



Sub-ambient CO oxidation over mesoporous Co_3O_4 : Effect of morphology on its reduction behavior and catalytic performance

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ARTICLE INFO

Article history:

Received 23 January 2012

Received in revised form 3 April 2012

Accepted 4 April 2012

Available online 25 April 2012

Keywords:

Cobalt oxide spinel

Morphology

Plane exposition

Reduction behavior

Low temperature CO oxidation

ABSTRACT

The influence of the Co_3O_4 morphology on its redox behavior and catalytic performance in the CO oxidation reaction is studied. Three different Co_3O_4 morphologies were synthesized by precipitation and hydrothermal methods. TEM and SEM observations clearly show the different obtained morphologies: rods, wires and a mixture of plates and cubes. The textural properties depend on the morphology and the redox ones on the particle size. XRD analysis reveals a spinel structure in all solids with a preferential exposition of the [1 1 0] plane in the Co_3O_4 rods sample. This preferential exposition, along with its higher specific surface area provides the rods with more efficient oxygen storage capacity resulting in an excellent catalytic performance compared to the other two morphologies.

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1. Introduction

Carbon monoxide is a well-known pollutant. Its complete oxidation to CO_2 and water over active catalysts is widely used to reduce its concentration in the air and reach the allowed concentration levels according to environmental regulations.

Almost all the catalysts used in CO elimination are based on supported noble metals: Pt [1–3], Pd [4,5], Rh [6,7] and Au [8–11]. The use of these expensive metals encourages the investigation of new, efficient and cheaper catalytic systems. Thus, the interest in transition metal oxide based catalysts for oxidation reactions is increasing nowadays [12]. Some metallic oxides such as Co_3O_4 [13], NiO and mixtures of MnO_2 and CuO (called hopcalite) are widely known for their activity at room temperature in CO oxidation [14].

Cobalt oxides show excellent activity towards CO oxidation even at very low temperatures [15,16]. Different activity values are reported in terms of T_{50} (temperature in which 50% of CO conversion is reached). Cunningham et al. [17] report a $T_{50} = -54^\circ\text{C}$ for pure Co_3O_4 and Thormählen et al. [15] report a $T_{50} = -63^\circ\text{C}$ for Co_3O_4 supported on alumina.

However, in heterogeneous catalysis, the catalytic properties of the solids are not only determined by the arrangement of atoms in the solid's bulk but also by the crystallographic structure of the surface particles [18], which is closely related to the morphology.

Thereby, the exposed planes in the metallic oxide play an important role in the catalytic activity. Experimental and theoretical measurements have demonstrated that metallic oxide particles with a FCC structure present different characteristics in the three lowest Miller index planes, [1 0 0], [1 1 0], [1 1 1]; having differences not only in the surface atomic density but also in the electronic structure, bonding and chemical reactivity [19].

Relating the catalytic activity to the morphology, Sadykov et al. [20] report that the catalytic activity of the Co_3O_4 depends upon the particles morphology. Xie et al. [21] studied the total CO oxidation at low temperature of Co_3O_4 nanorods, finding a 100% CO conversion at -77°C attributed to the preferential exposition of the [1 1 0] plane. Tang et al. [19] report the synthesis of Co_3O_4 octahedra with [1 1 1] plane preferential exposition, which suppresses its activity in the methane oxidation. Regardless of the diversity of the published results, there is general agreement on the importance of solid morphology control on the catalytic performance.

On the other hand, during heterogeneous catalytic reactions, the variations in oxidation states and interactions between the surface and the reactive gas define the mechanism by which the products are formed. In that way, knowing and characterizing the transition states of the studied systems is an important task. The transitory character of the reduction techniques at a programmed temperature, in which, the temperature, and therefore the surface coverage changes with time has the advantage of giving information that is not accessible by stationary techniques such as Raman or X-ray diffraction. For this reason, special attention is paid to the redox behavior of the samples.

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