion of volatile organic compounds, such as ethyl acetate, propane and ethanol. Pure oxides like Mn<sub>2</sub>O<sub>3</sub> and CuO are less active than the mixed oxides (Mn<sub>x</sub>Cu<sub>y</sub>). The catalytic system with a small amount of copper (Mn9Cu1), which prevents a big manganese oxide crystallite structure from arising, gives the best performance in ethanol combustion to CO<sub>2</sub>. The increase of copper content decreases the CO<sub>2</sub> yield [12]. Kandoi *et al.* [13] have shown that at low-temperatures catalysts containing Cu and Au should be more selective PROX catalysts than Pt.

The nanosized manganese and copper oxides particles are synthesized by various methods, *e.g.*, aqueous solution-based methods, such as the hydrothermal synthesis [14–16], electrospinning technique [17], co-precipitation [16, 18], sol-gel [19, 20] and modified spray pyrolysis process [21, 22]. The aerosol process has been used to synthesize a wide variety of materials in a powder form, *e.g.*, metals, metal oxides, nanophase materials [23, 24]. The spray pyrolysis is an effective process for the rapid synthesis (short residence time) of homogeneous materials with a controlled shape and usually aggregation-free. The morphological characteristics of materials were strongly affected by the preparation condition, such as precursor type or solution concentration.

In this work, powders were prepared by the spray pyrolysis process without milling. We investigated the influence of the method of preparation on the morphology and crystal phase of the formed powders and evaluated the catalytic performance of MO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> (M = Mn, Cu) for the CO oxidation reaction.

## 2. Experimental

### 2.1. Materials

The starting materials used in the work were aluminum nitrate hydrated (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), and manganese nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O).

### 2.2. Catalysts preparation

The supports were obtained by the spray pyrolysis method. The system consists of a droplet generator – ultrasonic nebulizer (2 MHz), a quartz reactor and an electrostatic precipitator. A 2-MHz ultrasonic nebulizer generated a large amount of droplets, which were carried into the quartz tube

situated in the high-temperature furnace by a carrier gas (Fig. 1). The oxides precursor used in this study was a mixture of aluminum and copper nitrates and aluminum and manganese nitrates with the proper mole ratio. The concentration for each nitrate solution was fixed at 0.12 M. The flow rate of the air used as a carrier gas was 170 dm<sup>3</sup>/h. Temperature of the furnace was 700°C.

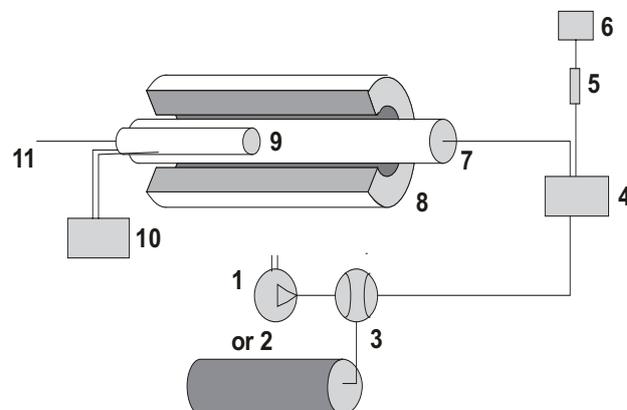


Fig. 1. Schematic diagram of the spray pyrolysis system: (1) air, (2) gas, (3) flow meter, (4) ultrasonic nebulizer, (5) peristaltic pump, (6) salt solution, (7) quartz tube, (8) furnace, (9) electro filter, (10) High voltage power pack, and (11) outlet.

Gold was supported on the mixed oxides by the deposition–precipitation method with the solution of HAuCl<sub>4</sub> (0,088 M). The suspension (oxides and 100 ml distilled water) was vigorously stirred and heated to 70°C. The solution of HAuCl<sub>4</sub> was added into the suspension. The pH of the solution was about 7 and was controlled by addition of NaOH. The suspension was cooled down after 2 hours of stirring, filtered and scoured away from the presence of Cl<sup>-</sup> ions. The resulting samples were dried over night at 40°C in air and calcinated at 300°C (heating rate, 5°C/min) for 2 h in the air nearby catalytic measurements. The content of Au was 2 wt% in all the samples.

