



Sub-ambient CO oxidation over Au/MO_x/CeO₂-Al₂O₃ (M = Zn or Fe)

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ABSTRACT

A series of ZnO and Fe₂O₃ modified ceria/alumina supports and their corresponding gold catalyst were prepared and studied in the CO oxidation reaction. ZnO-doped solids show a superior catalytic activity compared to the bare CeO₂-Al₂O₃, which is attributed to the intimate contact of the ZnO and CeO₂ phases, since an exchange of the lattice oxygen occurs at the interface. In a similar way, Fe₂O₃-modified supports increase the ability of the CeO₂-Al₂O₃ solids to eliminate CO caused by both the existence of Ce-Fe contact surface and the Fe₂O₃ intrinsic activity. All of the gold catalysts were very efficient in oxidising CO irrespective of the doping metal oxide or loading, with the ZnO containing systems better than the others. The majority of the systems reached total CO conversion below room temperature with the ZnO and Fe₂O₃ monolayer loaded systems the most efficient within the series.

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1. Introduction

In the last 20 years gold based catalysis has received considerable attention in the scientific community. The surprising discovery by Haruta et al. [1] that very small gold nanoparticles exhibit catalytic activity for oxidising CO at sub-ambient temperature, provoked enormous scientific interest and makes gold the most used and the most popular metal for CO catalytic oxidation reaction. There exist a huge number of publications on this subject, including several reviews and a book that endeavour to unite most of the information [2–5]. Despite the diversity of the proposed catalytic systems, published in the literature, there is a general agreement on the importance paid to the nature of the active phase, gold particle size and structural geometry (existence of defect sites) and to the nature of support and its interactions with gold. A general drawback of the gold nanoparticles is the fact that they are kinetically unstable and have higher tendencies to agglomerate in high temperature applications. However, the thermal stability could be improved by a careful choice of the support material, whose first role is to disperse and stabilise the nanoparticles against agglomeration.

CeO₂ has been broadly reported as an active support for oxidation catalyst due to its chemical properties [6–9]. As mentioned above, the principal role of the support is to stabilize and disperse the metal particles, and thus a high specific surface area is required to provide a high number of nucleation sites. The smaller the support crystallites are, the better the dispersion of the metal particles

[10]. It was reported by Andreeva et al. [11] that the addition of Al₂O₃ to CeO₂, as a textural promoter prevents the sintering of CeO₂ crystallites and avoids the agglomeration of Au during the WGS reaction thus maintaining a high catalytic activity in the steady state.

In addition, ceria is very useful in the oxidation reactions due to its redox behaviour allowing oxygen mobility and enhancing the oxygen exchange with the reaction flow in the gas phase oxidation reactions. Another feature of this support which should be taken into consideration is that ceria is an n-type semiconductor whose band structure can be modified by promoters. Several studies have demonstrated that doping of CeO₂ with elements of different ionic radii and oxidation state improves the exchange of oxygen in the oxide network by decreasing the energy barrier for oxygen migration [12–15]. Iron is an interesting dopant, especially because of its own redox behaviour (Fe³⁺/Fe²⁺). Zn has also been used as a CeO₂-doping metal and a positive effect of its addition on the catalytic performance has been reported [16]. Ce–Zn solid solution formation has not been reported, being the interface (or the perimeter of contact) between ZnO and CeO₂, the region where a strong Zn–O–Ce interaction is produced.

In gold-based catalysis not only is the high activity is important but also the stability of the system under operating conditions. It is likely, that the intimate interaction between gold and the support is crucial for the high performance. Fu et al. [17] have reported that the loss of activity in the WGS reaction could be due to the loss of surface area of the ceria support due to weakening of the Au/ceria interaction. In this context, supporting ceria on a high surface area oxide carrier should be a good solution to the problem of ceria crystallites sintering and the subsequent loss of activity.

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