

CO OXIDATION: EFFECT OF Ce AND Au ADDITION ON MnO_x CATALYSTS.

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Abstract - The effect of cerium and/or gold addition to a manganese oxide which was greatly active in CO oxidation was studied. The catalysts obtained by this way were characterized by N₂ adsorption, XRF, XRD and TPR, and their catalytic activity was measured in the CO oxidation reaction. The pure MnO_x catalyst was active in the CO oxidation but the addition of 5 wt % cerium decreased their catalytic activity. Adding 2 wt % gold improved the activity of MnO_x and Ce/MnO_x and caused a slight decrease of the catalyst specific area and of the average oxidation state of manganese in catalysts, which was found between 3.3 and 3.6. The order of activity found on the basis of T₅₀ for the four catalysts was: Au/MnO_x > Au/Ce/MnO_x > MnO_x > Ce/MnO_x, with T₅₀ of 89, 95, 99 and 139 °C, respectively. The solids Au/MnO_x and Au/Ce/MnO_x presented a T₁₀ of 30 and 49 °C, indicating that gold favored the conversion at room temperature. The effect of water vapor on the reaction was also analyzed, finding a decrease in the catalytic activity of all catalysts, due to the blocking of active sites in the catalyst surface.

Keywords: CO Oxidation; MnO_x; CeMnO_x; Au

I. INTRODUCTION

Manganese oxides are widely used in reactions of environmental interest such as the selective reduction of NO_x, total oxidation of CO and VOCs, due to their low cost and high activity, which is attributed to the labile lattice oxygen and their capacity of storing oxygen in the crystalline structure (Craciun *et al.*, 2003; Han *et al.*, 2006; Luo *et al.*, 2000; Tang *et al.*, 2007). In this sense, manganese oxides with mixed valence, where manganese atoms with different oxidation state are in the same net, proved to be the same as or more active than the manganese oxides with only one valence (Fouad *et al.*, 1998; Hasan *et al.*, 1999; Peluso *et al.*, 2003). The catalytic activity of manganese oxides could be enhanced by the combination with other metals. The presence in solid lattices of ions closely coupled to one or several metals (Mn-Ce, Mn-Cu, etc.) in different oxidation states results in a certain electronic mobility necessary to obtain a redox activity on the catalyst surface (Buciuman *et al.*, 1999; Dominguez *et*

al., 2009a; Hernández *et al.*, 2010). In this regard, mixed copper manganese oxides (Hopcalite) and cerium manganese oxides are well-recognized as low temperature CO oxidation catalysts (Martinez *et al.*, 2008; Njagi *et al.*, 2010; Zhang *et al.*, 2011). Apart from manganese based catalysts, gold supported catalysts are employed to oxidize CO. The role of the support in the reaction is believed to provide oxygen adsorption and activation sites for yielding a great amount of mobile oxygen capable of reacting with CO (Dominguez *et al.*, 2009b; Haruta *et al.*, 1993; Hernández *et al.*, 2009; Romero-Sarria *et al.*, 2007; Schubert *et al.*, 2001).

When the manganese oxides are combined with gold forming Au/MnO_x -type systems, the catalytic activity in CO oxidation reaction is significantly enhanced in some cases (Wang *et al.*, 2008). Some authors explained this behaviour by a synergistic interaction between Au and the MnO_x support. Recent studies have shown that Au/MnO₂-CeO₂ catalysts are more active in CO oxidation than Au/CeO₂ catalysts (Chang *et al.*, 2006; Tu *et al.*, 2009).

In this work it was studied the effect of Au and/or Ce addition on the physicochemical properties of a manganese oxide catalyst, which has shown good activity in the oxidation of VOCs (Peluso *et al.*, 2005). The catalytic activity of the mixed oxides was studied in the oxidation reaction of CO. In addition, the effect of water vapor in the CO feed on the activity of such catalysts was studied as well.

II. EXPERIMENTAL

A. Catalyst preparation

The preparation of the samples used in this work, along with their notation, is described as follows:

MnO_x: 10g of MnCO₃ were calcined in a glass reactor at 350 °C for 48 h, in a flow of 50 cm³ min⁻¹ of O₂ saturated in H₂O vapor. The H₂O vapor pressure was that corresponding to room temperature, 24.5 mmHg. Finally, the oxide was calcined in air for 2 h at 400 °C.