### 2.3. Characterization methods

The morphological characteristics of the particles was investigated using scanning electron microscopy (SEM, JEOL JSM 5400). Crystal structures were performed with the X-ray diffraction measurements (XRD), using Philips Analytical X'PERT PW-3710 equipped with an adapter for low-angular geometry GID. The specific surface area of the samples was determined by BET method using nitrogen adsorption-desorption isotherms with ASAP 2010 Micromeritics. The effluent gases descended from CO oxidation were analyzed online by the quadrupole mass spectrometer (Thermostar Balzers Instruments).

### 2.4. Catalyst activity test

The CO oxidation reactions were carried out in a flow reactor. Prior to the measurement the catalysts were heated at 300°C in air and kept for 30 min. The reactor was cooled under a flow of air before introducing the reactant flow. The catalysts were tested using a flow reactor at atmospheric pressure in the temperature range 25–300°C, using 0.3 g

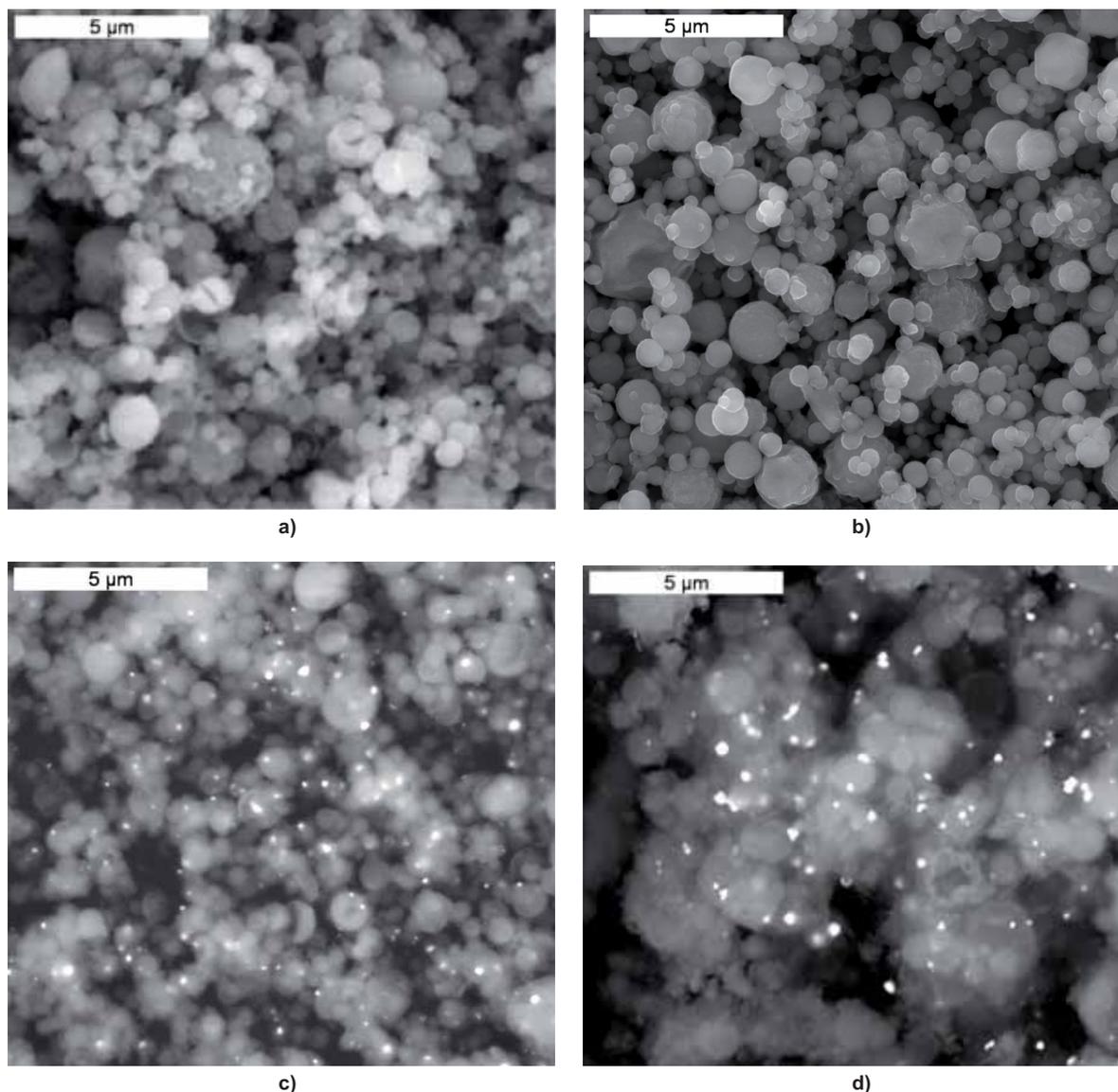


Fig. 2. SEM images of the support oxides and gold supported catalysts: a)  $Mn_2O_3-Al_2O_3$ , b)  $CuO-Al_2O_3$ , c)  $Au/Mn_2O_3-Al_2O_3$ , d)  $Au/CuO-Al_2O_3$ .

catalyst powder. The gas flow was  $6 \text{ dm}^3/\text{h}$  and consisted of 1 vol.% CO in experiment. The reactant flow ( $100 \text{ cm}^3/\text{min}$ ) consisted of 1 vol.% CO (18.8 vol.%  $O_2$ , 80.2 vol.%  $N_2$ ). The on line gas analysis was performed using a quadruple MS.

