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Silver/hydroxyapatite foam as a highly selective catalyst for acetaldehyde production via ethanol oxidation

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ABSTRACT

In this study, highly dispersed sliver (Ag) nanoparticles supported on a hydroxyapatite showed a surprisingly high activity (1.38 s^{-1} in turnover frequency (TOF)), selectivity (~100%) and durability (~100 h) for the oxidative dehydrogenation of ethanol to acetaldehyde. The structure of Ag nanoparticles is characterized using transmission electron microscopy (TEM), X-Ray Diffraction (XRD), in-situ and ex-situ X-ray photoelectron spectroscopy (XPS) and temperature-programmed surface reaction (TPSR). Density Functional Theory (DFT) calculations on Ag(1 1 1) were performed to understand the mechanism of catalytic reactions at a molecular level. The calculation results revealed that the barrier for the formation of acetaldehyde is 38.6 kJ/mol, and 126.4 kJ/mol for CO_2 formation, thus leading to high selectivity to acetaldehyde. By combination of DFT calculation and experimental work, it can be concluded that ethanol oxidation predominantly took place on the terrace surface although step surface are more active. This study provides a methodology to develop completely selective practical catalysts especially for the utilization of biomass.

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1. Introduction

Selective oxidation/dehydrogenation of ethyl alcohols to aldehydes, ketones and carboxylic acids is both technically and fundamentally important, and found to be an essential reaction in the utilization of biomass [1–3]. Bioethanol has been regarded as a key building block in future biorefinery industry. The transformation of bioethanol to value-added chemicals has attracted growing concerns in the last decades [4–7].

Acetaldehyde is an important intermediate for the production of chemical commodities such as acetic acid, acetic anhydride, hydrocyanic acid, ethyl acetate, alkylamines and pyridines [8]. Commercial processes for acetaldehyde production include the oxidation or dehydrogenation of ethanol, the addition of water to acetylene, the partial oxidation of hydrocarbons and the direct oxidation of ethylene. The last route, also named as the Wacker process, is the primary method for industrial production [8].

With the ever-growing of the world output of bioethanol, the production of acetaldehyde *via* alcohol oxidation has been gradually considered a feasible process. Indeed, a gas-phase process was commercialized by passing alcohol vapors and preheated air over silver (Ag) catalysts at 753 K, with a conversion of 74–82% and a selectivity of ca. 80% [9]. However, the high cost of Ag catalysts (Ag powder or inorganic Ag compounds) became the major drawback of this process [10,11]; Ag nanocatalysts may be a promising alternative. However, owing to the poor thermal conductivity of Ag, highly dispersed Ag particles are easily sintered and aggregated at elevated temperatures, which usually leads to a remarkable catalyst deactivation. In addition, acetic acid, as a byproduct, even with a trace amount in the reaction system, can erode the reactor seriously at high reaction temperatures, thus leading to the rise of the operational cost. Platinum group elements, IB and IIB group elements have also been studied for this reaction; however, either the selectivity or activity of those catalytic reactions doesn't meet the industrial demands [12,13]. Therefore, the development of novel catalysts for this process is highly desired in biorefinery industry. Aldehydes production with a complete selectivity from oxidation/dehydrogenation of alcohols is both technically and fundamentally challenging. In general, for the sustainable development of economics, the complete selectivity reaction is a main mission in catalysis field in the future.

For the fundamental aspects, the studies of oxidative dehydrogenation of ethanol over Ag catalysts have rarely been reported so far [14–16]. Wachs and Madix [17,18] have proposed a