Ce/MnO_x: Sample MnO_x was impregnated at pore volume with an aqueous solution of Ce(NO₃)₃·6H₂O of such concentration to obtain a 5 wt% Ce. After filtered and washed with distiller water, the obtained solid was dried at 120°C for 12 h and calcined in air for 2 h at 400 °C.

Au/MnO_x: an aqueous solution of HAuCl₄·3H₂O, of such concentration in order to obtain 2.5 wt% Au, was prepared and kept at 70 °C. Then MnO_x was added to the solution and maintained at 70°C for 20 min under constant stirring. After this time, NH₄OH was added and kept for 20 min under constant stirring. Then, the solid was filtered, dried and finally calcined in air for 2 h at 300 °C (Ivanova *et al.*, 2004).

Au/Ce/MnO_x: It was prepared using the same procedure as the Au/MnO_x catalyst, except that Ce/MnO_x was added to the HAuCl₄·3H₂O solution.

B. Characterization

By means of X-ray diffraction, the material structure was analyzed using a X'Pert Pro Philips diffractometer working with Cu K α radiation ($\lambda=1.5404$ Å) in continuous scan mode from 5° to 70° of 2 θ using 0.05° sampling interval and 1.0 s.

The chemical composition of the materials was determined by X-Ray fluorescence (XRF) using a spectrophotometer Siemens SRS 3000 equipped with a rhodium tube.

The textural properties were studied by N₂ adsorption measurements at liquid nitrogen temperature. The experiments were carried out in micromeritics ASAP 2020 equipment. Before analysis, the samples were degassed for 2 h at 150 °C in vacuum.

The sample reducibility was analyzed by hydrogen temperature-programmed reduction (H₂-TPR) tests using a 5% H₂/Ar reducing mixture carrier flowing at 40 cm³ min⁻¹. The experiments were carried out with a heating rate of 10 °C min⁻¹ from room temperature to 900 °C using 40-50 mg of sample. A calibration curve of the TCD response signal expressed by the integral area of peaks as a function of the amount of the hydrogen consumption was established by reducing known amounts of pure CuO to Cu.

C. Catalytic activity

The activity measurements were carried out in a flow U-shape glass reactor at atmospheric pressure. 80 mg

of catalyst were placed into the glass reactor and a reactive flow (3.4% CO and 21% O₂ balanced by helium) was passed through it. The total flow was 42 cm³ min⁻¹ and the quantitative analysis was carried out with a Balzers Omnistar Bentchop mass spectrometer. The catalyst was activated in a flow containing 21% O₂ in helium (total flow 30 cm³ min⁻¹) at 300 °C for 1 h. Then, the system was cooled down and stabilized at room temperature and the light-off curve (from RT to 300 °C at 5 °C min⁻¹) was started.

In order to determine the effect of water in the catalytic activity, a second test was carried out by bubbling the feed through a water saturator at RT. It is assumed that water vapor pressure was that corresponding to 25 °C, (24.5 mmHg) which yielded a concentration of 3.2 v/v % H₂O.

III. RESULTS AND DISCUSSION

A. Ce influence on MnO_x

The Ce content calculated by XRF, together with the results of the textural properties of catalysts is shown in Table 1.

The addition of cerium to the manganese oxide catalyst did not modify substantially its textural properties. The X-ray diffraction diagrams of the catalysts are shown in Fig. 1.

The MnO_x XRD pattern was characterized by some intense diffraction lines and some broad and poorly resolved peaks, which could correspond to a α -MnO₂ phase (JCPDS 44-0141) or α -MnO_x·nH₂O hydrated oxide (JCPDS 81-1946). These manganese ox-

Table1. Textural properties of catalysts.

Catalyst	Au ^a	Ce ^a	S _{BET} (m ² g ⁻¹)	Vp (cm ³ g ⁻¹)	Dp (Å)
MnO _x	0	0	50	0.158	99
Au/MnO _x	2.8	0	41	0.153	113
Ce/MnO _x	0	5.8	52	0.167	101
Au/Ce/MnO _x	2.5	3.5	41	0.153	112

^a (wt%) Measured by XRF.