### 3. Results and discussion

#### 3.1. BET specific surface area

The specific surface area of samples are reported in Table 1. It can be observed that after deposition of gold the specific surface area of the respective samples increased considerably. This suggests very fine size of gold particles.

#### 3.2. The SEM observations

The SEM investigations were made to observe the morphology of the particles produced by spray pyrolysis and particle size of the catalysts. The SEM micrographs of catalysts are shown in Fig. 2. The catalysts have micron sizes and/or even less, spherical shapes and hollow morphologies. The EDS spectra (not included) of each

Table 1. Specific surface area ( $S_{BET}$ ) for various catalysts.

Catalyst	$S_{BET} [\text{m}^2\text{g}^{-1}]$
$CuO - Al_2O_3$	$22.43 \pm 0.07$
$Au/CuO - Al_2O_3$	$133.67 \pm 0.18$
$Mn_2O_3 - Al_2O_3$	$127.04 \pm 0.45$
$Au/Mn_2O_3 - Al_2O_3$	$210.12 \pm 0.58$

catalyst show that the element compositions are related to the assumed catalysts.

#### 3.3. X-ray diffraction (XRD)

The results of XRD are shown in Fig. 3. XRD was used to identify the crystalline phases present in the catalysts. The crystalline phases were identified using JCPDS-ICDD files. In the case of catalysts containing manganese-aluminium oxides, diffraction peaks of Au and  $Mn_2O_3$  were observed. The samples were characterized by a large content of the amorphous phase, in particular manganese-alumina oxides.

Diffraction peaks corresponding to crystalline Mn<sub>2</sub>O<sub>3</sub> were detected in both samples. The nature of the phase depends strongly on the method of preparation and synthesis condition.

