Catalytic MnO_2-Pt Nanohybrid for CO Oxidation: Insights on the Crystallographic and Mechanistic Aspects

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Abstract: The discussion will be focusing on scalable synthesis, characterization and CO oxidation activity of Pt nanoparticles supported on nanoscale Manganese dioxide (MnO_2) nanorods. A low-temperature hydrothermal technique is employed in this work to generate different phases, (*viz.* α and β) of the 1-D MnO_2.. Further tuning of reaction duration leads to formation of a flower morphology of α-MnO_2. The work encompasses detailed microstructural and crystallographic characterization to address the different phase formation of MnO_2 support. Interestingly, the α-MnO_2 rods show a higher extent of surface reducibility, in sync with their better catalytic activity in the CO oxidation process.

On the different phases of MnO_2 nanorods, Pt nanoparticles have been nucleated through a rapid microwave based technique. Owing to highest surface reducibility of the support, the best catalyst was found to be 2 wt% Pt-decorated-α-MnO_2 (flowers) with a CO conversion temperature with a range of 50-90℃. The work will encompass the aspects of activation energies, rate of the reactions, cyclic stabilities, and their justifications from the *ab initio* viewpoint.

Keywords: Pt-MnO_2, EELS, CO oxidation, DFT.

1. Introduction

The low-temperature catalytic oxidation of CO is of great interest due to its relevance in various practical applications, [1-3] such as CO removal from PEMFC feed, environmental cleaning and as a model to understand catalytic mechanisms. The noble metal-supported transition metal oxides have been widely explored as catalysts due to their low cost and high thermal stability. Among the transition metal oxides, MnO_2 exhibits good oxygen storage/release ability [4] due to its easy reduction–oxidation cycles through its interaction with the reducing and oxidizing environment. It exists in various structural phases and its different polymorphic forms [5] are believed to be responsible for their physicochemical properties and catalytic performance.

In this study, different phases of MnO_2 *viz.* α and β, are synthesized using a scalable low-temperature hydrothermal method, and their CO oxidation activity was explored. Detailed microstructural and crystallographic analysis were used to explain the reasons for the formation of different phases. The chemical reaction parameters during synthesis were tuned to obtain various morphologies (nanorods and nano-flowers) of MnO_2. Ultra-fine Pt nanoparticles were decorated on the oxide support using a rapid microwave technique. The CO oxidation activity on 2 wt% Pt-α-MnO_2 (flowers) was observed to be the best with the conversion temperatures ranging from 50 ^oC to 90 ^oC.

2. Experimental

Preparation of catalysts

The α- and β-MnO_2 nanorods were synthesized by a facile hydrothermal technique mentioned elsewhere [6]. The black powders were calcined at 300 ^oC for 2 h to remove impurities. To load 2 wt% Pt over the MnO_2 substrate [7], 50 mg of the black product was dispersed in ethylene diamine (EG) and appropriate amount of H_2PtCl_6 salt was added. After ensuring a homogeneous dispersion, the solution was subjected to microwave for 5 min. The resulting precipitate was washed and dried in a similar fashion as mentioned above.

Catalytic Experiments

The catalytic activity of catalysts for CO oxidation were measured in a plug flow reactor by using 100 mg of catalyst in a gas mixture of 2 vol % CO, 2 vol % O_2, and N_2 as balance at a flow rate of 100 mL min^{-1}.

3. Results and discussion

Wide angle XRD of hydrothermally synthesized MnO_2 powders show that the phases are α-MnO_2 (JCPDS 44-0141) and β-MnO_2 (JCPDS 24-0735). Low magnification bright field TEM images, along with the selected area diffraction patterns show the 1-D nanorod morphology of the α– and β– phases (Fig. 1a and 1b). Further tuning of the reaction condition to a lower temperature yields a flower-like morphology of the α-MnO_2. Followed by this, Pt nanoparticles were nucleated on the rods/flowers to make the inorganic catalyst nanohybrid. Fig. 1d shows the atomic structure of the [001]-oriented a- and b- MnO2 nanowires, depicting a clear difference in surface termination, which might be a reason of their different reducibility.

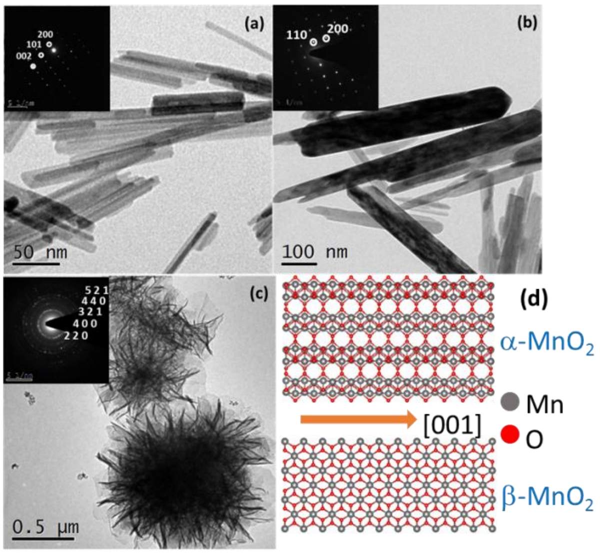

Figure 1. TEM bright field images of the catalysts: (a) α-MnO_2 nanorods, (b) β-MnO_2 nanorods and (c) α-MnO_2 flowers - their respective electron diffraction patterns are shown in the insets. (d) Schematic showing the atomic arrangements of [001]-oriented MnO_2 nanowires of the two different phases.

	α-MnO_2 rods-2%Pt	α-MnO_2 flowers-2%Pt	β-MnO_2 rods-2%Pt
T_{100} (°C)	120	90	140
Activation Energy (E_a) kJ/mol	96.10	83.06	102.53
BET specific S.A. m^2/g	54	118	42
Stability studies (h) at T_{100}	24	11	24

Table 1. Summary of catalytic activities (T_{100}) and the specific surface area of Pt-decorated MnO_2 supports.

The CO oxidation profiles for all the catalysts were thoroughly studied and activation energies are represented in Table 1. Owing to higher reducibility, catalytic hybrids with the α-phases exhibit better activity.

4. Conclusions:

α- and β- phases of MnO_2 with different morphologies were synthesized by a facile hydrothermal technique, followed by the nucleation of Pt nanoparticle by a microwave technique to make catalytic hybrids for CO oxidation. These hybrids show high CO oxidation activity in a temperature range of 50-150 °C. The CO oxidation experiments were also done on bare oxides to compare their performances. The Interestingly, the best activity is shown by 2 wt% Pt decorated-α-MnO_2 flowers which gives a full conversion of CO at 90 °C. The stability studies suggest that this catalyst is stable at T_{100} for 11 h. The high activity of the catalyst is supported by the activation energy calculations (83.06 kJ mol^{-1}) and the specific surface area measurements (118 m^2 g^{-1}), along with the higher reducibilityof α-MnO_2 surfaces compared to that of the β-phase.

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