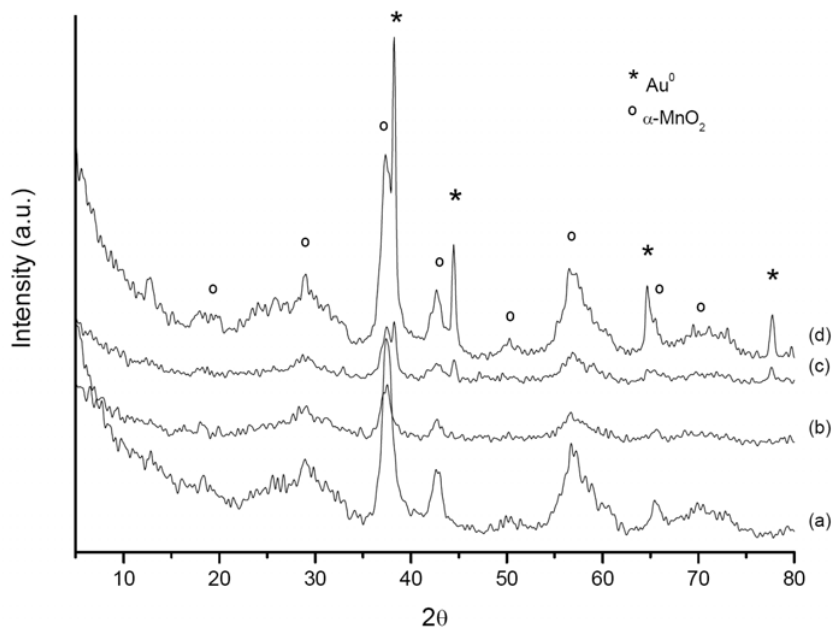


Figure 1. X-ray diagram of MnO_x -based catalysts: (a) MnO_x ; (b) Ce/MnO_x ; (c) $\text{Au}/\text{Ce}/\text{MnO}_x$ and (d) Au/MnO_x .

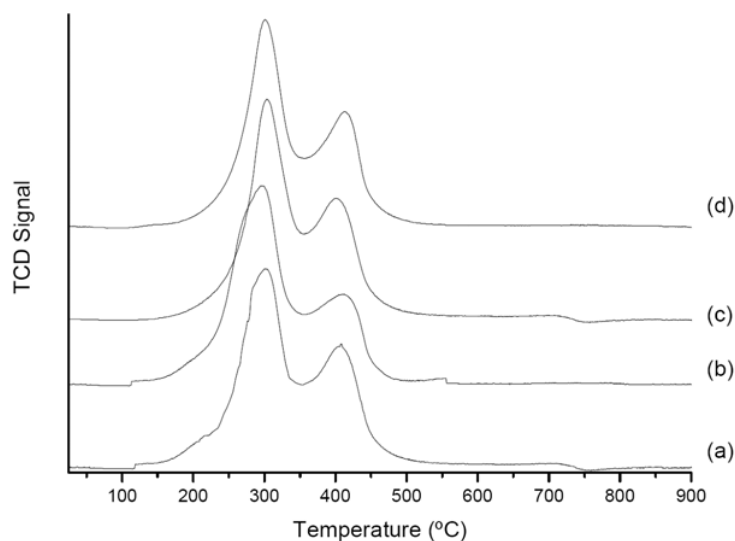


Figure 2. Thermal programmed reduction curves of MnO_x -based catalysts: (a) MnO_x ; (b) Ce/MnO_x ; (c) Au/MnO_x and (d) $\text{Au}/\text{Ce}/\text{MnO}_x$.

Table 2. Quantification results of TPR.

