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Gas-phase selective oxidation of alcohols: In situ electrolytic nano-silver/zeolite film/copper grid catalyst

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Abstract

The selective oxidation of a series of alcohols to their corresponding carbonyl products was carried out over a rationally designed in situ electrolytic nano-silver/zeolite film/copper grid (SZF) catalyst, which was prepared by a combination of the seed-film method for the fabrication of an ultrathin zeolite film and the in situ electrolytic process for the formation of highly dispersed silver nanoparticles. At a relatively low reaction temperature (ca. 320 °C), the SZF catalyst with highly dispersed in situ electrolytic silver nanoparticles exhibited much higher activity for the oxidation of mono-alcohols and higher selectivity for ketonic aldehyde in the oxidation of di-alcohols than the conventional bulk electrolytic silver catalyst. On the basis of the combination of diffuse reflectance ultraviolet visible spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and thermoanalysis, the remarkably high activity and selectivity of the SZF catalyst was attributed to the highly dispersed silver nanoparticles, which were stabilized by the zeolite film against sintering, and, accordingly, a large amount of Ag^+ ions and $Ag_n{}^{\delta+}$ clusters existed in the silver nanoparticles. The improvements of the catalytic performance of the SZF catalyst in a wide application extension will bring new concerns in both theoretical and applied fields.

Keywords: In situ electrolytic silver nanoparticles; Zeolite film; Alcohol; Carbonyl; Selective oxidation

1. Introduction

Selective oxidation of alcohols to carbonyls in the gas phase is one of the most important chemical transformations in industrial chemistry because of the significance of ketones and aldehydes in the syntheses of drugs, vitamins, and fragrances, as well as in many complex syntheses [1–3]. Currently the focus is on two types of reactions: the selective oxidation of mono-alcohols (Eq. (1)) [4,5], where the desired products are often those of moderate oxidation (i.e., aldehydes and ketones), and the selective oxidation of polyhydric alcohols (Eq. (2)) [1,2,6], where the target products are often moderately oxidized compounds. Products of lean oxidation (α-hydroxyketone), and overoxidation (carboxyl acid, CO_2) or cracking should be avoided. The complexity of the selective oxidation of polyhydric alcohols is due more to the catalyst design.

Up to now, several silver-based catalysts, including bulk silver and supported silver catalysts, have been developed for the oxidation of alcohols [7–10]. However, some serious problems are still encountered in the application of such catalysts. For example, in conventional bulk silver (e.g., industrial electrolytic silver), the low catalytic activity at low temperature often leads to the formation of byproducts of lean oxidation (e.g., α-hydroxyketone). In contrast, at a higher reaction temperature (>500 °C), the products of cracking and/or overoxidation are mainly obtained. Attempts have been made to improve the catalytic performance of silver-based catalysts by either adding additives to bulk silver catalysts [7] or dispersing the silver particles on suitable supports [11]. Supported silver is expected to enhance the dispersion and stability (i.e., antisintering ability) of silver, and thus also enhance its catalytic activity at relatively low temperatures. However, compared with bulk silver cata-

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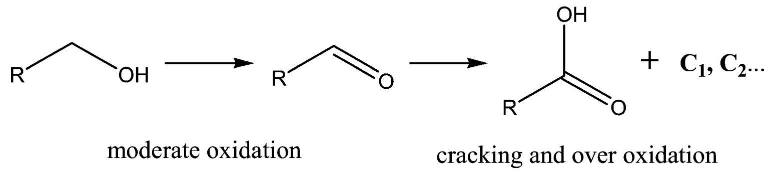
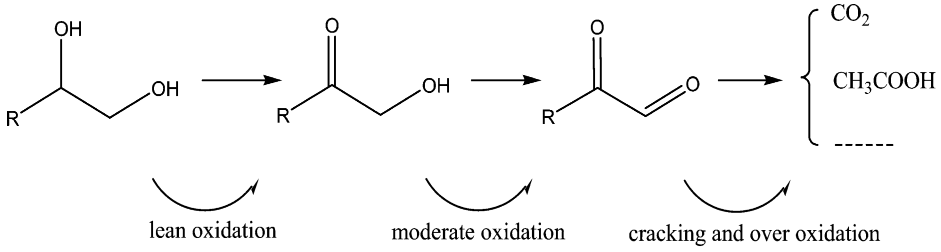


(1)



(R= H, CH_3, CH_3CH_2......)

