Efficient hydrogenation of dimethyl oxalate to methyl glycolate over highly active immobilized-ruthenium catalyst

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ABSTRACT

Highly active and stable catalysts for hydrogenation of dimethyl oxalate (DMO) to methyl glycolate (MG) were desirable but highly challengeable. In this study, a kind of immobilized Ru based catalyst for the hydrogenation of DMO has been developed. The catalyst was synthesized by covalently bonding a ruthenium complex onto the modified-SiO_2 surface, which was modified by 3-aminopropyltriethoxysilane (KH550), through coordination interaction with aminosilane ligands. Compared with the traditional Ru/SiO_2 catalyst, the immobilized $Ru-NH_2-SiO_2$ catalyst exhibits significantly enhanced catalytic performance and high stability towards hydrogenation of dimethyl oxalate to MG at temperatures as low as 80 °C. The yield of MG was 86.8% over $Ru-NH_2-SiO_2$ catalyst, while the yield of MG was only 34.5% over Ru/SiO_2 catalyst. A series of characterization revealed that the excellent catalytic performance of $Ru-NH_2-SiO_2$ was resulted from the superior dispersion of Ru NPs on the surface of support and the electron-rich state of Ru centers.

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1. Introduction

With the increasing concerns of energy shortage and environmental pollution, great efforts have being devoted to develop the way of green and eco-friendly utilization of coal resources and further synthesis of highly value-added compounds. Among these coal resources, C1 chemical research has attracted much more attention all over the world. Hydrogenation of dimethyl oxalate (DMO) synthesized from syngas to methyl glycolate (MG) is one of the great productive applications for the C1 chemistry [1,2].

The use of MG is widespread as its unique molecular structure, which has both hydroxyl and ester groups in the molecule. MG is an important fine chemical intermediate, which can be used as a raw material for the synthesis of glycol, glycollic acid, polyglycolic acid and other organic chemicals [3]. Recently, several methods for the production of MG have been developed. For example, it can be synthesized from the carboxylation of formaldehyde, the coupling method of methyl formate and the hydrogenation of DMO [4–6]. Typically, the hydrogenation of DMO to MG is more attrac-

tive for that it is more economical and eco-friendly compared with its synthesis from methyl formate and formaldehyde.

Several metal catalysts have been reported to be active in the hydrogenation of DMO to MG. High conversion of DMO and high yield of MG (97%) can be achieved over Ru-based homogenous catalysts [7,8]. However, the challenges in the homogenous catalyst separation and recycling greatly restricted its widespread application in industry. To address these problems, some heterogeneous catalysts are proposed to catalyze DMO to MG, such as non-noble metal Cu-based and Ni-based catalysts [9,10]. However, the yield of MG on the Cu or Ni based catalyst is extremely low at low temperature as the low activity of non-noble metal, due to low conversion of DMO. Severe reaction conditions (>200 °C) were required to obtain high conversion of DMO. Nevertheless, high temperature was in favor of the hydrogenation for another ester group of MG to ethylene glycol (EG), which drastically decreased the selectivity of MG. The MG would be the main products only when the conversion of DMO is below 70% [11]. Additionally, for the Cu-based catalyst, Cu NPs are unstable and tend to sinter at moderate-to-high temperatures during calcinations, pretreatment and catalytic process, due to the low Tammann temperature (405 °C) of copper [12]. To improve the selectivity of MG in hydrogenation of DMO, it is necessary to introduce a high activity metal, i.e. noble metal, to the catalytic system. For example, Cu/Au alloy nanoparticles were
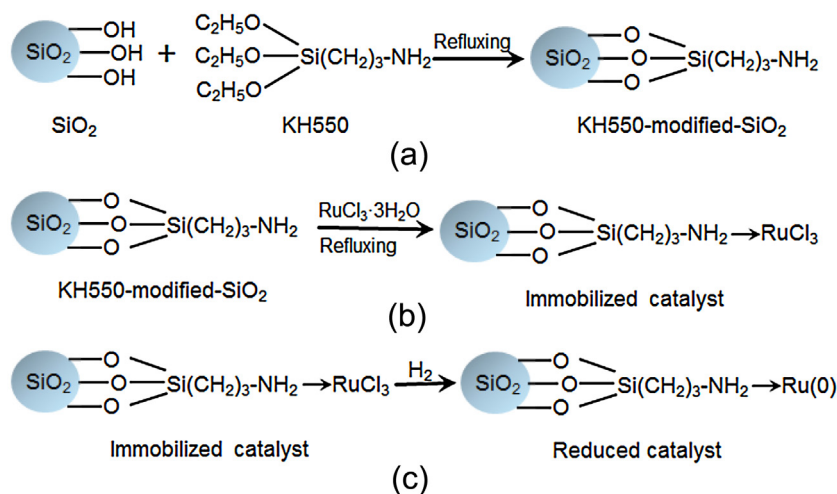
Scheme 1. (a) SiO$_2$ surface modification by KH550; (b) synthesis of the immobilized Ru-based catalyst; (c) reduction of immobilized Ru-based catalyst.

