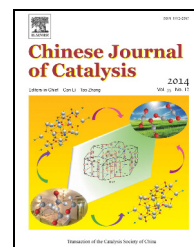


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Article

Formaldehyde catalytic oxidation over hydroxyapatite modified with various organic molecules

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ABSTRACT

Hydroxyapatite (HAP) was modified by adding various organic molecules, such as cetyltrimethylammonium bromide, sodium dodecyl sulfate, and sodium citrate, during the precipitation of HAP. Sodium citrate-modified HAP displayed the best activity for formaldehyde oxidation, achieving complete conversion at 240 °C. The influence of the organic modifiers on the structure of HAP was assessed by X-ray diffraction, Fourier transform infrared spectroscopy, N₂ adsorption-desorption, scanning electron microscopy, and thermogravimetry/derivative thermogravimetry. The higher specific surface area and pore volume, and smaller pores, owing to modification with sodium citrate, favored adsorption, mass transfer, and interaction process during formaldehyde oxidation. Furthermore, the higher hydroxyl group content observed in sodium citrate-modified HAP enhanced interactions between formaldehyde and HAP, thus resulting in higher catalytic activity.

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1. Introduction

As one of the most common volatile organic compounds, formaldehyde (HCHO) is generating increasing attention as it poses potential health risks to humans even at low concentrations. Thus, the removal of HCHO has become an important issue [1,2]. Numerous studies have been carried out for the abatement of HCHO; the main techniques being investigated are adsorption, plasma decomposition, biological/botanical filtration, and catalytic oxidation [1]. Among all these techniques, catalytic oxidation is a promising method for HCHO removal because of its efficiency, convenience, and no secondary pollution. Commonly studied catalysts include noble metals (e.g., Pt, Au, Pd, and Ag) [3–6] and transition metal oxide catalysts (e.g., MnO_x and CeO₂) [7–9]. Moreover, transition metal

oxides are usually employed as substrate for loading noble metal catalysts [10–13]. Noble metal-loaded catalysts show relatively better activities towards HCHO oxidation (complete conversion is generally achieved at around 100 °C or below) [5,14]. However, the high cost of noble metal limits the wide practical application of noble metal catalysts. For transition metal oxides, complete HCHO conversion temperatures are generally above 100 °C, and even above 200 °C under some circumstances [7,9,13]. Besides poor performance, the toxicity of some commonly used transition metal oxides (MnO_x) limits the application of such catalyst systems [15,16]. In recent years, many studies on HCHO catalytic oxidation have been conducted to improve the catalytic performance. However, the studied catalytic systems are still focused on noble metal catalysts and transition metal oxides such as MnO_x, Ag/CeO₂, Co₃O₄, and

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Pt/CeO₂ [17–22]. The drawbacks of such catalytic systems are yet to be addressed. Thus, economical, safe, and non-toxic novel materials are required for HCHO catalytic oxidation.

As the main inorganic component of natural bone and teeth, with a wide application in the field of biomedical materials as biological active materials, hydroxyapatite (HAP) is safe and non-toxic [23]. Moreover, unlike noble metals, HAP is a cheaper alternative. In 2010, Xu *et al.* [24] reported HAP as a promising novel, non-precious metal catalyst for HCHO combustion, whereby the hydroxyl groups bonded to the Ca²⁺ channels may act as active sites.

To date, the examination of HAP as a catalytic material for HCHO oxidation remains rare. However, as a novel, non-precious metal catalyst with demonstrated activity towards HCHO oxidation, HAP is worth exploring further. It is well known that the catalyst performance is closely related to its structure. Based on the reported study [1], HCHO adsorption and its interaction with the support are related to the HCHO oxidation process. In that case, larger adsorption areas and abundant interaction between the reaction gas and catalyst will be important for activity enhancement. Organic modifiers have been widely used in morphology- and size-controlled synthesis of nano-sized metals and inorganic materials, as well as for the generation of pores and vacancies in the structure [25–30]. To this effect, in this study, organic modifiers (*i.e.*, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and sodium citrate (SC)) were employed during the synthesis of HAP to modify its structure. Various characterization techniques and subsequent activity tests were conducted to elucidate the structure-performance relationship.