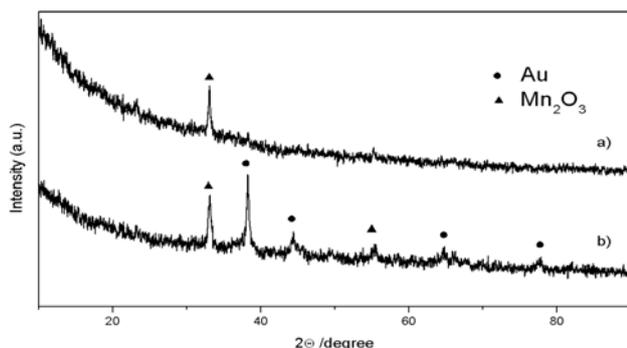


Fig. 3. X-ray diffraction patterns: a) Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and b) Au/Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts.

Fig. 4 shows the XRD patterns of gold catalysts supported on copper-aluminium oxides. For the catalysts containing copper oxide diffraction peaks due to CuO and CuAl<sub>2</sub>O<sub>4</sub> were observed. The results show that the samples with copper oxide are more complex than the samples with manganese oxide. The intensity of the CuO diffraction peaks is weaker in the Au/CuO-Al<sub>2</sub>O<sub>3</sub> than in the CuO-Al<sub>2</sub>O<sub>3</sub> catalysts.

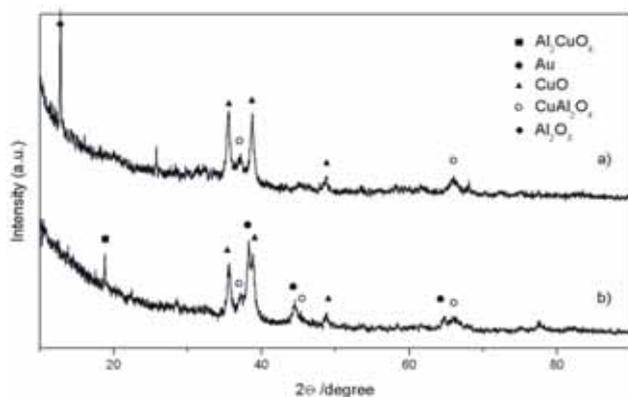


Fig. 4. X-ray diffraction patterns: a) CuO-Al<sub>2</sub>O<sub>3</sub> and b) Au/CuO-Al<sub>2</sub>O<sub>3</sub> catalysts.

### 3.4. Catalytic activity

The results of catalytic activity in carbon monoxide oxidation are shown in Fig. 5.

Au/CuO-Al<sub>2</sub>O<sub>3</sub> catalysts are more active than CuO-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> pure oxides for 1 vol.% carbon monoxide content. After gold deposition the catalytic activity Au/CuO-Al<sub>2</sub>O<sub>3</sub> catalysts remarkably increase. It is possible to specify the catalytic activity in three different stages. First, the catalytic activity rises fast at room temperature to 100°C, next it is stopped and remains on this level to 150°C, and subsequently rises again to 300°C.

In Fig. 6 the CO conversion for Au/Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are presented. The addition of gold brings about an insignificant increasing catalytic activity in comparison to pure support. The catalytic activity arises at about 130°C. In the presence of higher vol.% of CO, the CO conversion remains at the same level.

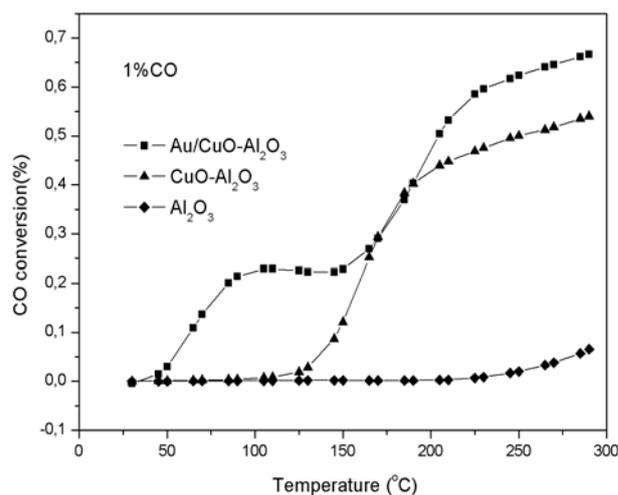


Fig. 5. CO oxidation activity of catalysts with 2 wt% gold loadings and 1 vol.% CO in feed gas: (■) Au/CuO-Al<sub>2</sub>O<sub>3</sub>, (▲) CuO-Al<sub>2</sub>O<sub>3</sub>, (□) Al<sub>2</sub>O<sub>3</sub>.