Catalyst	T_1 (°C)	T_2 (°C)	Mmol H_2 (g^{-1})	O/Mn
MnO_x	297	406	9.64	1.81
Au/MnO_x	304	402	8.18	1.67
Ce/MnO_x	295	412	9.88	1.83
$\text{Au}/\text{Ce}/\text{MnO}_x$	301	413	9.01	1.75

T_1 and T_2 : The temperatures at the maximum of the first and second reduction peaks, respectively, in the TPR profiles.

ide phases were characterized by the presence of Mn^{4+} and Mn^{3+} cations (Post *et al.*, 1982). When a 5 wt % Ce was added to the manganese oxide, Mn species still crystallized in the same MnO_x structure and there was no diffraction peaks attributable to cerium oxide, indicating either a high Ce dispersion on the surface or a very small size of its crystalline domain. Nevertheless, the intensity of the Mn oxide-related peaks de-

creased, indicating a lower degree of crystallinity. These results are coincident with those reported for mixed manganese-cerium oxides (Chen *et al.*, 2001).

The thermal reduction curves of catalyst curves are shown in Fig. 2. In addition, the results obtained from TPR quantification curves, together with temperature values of the reduction peak maxima are shown in Table 2. MnO is assumed to be the final phase after the reduction at temperatures below 900 °C (Kapteijn *et al.*, 1994).

For both samples, MnO_x and Ce/MnO_x , two reduction peaks were observed. The low reduction peak can be explained as the reduction of MnO_2 and or Mn_2O_3 to Mn_3O_4 , and the high reduction peak represented the reduction of Mn_3O_4 to MnO (Gil *et al.*, 2004; Kapteijn *et al.*, 1994; Tang *et al.*, 2008) in

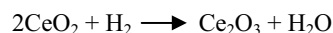
MnO_x and the combined reduction of Mn₃O₄ to MnO and surface Ce⁴⁺ to Ce³⁺ species in Ce/MnO_x (Tang *et al.*, 2006). Additionally, in the Ce/MnO_x sample it was not detected the high temperature cerium reduction peak. Based on the O/Mn ratio, it is deduced that Mn presented an average oxidation state between 3.62 and 3.66, indicating the presence of Mn⁴⁺ cations together with Mn³⁺ or Mn²⁺ cations. These results are in agreement with the manganese oxide phase detected by XRD, which contained Mn⁴⁺ and Mn³⁺.

In the case of Ce/MnO_x catalyst, it is observed that the reduction signal of low temperature presented a broadening towards the area of lower temperatures in relation to MnO_x, indicating a greater heterogeneity of reducible species at low temperature.

On the other hand, the presence of cerium did not change the average Mn oxidation state, and shifted the second reduction peak to higher temperatures with respect to the starting oxide.

However, this second peak could have been influenced by Ce reduction (Tang *et al.*, 2006), which could have resulted in the slight observed shift.

Assuming that the reduction of Ce occurs as follows:



where one cerium mol is reduced by 0.5 H₂ mol.

Taking into account that Ce/MnO_x contained 5.8 wt %, and assuming that cerium was in the Ce⁴⁺ form, it was necessary 0.21 mol of H₂ to reduce all the cerium in one gram of catalyst. As the overall consumption of H₂ to reduce 1g catalyst was 9.88 mols, the number of H₂ mols to reduce the MnO_x phase was 9.67, a value close to 9.64 obtained for the pure MnO_x catalyst.

The results of CO oxidation on the catalysts as a function of temperature are represented in Table 3 and Fig. 3. The temperature at which the CO conversion reached 10, 50 and 90% (T₁₀, T₅₀, T₉₀) was taken as a measurement of catalytic activity.

Over pure MnO_x, CO oxidation started at about 40 °C and complete conversion was reached at temperatures below 150 °C. The catalytic properties of manganese oxides are related to the presence of the Mn⁴⁺-Mn³⁺ redox pairs (Peluso *et al.*, 2003).

Surprisingly, the addition of cerium to the manganese oxide prepared in this work moved the ignition curve to higher temperatures, giving a T₅₀ about 40 °C higher than MnO_x.