(2)

lysts, supported silver catalysts usually have a low heat conductivity, which greatly restricts their practical application, especially in some strongly exothermic oxidation reactions. Hence the design of a catalyst with elaborate structure and better performance remains a challenge for research on alcohol catalytic oxidation, especially those with relatively complex molecular structures (e.g., polyhydric alcohols), for which the currently available catalysts are inapplicable because of their complex selectivity and/or low activity at low temperatures. The development of a catalyst combining the advantages of both the bulk silver catalysts (e.g., conventional electrolytic silver) and the supported silver catalysts would be highly desirable for this purpose.

In our previous communication [1], we developed a novel silver-based catalyst for the selective oxidation of 1,2-propylene glycol through the in situ generation of electrolytic silver nanoparticles over an ultra-thin zeolite film precoated on a copper grid. It was suggested that the zeolite film would hinder sintering of the highly dispersed silver nanoparticles [12,13] and thereby endow the catalyst with high activity and selectivity for the selective oxidation of 1,2-propylene glycol at a relatively low temperatures. Furthermore, because of the existence of the copper grid substrate, the catalyst has a high thermal conductivity, which is beneficial to the exothermal oxidation reaction. In this paper we report an in-depth and wide-ranging investigation of the origin of the high activity of this novel nanosilver/zeolite film/copper grid (SZF) catalyst at low temperature and the possibility that excellent catalytic performance can be embodied in selective oxidation covering a wide range of alcohols with different physical and chemical features. A series of alcohols with different molecular structures and/or numbers of hydroxyl groups are used as the reactants to investigate the applicability of the SZF catalyst. The reasons for the SZF catalyst's high activity and selectivity are explored through detailed characterizations of the prepared catalyst by diffuse reflectance ultraviolet visible spectroscopy (UV–vis DRS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and thermoanalysis.

2. Experimental

2.1. *Catalyst preparation*

The copper grid was coated with a thin zeolite film by a previously developed seed-film method [14]. Typically, the copper grid was first seeded with a monolayer of nanosized zeolite LTA with the aid of cationic polyelectrolytes. Then the seeded copper grid was immersed in a solution with the molar ratio of 80 Na_2O:Al_2O_3:9 SiO_2:5000 H_2O at 80 °C for 5 h to fabricate the zeolite film-coated copper (ZFC) grid. Afterwards, the ZFC grid was used as the cathode in an electrolytic cell containing 5 wt% $AgNO_3$ solution to prepare the target SZF catalyst. The electric current density of the electrolytic process was 16 $\mathrm{A\,dm^{-2}}$, the electrolysis temperature was 55 °C, and the time was 1 min. The catalyst was finally calcined in air at 400 °C for 2 h.

For comparison, a bulk electrolytic silver catalyst was prepared by a traditional electrolytic process with silver as an anode and platinum plate as a cathode under the same conditions as the SZF catalyst.

The silver content in the SZF catalyst was determined to be 7 wt% by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis, and the Si/Al ratio of the zeolite film was measured as 1 (the typical value of zeolite LTA) by energy-dispersive X-ray (EDX) analysis. The surface area of silver in the two catalysts was measured through the hydrogen–oxygen titration method. The surface area of the in situ electrolytic silver nanoparticles in the SZF catalyst was about 74 $\mathrm{m^2\,g^{-1}}$, whereas that of the bulk electrolytic silver prepared by conventional process was $<1\ \mathrm{m^2\,g^{-1}}$.

2.2. *Catalyst characterization*

The SEM and TEM images of the catalysts were obtained on Philips XL30 and JEOL JEM-2010 instruments with acceleration voltages of 20 and 200 kV, respectively. The TG and DTA data were recorded in air atmosphere on a Perkin–Elmer 7 thermal analyzer. The XPS analysis was carried out with a