2. Experimental

2.1. Preparation of catalysts

HAP powder was prepared through an aqueous precipitation-hydrothermal method using (NH₄)₂HPO₄ (AR, Kemiou Chemical Reagent Co., Ltd, Tianjin) and Ca(NO₃)₂·4H₂O (AR, Damao Chemical Reagent Factory, Tianjin) as precursors. Ammonia (NH₃) solution (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai) was used for pH adjustments during the precipitation process. A solution of 0.2 mol/L Ca(NO₃)₂·4H₂O (4.72 g in 100 mL deionized water) containing an organic modifier (5 wt%, CTAB (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai), SDS (AR, Kemiou Chemical Reagent Co., Ltd, Tianjin), or SC (AR, Reagent No. 1 Factory of Shanghai Chemical Reagent Co., Ltd., Shanghai)) was stirred under a constant temperature of 40 °C. A solution of 0.3 mol/L (NH₄)₂HPO₄ (1.58 g in 40 mL deionized water) was added dropwise to the Ca(NO₃)₂·4H₂O solution. Then, the pH of the suspension was adjusted to 10 with ammonia solution (35%), followed by 8 h of reaction under stirring. Subsequently, the reaction solution was transferred to a Teflon-lined autoclave and heated at 100 °C for 12 h. Finally, the resulting powders were centrifuged and washed multiple times and dried at 100 °C overnight and then calcined at 700 °C for 2 h. The obtained HAP samples were denoted as HAP_{CTAB}, HAP_{SDS}, and HAP_{SC}. Non-modified HAP was also syn-

thesized using the same procedure for comparison studies and denoted as HAP_{BLANK}.

2.2. Characterization of catalysts

The crystallinity of the catalysts was established and identified by X-ray diffraction (XRD, Rigaku D/max- γ b X-ray diffractometer, Japan) using Cu K α radiation in the 2 θ range of 10°–80° at room temperature. Fourier transform infrared spectroscopy (FTIR) was carried out on specimens that were prepared into pellets containing the HAP samples and KBr. FTIR spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer (Japan) in the range of 4000–400 cm⁻¹. A background spectrum of KBr was subtracted from each sample spectrum. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6360 scanning electron microscope (USA) operating at an acceleration voltage of 20–30 kV. N₂ adsorption-desorption measurements were carried out on a Quantachrome Quadrasorb S1 (USA). Prior to analysis, each sample was heated at 200 °C for 4 h under vacuum. Surface areas were calculated using the BET method. The pore size was calculated using the BJH model. Thermogravimetry/derivative thermogravimetry analysis (TG/DTG) was performed on a WCT-1C thermobalance (Beijing) in the temperature range of 20–900 °C.

2.3. Catalytic activity tests

HCHO oxidation activity tests were carried out in a fixed-bed flow reactor under atmospheric pressure. Typically, 0.2 g catalyst was loaded in a quartz tube reactor for activity test. The catalyst was calcined at 400 °C for 1 h in an O₂/Ar flow before the reaction. During the reaction, gaseous HCHO was generated by flowing He over trioxymethylene (99.5%, Acros Organics) in an incubator placed in an ice-water mixture. The feeding stream consisted of 500 ppm HCHO, 20 vol% O₂, and balanced He; the total flow rate throughout the reactor was maintained at 30 mL/min by a mass flow meter. The effluents from the reactor were analyzed by an online gas chromatograph (GC 7890II, Techcomp, China) equipped with a flame ionization detector (FID). To determine the exact concentration of produced CO₂, a nickel catalyst converter was positioned in front of the FID to convert CO₂ quantitatively into methane in the presence of hydrogen. Generally, the reaction data were collected until reaction balance was reached. No other carbon-containing compounds except for CO₂ in the products were detected for all the tested catalysts. Thus, the HCHO conversion was calculated as: HCHO conversion = [CO₂]/[CO₂]* × 100%, where [CO₂]* and [CO₂] represent respective concentrations of CO₂ detected in the effluent when HCHO is completely oxidized and at a given reaction temperature, respectively.

3. Results and discussion

3.1. Catalytic activity for HCHO oxidation

The catalytic activities of HAP_{BLANK} and modified HAP sam-

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