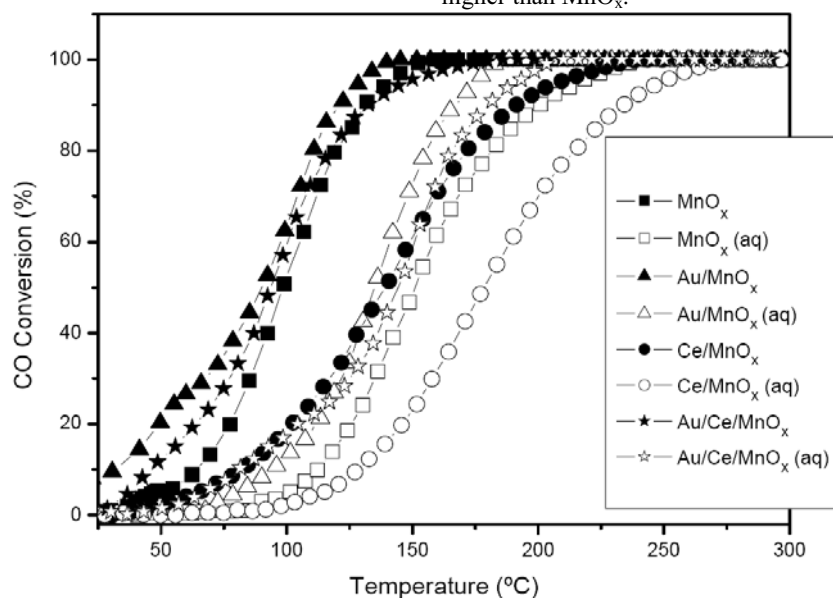


Figure 3. CO ignition curves on MnO_x based catalysts. (The full symbols represent the reaction without water, while the empty symbols represent the reaction with water in the stream)

Table 3: Catalytic activity in CO combustion with and without water vapor on MnO_x catalysts.

Catalyst	CO			CO + H ₂ O		
	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
MnO _x	65	99	132	113	151	202
Au/MnO _x	30	89	122	95	135	167
Ce/MnO _x	85	139	191	129	179	235
Au/Ce/MnO _x	49	95	136	81	144	181

T₁₀, T₅₀ and T₉₀: reaction temperatures corresponding to 10%, 50% and 90% of CO conversion.

Several mixed manganese-cerium oxides prepared by co-precipitation have been reported to present a favorable synergetic effect between MnO_x and CeO₂ and as a consequence, an improvement in their oxidation abilities (Chang *et al.*, 2006; Chen *et al.*, 2001; Zhang *et al.*, 2011). The Ce/MnO_x catalyst prepared in this

work by impregnation of a cerium salt over MnO_x, did not improve the catalytic activity, moreover, it had a detrimental effect on the activity.

Assuming that a CeO₂ has a cubic structure and a lattice parameter *a* of 0.5411 nm, the amount of cerium molecules to form a theoretic monolayer over a 1g

of $50 \text{ m}^2 \text{ g}^{-1} \text{ MnO}_x$ is 1.71×10^{20} , which corresponds to 5 wt% CeO_2 . According to FRX result, Ce/MnO_x presented a 5.8 wt% Ce, or 7 wt% CeO_2 , indicating that Ce formed a theoretical monolayer onto MnO_x . This monolayer could block the intrinsic active sites of the MnO_x oxide. This effect could be related with the TPR result where the bulk CeO_2 reduction event was not observed.

B. Effect of Au addition

The Au content and the textural properties of gold catalysts are shown in Table 1. It can be seen that after adding Au either to MnO_x or Ce/MnO_x catalyst, a decrease in the specific surface took place together with an increase of the pore diameter, in agreement with other authors (Cole *et al.*, 2010; Dominguez *et al.*, 2006). The cerium content in Au/Ce/MnO_x decreased from 5.8 to 3.6 wt %, indicating that the impregnation method to deposit gold causes a partial dissolution of cerium. Several authors have reported that on Mn-Ce mixed oxides where a solid solution is formed (with the subsequent displacement of the TPR peaks to lower temperatures) no leaching of cerium occurs (Hussain *et al.*, 2001). In the Ce/MnO_x prepared in this work, neither TPR displacement to lower temperatures nor CeO_2 diffraction peaks were observed. It is likely that cerium was dissolved in the acidic medium of the HAuCl_4 solution.