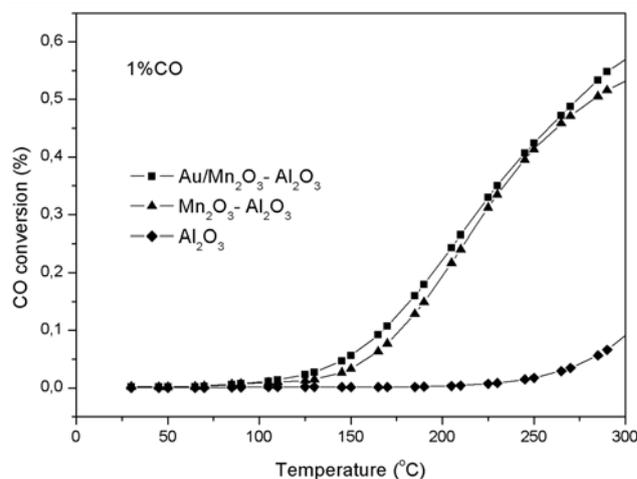


Fig. 6. CO oxidation activity of catalysts with 2 wt% gold loadings and 1 vol.% CO in feed gas: (■) Au/Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, (▲) Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, (□) Al<sub>2</sub>O<sub>3</sub>.

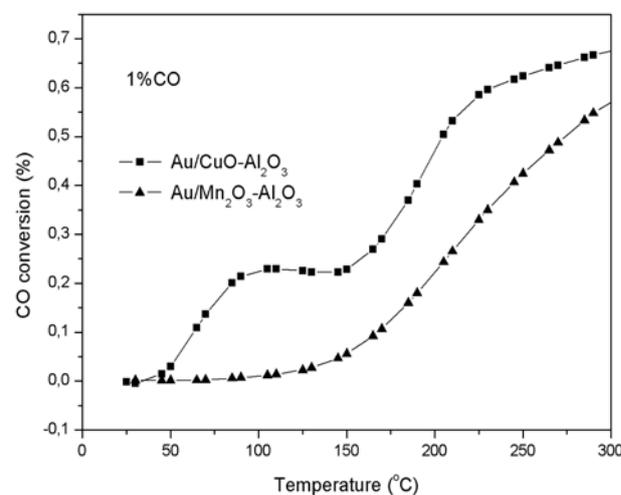


Fig. 7. CO oxidation activity of catalysts with 2 wt% gold loadings and 1 vol.% CO in feed gas: (■) Au/CuO-Al<sub>2</sub>O<sub>3</sub>, (▲) Au/Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>.

Fig. 7 shows the dissimilarity between these systems in CO oxidation reaction. The Au/CuO-Al<sub>2</sub>O<sub>3</sub> catalysts are more active than catalysts containing manganese oxide.

#### 4. Conclusions

The catalysts Au/CuO-Al<sub>2</sub>O<sub>3</sub> and Au/Mn<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> have been prepared by the spray pyrolysis method. The morphology of metal oxides is similar to both samples. The SEM analysis showed that all the catalysts have spherical-shape particles with a hollow structure. From XRD analysis it was found that there are significant differences in the phase composition between the catalysts. The catalysts with manganese oxide contained only one crystalline oxide phase: Mn<sub>2</sub>O<sub>3</sub>. In the catalyst with copper oxide the spinel type compounds, like Al<sub>2</sub>CuO<sub>4</sub> and CuAl<sub>2</sub>O<sub>4</sub>, have been found. The higher activity for CO oxidation showed Au/CuO-Al<sub>2</sub>O<sub>3</sub> in the whole temperature region investigated.

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