CO OXIDATION: EFFECT OF Ce AND Au ADDITION ON MnOx 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 MnOx 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 MnOx and Ce/MnOx 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/MnOx > Au/Ce/MnOx > MnOx > Ce/MnOx, with T50 of 89, 95, 99 and 139 ºC, respectively. The solids Au/MnOx and Au/0.5%Ce/MnOx presented a T10 of 30 and 49 ºC, 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; MnOx; CeMnOx; Au

1. INTRODUCTION

Manganese oxides are widely used in reactions of environmental interest such as the selective reduction of NOx 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/MnOx –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 MnOx support. Recent studies have shown that Au/MnOx–CeO2 catalysts are more active in CO oxidation than Au/0.5%Ce 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: MnOx: 10g of MnCO3 were calcined in a glass reactor at 350 ºC 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 ºC. Ce/MnOx: Sample MnOx 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 ºC for 12 h and calcined in air for 2 h at 400 ºC.