The X-ray diffraction diagrams of the catalysts are shown in Fig. 1. In the two samples containing Au, it is observed diffraction lines in $2\theta = 38.2; 44.5; 64.5$ and 77.6° ; assigned to metallic gold planes (111), (200), (220) and (311), respectively. These results show that the sample calcination, even in presence of oxygen, produced the gold self-reduction and the formation of metallic gold particles (Mihaylov *et al.*, 2007). The diffraction lines of metallic gold in Au/Ce/MnO_x are also less intense than in Au/MnO_x catalyst. This effect could be related to the presence of Ce which it has been reported that favors the dispersion of metallic phases (Carriazo *et al.*, 2007; Centeno *et al.*, 2006). Analysis of the peak widths by Scherrer equation showed that the mean gold particle size for the gold promoted catalysts was *ca.* 40-50 nm. Shimada *et al.* (2010) have reported that the mean particle size of Au on Au/CeO_2 prepared by impregnation of HAuCl_4 is 53 nm. They have reported that during calcination, small metal particles are agglomerated by the aid of chloride ion to form larger particles.

The H_2 -TPR profiles of gold catalysts are displayed in Fig. 2. Compared with the H_2 -TPR behavior of the MnO_x and Ce/MnO_x , the addition of gold did not modify the reduction features. As in the case previously described, the reduction took place in two stages, which can be explained as the reduction of MnO_2 and Mn_2O_3 to Mn_3O_4 and as the reduction of Mn_3O_4 to MnO (Gil *et al.*, 2004; Kapteijn *et al.*, 1994; Tang *et al.*, 2006). Nevertheless, the addition of gold resulted in a decrease in the H_2 consumption per catalyst gram, and therefore, in the average Mn oxidation state.

On the other hand, the reduction peaks in the catalyst Au/MnO_x appeared at almost the same temperature as in the pure oxide, indicating the absence of the hydrogen spillover effect, differently from what has been reported by other authors in the case of gold catalysts supported on manganese oxides (Tu *et al.*, 2009; Wang *et al.*, 2008). This allows us to think that there was a strong metal-support interaction that decreased oxygen mobility, which was favorable to suppress the hydrogen dissociation (Tu *et al.*, 2009), which could be interesting for the PROX reaction where it is required a high selectivity of oxygen towards CO_2 .

The results of CO oxidation of the gold catalysts in function of temperature are represented in Table 3 and Fig. 3. The addition of gold to the MnO_x improved the catalytic performance, unlike the addition of cerium to MnO_x . Au/MnO_x yielded a T_{50} about 10°C lower than the pure oxide and presented a T_{90} of 122°C , also about 10°C lower than that of MnO_x .

The addition of gold to Ce/MnO_x greatly improved the catalytic activity. Au/Ce/MnO_x yielded a T_{50} about 55°C lower than that of the cerium manganese oxide. Nevertheless, Au/MnO_x presented higher conversion than Au/Ce/MnO_x . The increment in CO oxidation on both catalysts containing gold, Au/MnO_x and Au/Ce/MnO_x , was accompanied by a decrease in the catalyst specific area (Table 1). Taking into account that in the Au/Ce/MnO_x preparation part of the cerium was removed by leaching, and the initial Ce concentration was necessary to form a monolayer, the great increment in activity could be related to the breaking of the monolayer, which favoured the access of the reactant to the active sites.

Taking into account the XRD results, where in Au/Ce/MnO_x the diffraction lines of metallic gold are less intense than in Au/MnO_x , if the former presents a higher dispersion of metallic gold particles, a significant change of particle size and a correlation with the catalytic activity should be observed. So, possible explanation could be that Au is not completely reduced to metallic Au in Au/Ce/MnO_x catalyst. Probably, the presence of Ce in the catalyst modifies the surface conditions during the calcination limiting gold reduction. This effect also could explain the lower hydrogen consumption in the TPR analyses of Au/MnO_x in comparison to Au/Ce/MnO_x catalyst.

