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A novel catalyst with high activity for polyhydric alcohol oxidation: nanosilver/zeolite film†

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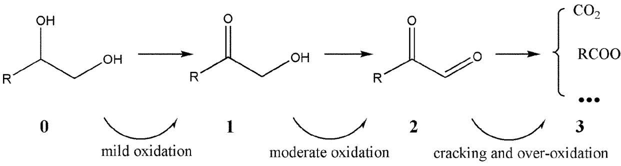
A novel catalyst of silver nanoparticles over a zeolite film-coated copper grid (SZFC) has been fabricated *via* an *in situ* electrolytic method; it exhibited high catalytic activity and selectivity at a relatively low temperature for the partial oxidation of 1,2-propylene glycol to methyl glyoxal.

Nowadays tens of millions of chemical products are obtained through industrial processes involving silver-based catalysts, *e.g.* oxidation of ethylene to ethylene oxide,[1] methanol to formaldehyde,[2] ethylene glycol to glyoxal,[3,4] and 1,2-propylene glycol to methyl glyoxal. Recently, there has been great interest in the application of silver-based catalysts in the field of fine chemistry such as the partial oxidation of polyhydric alcohol. The reactions involved in this process include:



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

Generally, it is desired for the reaction process to stop at product **2**, avoiding both mild oxidation product **1** and the over-oxidation products **3**. However, for commercial silver catalysts (*e.g.* electrolytic silver), insufficient catalytic activity often results in the generation of a large amount of the mild oxidation product, α-hydroxyketone, at low temperature. To obtain the required oxidation activity for the target product **2**, a higher reaction temperature (*e.g.* 600 °C) is usually adopted. However, such a high reaction temperature would often lead to the over-oxidation of the reactant to CO_2, the cracking of C–C chains as well as the sintering of the silver catalyst. To avoid these side-reactions at high temperature and enhance the activity of the silver catalyst at low temperature, one of the most effective methods is to load silver nanoparticles onto suitable supports to realize a high degree of dispersion of the silver.[5] However, compared with commercial electrolytic silver catalysts, the supported silver catalysts often bring about low heat conductivity, which becomes a barrier to their practical application, especially for strongly-exothermic oxidation reactions.

In this paper, we developed a novel silver-based catalyst by *in situ* generation of the electrolytic silver nanoparticles over a thin zeolite film which was pre-coated on a copper grid. Because of the strong hindering effect of zeolitic pores/cages for the agglomeration of metal nanoparticles,[6,7] the silver component could remain highly dispersed. As a result, this catalyst not only possesses a suitably high activity in the partial oxidation of polyhydric alcohol to product **2** at a relatively low temperature, it also eliminates the over-oxidation and/or C–C bond cracking of the polyhydric alcohol at a high temperature as had occurred on the conventional electrolytic silver catalyst. Moreover, its high heat-conductivity and the flexible shape of the copper substrate made the catalyst suitable for exothermic reactions and facilitated the design of reactors.

The detailed procedure for the catalyst preparation is shown in Fig. 1. The copper grid was coated with a thin zeolite film by a previously developed seed-film method.[8] Typically, the copper grid was first seeded with monolayer nanosized zeolite LTA[9] through a layer-by-layer method.[10] 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 grid (ZFC). In order to obtain the target silver-loaded ZFC catalyst (SZFC), the ZFC was placed in an electrolytic cell with 5 wt% $AgNO_3$ solution as the electrolyte, ZFC as the cathode and silver as the anode. The electrolytic process was carried out at an electric current density of 16 A dm^{-2} at 55 °C for 60 s. The final catalyst was obtained *via* calcination at 400 °C for 2 h.

Fig. 2a shows a typical SEM image of the prepared ZFC. As

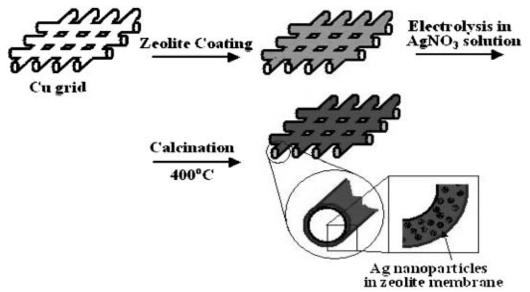


Fig. 1 The schematic illustration for the fabrication of the SZFC catalyst.

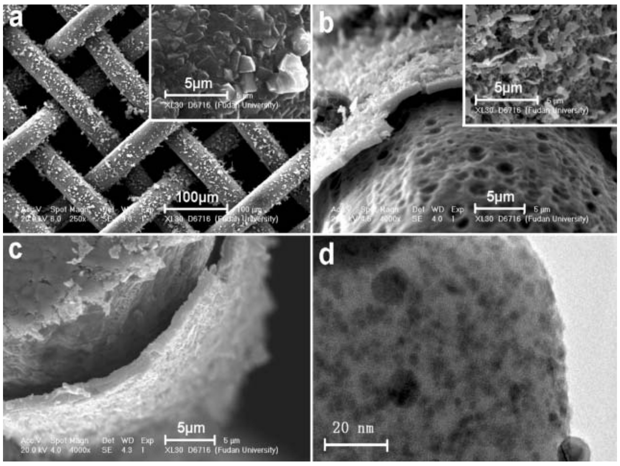


Fig. 2 SEM images of ZFC (a), SZFC before (b) and after calcination (c) and TEM image of SZFC after calcination (d).

