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Gold supported cryptomelane-type manganese dioxide OMS-2 nanomaterials deposited on AISI 304 stainless steels monoliths for CO oxidation

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ABSTRACT

Gold supported on cryptomelane-type OMS-2 catalysts deposited on AISI 304 stainless steels monoliths have been prepared for the first time, characterised and tested in the CO oxidation reaction. An easy and non-conventional method of incorporation of gold to the cryptomelane solid is used. This method allows the preparation of the monolithic catalysts without altering the structural and textural characteristics of the parent OMS-2 material. Although these catalysts do not show an optimal performance for the oxidation of CO, the presence of small gold particles enhances the catalytic performances of the cryptomelane producing promissory CO oxidation catalysts. The non-conventional gold deposition favours a partial loss of K^+ into the channels, resulting in an increment of the average oxidation state of manganese which favours the catalytic behaviour of these kinds of materials. This study can be taken as a starting point to obtain very active gold catalysts supported on OMS-2 materials through the optimisation of the gold–support interaction and the decrease in the gold particle size.

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1. Introduction

Carbon monoxide is a strongly toxic gas for the people and the environment. It takes part directly in the formation of ground-level ozone and it favours the greenhouse effect. Besides this, CO goes along with the hydrogen in the reforming gases and it is a poison for the platinum-based catalysts of the PEM fuel cell. For all above, nowadays, the interest in developing catalysts very active and selective to CO oxidation reactions at low temperature has increased significantly.

In the latest years catalysts based in supported gold nanoparticles have demonstrated to be very active for CO oxidation reaction at low temperatures [1–3]. However, in this type of catalysts, not only the gold particle size but also the choice of the support plays a determinant role in the catalytic activity of the system. Although non-reducible metal oxides have been successfully used as supports [4–6], it is generally accepted that supports based on reducible transition metal oxides such as MnO_x, Fe_2O_3, TiO_2, CoO_x, NiO_x and CeO_2 are the best option due to their ability to provide reactive oxygen [5,7–10]. Manganese oxides are one of these reducible metal oxides suitable to be used as active support of gold nanoparticles. Even more, unsupported MnO_x catalysts, for instance, MnO_2 [11], Mn_2O_3 [12,13] MnO [13] as well as copper manganese oxide [14], has been reported as active catalysts in oxidation reactions, among them CO oxidation. When doping with gold nanoparticles a significantly enhanced activity is obtained [12,14,15].

Among the different structural forms and crystallographic phases of manganese studied in oxidation reactions, the cryptomelane-type manganese oxide octahedral molecular sieves (OMS-2) ones are of special interest due to their tunnel structures and related properties and applications [16]. OMS-2 materials are formed by double chains of edge-shared MnO_6 octahedra and corner sharing of the double chains. The structure forms 2×2 tunnels with a pore size of about 4.6 Å [17]. The average oxidation state of manganese is around 3.8 due to the coexistence of Mn^{4+} and Mn^{3+} species. To stabilise the structure and provide charge balance, cations (typically K^+) and water molecules are placed in the tunnels. Moreover, the tunnel species are exchangeable allowing the change of the properties of the material [18,19]. The conjunction of the characteristic tunnel and porous structure and the mixed of oxidation state of the manganese species makes the OMS-2 solids very interesting materials with potential applications in a large variety of processes [20–23]. In particular, they have been reported as excellent catalysts for volatile organic compounds (VOCs) [24–28] and CO oxidation [14,29–31]. The doping or modification of the cryptomelane materials with transition (Cu, Co, Ni and Zn) or noble metals (Ag, Pt, Pd) improves greatly the oxidation performances of the OMS-2. However, up to our knowledge there is no published papers concerning the effect of the incorporation of gold nanoparticles in this type of manganese molecular sieves for CO or gaseous VOCs oxidation, although one recent paper evidences the positive

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