Comparing the four catalysts studied, the activity order found based on T_{50} was: $\text{Au/MnO}_x > \text{Au/Ce/MnO}_x > \text{MnO}_x > \text{Ce/MnO}_x$. However, MnO_x had a lower T_{90} than Au/Ce/MnO_x . It is worth pointing out that Au/MnO_x and Au/Ce/MnO_x catalysts presented the lowest T_{10} ; (30 and 49°C , respectively). This fact indicates that gold mainly favored the conversion to temperatures close to room temperature.

The enhancement of the catalytic activity, when supporting Au on Mn, can be attributed to what has been remarked by Srinivasan and Gradner (1998), who state that a synergetic effect takes place producing an enhancement in the electric conductivity properties of the solid, with the subsequent increment in

the catalytic activity according to Wolkstein electronic theory of catalysis.

The slight activity increase of Au/MnO_x compared to MnO_x could be related to the presence of large Au particles (Haruta *et al.*, 1989).

C. Effect of H₂O vapor on the CO oxidation

Despite the great number of works focused on CO oxidation, there is no agreement about the role of water on the reaction. According to literature, the presence of 10% water in the gaseous stream causes the activity decrease in CO oxidation in CuO/CeO₂ (Avgouropoulos *et al.*, 2006) catalysts, and has no effect on Au/MnO_x and Au/FeO_x catalysts (Luegnaruemitchai *et al.*, 2005). On the other hand, Bocuzzi *et al.* (1996) have found that a small amount of water promotes the CO oxidation on Au/TiO₂ catalysts, with a maximum activity at a water concentration of 200 ppm. Besides, Haruta *et al.*, (2001) have also found that low water concentrations (1-200 ppm) in the current result in a positive effect in CO oxidation reaction, whereas high water concentrations (6000 ppm) suppress the activity. Recent results on Au/CeO₂ catalyst detected that a 3 v/v% H₂O has a positive effect on CO oxidation (Romero-Sarria *et al.*, 2008).

The water vapor effect on the gaseous current in relation to the catalysts prepared in this work is shown in Fig. 3 (empty symbols).

In all cases, a significant decrease occurred in the conversion in presence of 3 v/v% water vapor due to the interaction of the active sites between CO and H₂O molecules. (Avgouropoulos *et al.*, 2006; Lahousse *et al.*, 1998; Parida and Samal, 1999). The conversion order of the catalysts based on their T₅₀ and T₉₀ in presence of water was: Au/MnO_x > Au/Ce/MnO_x > MnO_x > Ce/MnO_x. However, it is worth pointing out that Au/Ce/MnO_x yielded the lowest T₁₀ when water vapor was added to the CO feed. Over gold supported catalysts, the presence of Ce could promote the resistance to water during the reaction at low temperatures, as it has been reported by Centeno *et al.* (2005) who have concluded that on Au/CeO₂ catalysts, the presence of water in the feed increases the catalytic activity towards CO oxidation at temperatures lower than 120 °C, whereas the effect of water is negative at higher temperatures. The positive effect of the presence of water at low temperatures was ascribed to the improved control of the redox reactions implied in the reaction mechanism of the catalytic system.

IV. CONCLUSIONS

A manganese oxide (MnO_x) which showed great activity in VOCs oxidation was impregnated with gold and/or cerium in order to enhance its activity in CO oxidation. The MnO_x impregnation with gold led to an activity increase, reducing T₅₀ and T₉₀ both in 10 °C. The manganese oxide impregnation with cerium resulted in a catalyst much less active than the starting oxide. However, after the subsequent impregnation with gold there was a significant increase in the catalytic activity. Based on T₁₀ values of catalysts, it was

observed that gold favored the CO conversion, especially at temperatures close to room temperature. The increment in activity produced when adding gold is related to the fact that the impregnation with Au enabled Mn³⁺ formation, which gave rise to an increase in the number of Mn⁴⁺/Mn³⁺ pairs.

The water vapor in the gaseous current resulted in a decrease of catalytic activity, possibly due to the blocking of MnO_x active sites by water molecules.

ACKNOWLEDGEMENTS

Programme AlBan-European Union Programme of High Level Scholarships for Latin America (W.Y. Hernández Ph.D. UE E06D101739CO Scholarship)

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Received: September 8, 2011

Accepted: January 6, 2012

Recommended by subject editor: Pedro de Alcântara Pessôa