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† Electronic supplementary information (ESI) available: XRD pattern and stability tests of SZFC. See http://www.rsc.org/suppdata/cc/b4/b412986e/
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Table 1 Conversion and product distribution of 1,2-propylene glycol oxidation over SZFC and electrolytic silver catalysts[a]

					Selectivity/mol %		
Catalyst	Weight/g	LHSV/g h^{-1} g^{-1}	Temperature/°C	Conversion (%)	α-Hydroxyacetone	Methyl glyoxal	Over-oxidation & cracking product
SZFC	0.08	40	240	70.2	31.9	60.8	7.3
			280	81.4	21.2	69.3	9.5
			320	92.8	10.6	75.6	13.8
			360	94.3	7.7	69.2	23.1
Electrolytic silver	1.0	3.2	240	60.7	76.4	21.4	2.2
			280	76.4	68.1	28.5	3.4
			320	83.6	64.5	32.2	3.3
			360	89.8	58.4	37.9	5.7
ZFC	0.08	40	360	1.3	95.1	3.2	1.7

[a] A continuous fixed bed reactor system was adopted; O_2/alcohol = 1.2; O_2 flow = 19 ml min^{-1} (STP); N_2 flow = 300 ml min^{-1} (STP); amount of alcohol inlet = 3.2 g h^{-1}.

shown in the inset of Fig. 2a at high magnification, the surface of the copper grid has been covered with a compact zeolite film with a mean crystal size of *ca.* 1 μm (Fig. 2a, inset) and a film thickness of *ca.* 1 μm (*cf.* Fig. 2b) through hydrothermal treatment. It is clear that after electrochemically treating ZFC in the $AgNO_3$ solution, a layer of silver nanoflakes has grown from the pre-coated zeolite film. After calcination at 400 °C, the silver flakes disappeared and were converted to highly-dispersed silver nanoparticles in the zeolite film, as shown in Figs. 2c and 2d. Almost all of the silver nanoparticles were averagely dispersed at a size of 2–3 nm except for a few larger ones of 10 nm (Fig. 2d). The XRD pattern of the product (see ESI†) clearly shows the diffraction peaks of metallic Ag, and the ICP analysis result shows that the silver content in the catalyst was about 7 wt%. The EDX analysis shows that the Si : Al ratio of the zeolite film was *ca.* 1, the typical value for zeolite LTA.

The oxidation of 1, 2-propylene glycol in oxygen was adopted to investigate the catalytic performance of SZFC for the partial oxidation reactions of polyhydric alcohols. The target product of this reaction is the moderate oxidation product, methyl glyoxal, a very important fine chemical applied as an intermediate in imidazole synthesis[11] and the research and application of biochemistry.[12] Table 1 displays the relationship between the conversion/selectivity of 1,2-propylene glycol oxidation and reaction temperature of both SZFC and a commercial electrolytic silver catalyst. ZFC is almost catalytically inert to the reaction as shown in Table 1. It is clear that the SZFC presents higher activity than that of a conventional electrolytic silver catalyst even when the weight of the former catalyst is much lower (or the LHSV of the former is much higher) than that of the latter (Table 1). The activity improvement of the silver component in the SZFC could be further reflected by the distribution of products. The dominant product on the electrolytic silver catalyst is the mild oxidation product, α-hydroxyacetone, in the experiment temperature range of 240 to 360 °C. However, for the SZFC, the target product with a moderate degree of oxidation, methyl glyoxal, becomes the prominent product even at 240 °C, and reaches an optimal selectivity of 75.6% at 320 °C. When the reaction temperature was raised further, the by-product of over oxidation and cracking considerably increased, leading to a decrease of selectivity. The high activity and selectivity to methyl glyoxal of the SZFC at a relatively low temperature could be attributed to the high dispersion of silver in the zeolite film of SZFC.

In conclusion, a novel silver catalyst was fabricated by *in situ* generation of electrolytic silver nanoparticles on the ZFC based on the strong hindering effect of zeolite film on the agglomeration of metal nanoparticles. The catalyst with highly dispersed silver nanoparticles exhibits a suitable oxidation activity of 1,2-propylene glycol to methyl glyoxal, the moderate oxidation product, at a relatively low temperature. The performance of SZFC effectively avoids the problems of either over-oxidation and C–C bond cracking at a high temperature or the mild oxidation at a low temperature as in the case of the practical electrolytic silver catalyst. In addition, the copper substrate of the catalyst provides high heat-conductivity that benefits the strongly-exothermic oxidation reactions.

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