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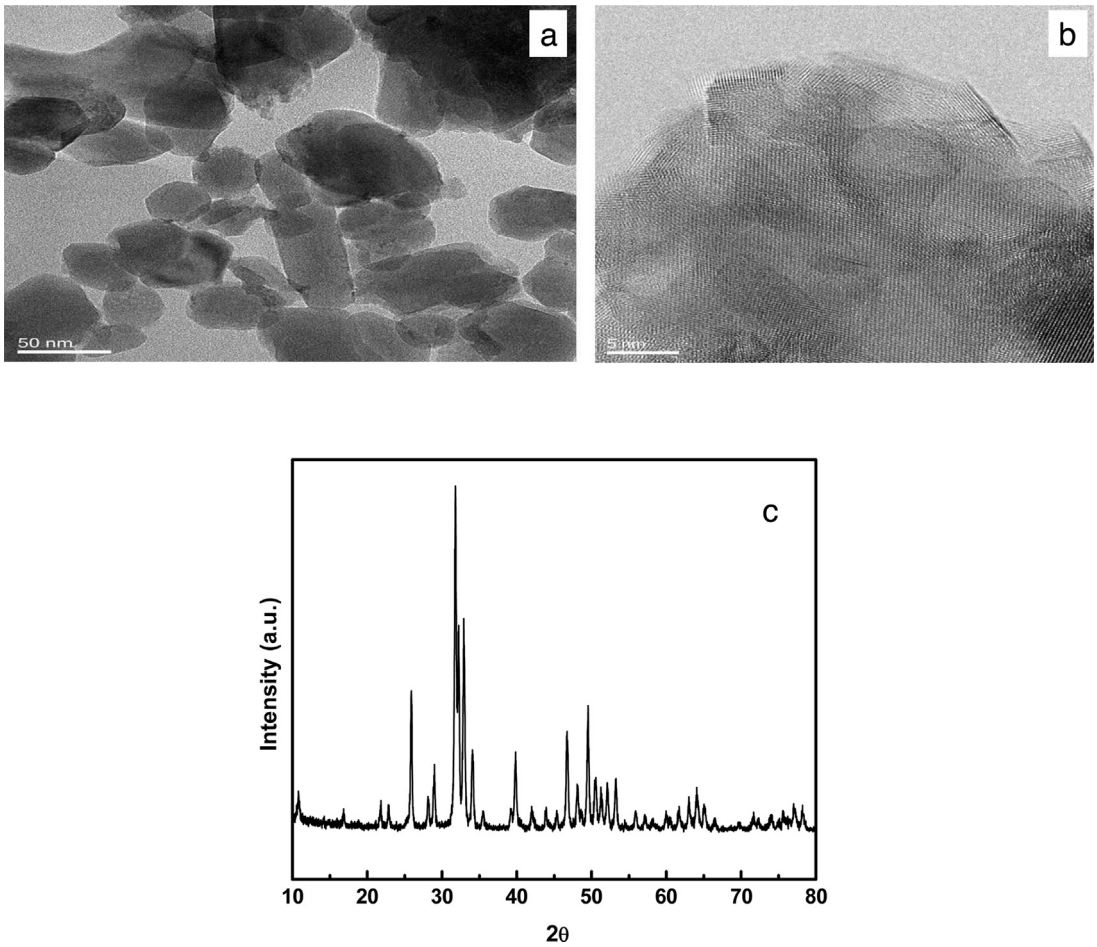

Fig 1. (a,b) TEM images and (c) XRD patterns of HAp.

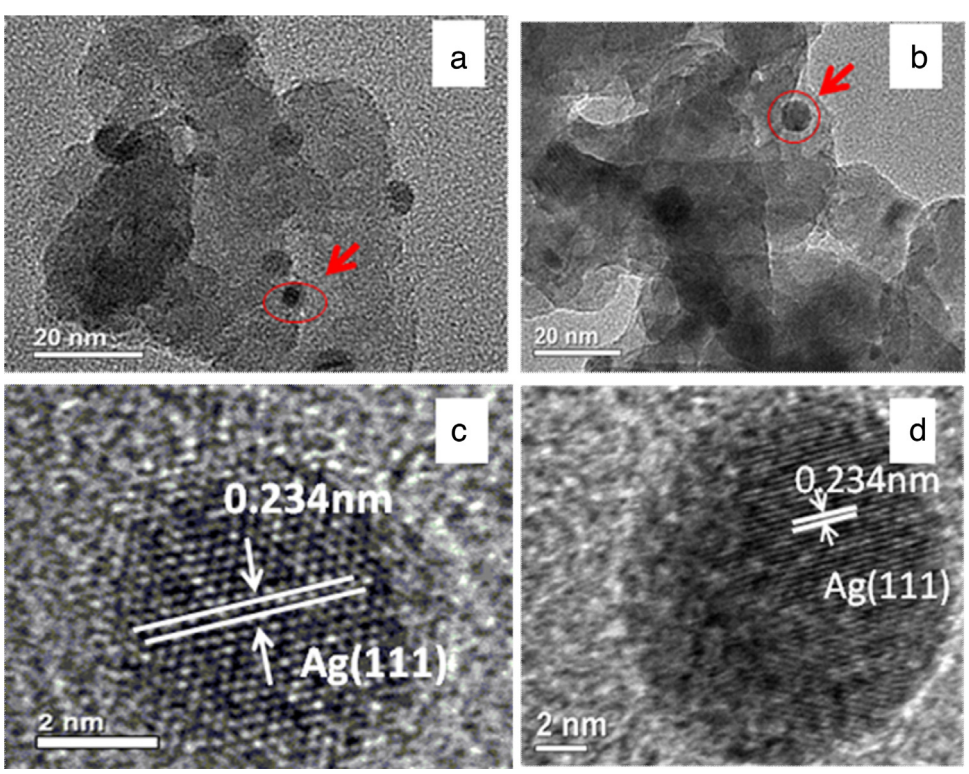

Fig. 2. Morphology of Ag nanoparticles over the fresh (a and c) and spent (b and d) (0.5 wt%)/HAp catalyst by TEM.

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