applied for the hydrogenation of DMO to obtain a yield of MG (90%) at 453 K [13]. Another type of bimetallic catalyst of Au-Ag/SBA-15 was studied for the selective hydrogenation of esters, over which DMO had high conversion and excellent selectivity to MG at 418 K [14]. However, the requirement of the noble metal Au limited its further application in industry. In order to decrease the cost, some efforts pay much attention to the catalysts of Cu/Ag or Ag-based catalyst. For example, Wang et al. reported that the high conversion of DMO can be achieved over Cu-Ag catalyst, yet the yield of MG was only 69% at 473 K [15]. Recently, Ag/SiO$_2$ catalysts were identified to be an efficient catalyst for the conversion of DMO to high yield of MG at 493 K [16]. However, the reaction temperature was still severe. As the thermosensitive substance, DMO and MG were susceptible to polymerization to produce macromolecule at the high reaction temperature. It is hence the high temperature is still a block for the hydrogenation of DMO to MG on Ag based catalysts.

Thus, it is desirable but more challenging to design an efficient catalyst to catalyze the hydrogenation of DMO to MG under mild conditions. Because of their high catalytic efficiency and stability, Ru-based catalysts have been widely used in the hydrogenation of —C=O compounds, such as the aqueous hydrogenation of levulinic acid to γ-valerolactone [17], aqueous hydrogenation of carboxylic acid [18], hydrogenation of lactic acid [19]. Among these —C=O hydrogenation reactions, the Ru-based catalysts display superior catalytic performance respectively, particularly low temperature catalytic activity. Our previous studies reported that Ru/TiO$_2$ catalyst can efficiently catalyze the hydrogenation of levulinic acid to a high yield of γ-valerolactone at the low temperature as 70 °C [17][17a]. Primo et al. demonstrated that the hydrogenation of lactic acid to 1,2-propanediol could be achieved at 150 °C 0.3 MPa over 0.64%Ru/TiO$_2$ catalyst [19]. To the best of our knowledge, the heterogeneous Ru-based catalysts have scarcely been reported in the hydrogenation of DMO to MG. Based on the above understandings, we envisage that it would be a huge breakthrough if the DMO hydrogenation efficiently to MG at low temperatures over heterogeneous Ru-based catalyst. It is hence that the metal Ru was selected as the catalytic active centers for the hydrogenation of DMO.

Some efforts reported that the support has a significant effect on the activity of the catalyst [17,20], which can be used to disperse and stabilize the metal active centers. SiO$_2$ is a common support used in preparing majority of metal based catalysts. As a kind of neutral oxide, it has good mechanical property, large surface areas and could prevent some other side reactions [21]. At present, most of supported metal catalysts are prepared by impregnation method which is relatively easy to manipulate and economical. However, there are some defects for the impregnation method. The dispersion and stability of the active metal center was poor for the catalysts as the interaction between the metal and the support was Van der Waals' force, electrostatic adsorption or weak covalent bonding. Compared to the conventional supported metal catalyst, the dispersion and stability of immobilized catalyst was better for the interaction between the metal and the support was strong covalent bonding. Our previous study revealed that the catalytic performance of Ru-NH$_2$-Al$_2$O$_3$ catalyst in the hydrogenation of levulinic acid to γ-valerolactone was significantly enhanced by immobilized method [17][17a]. By immobilization, the active metal was combined strongly with the surface of support in the form of covalent bond, which enormously improved the dispersion of active metal and stability, leading to a great potential in industrialization.

Based on the understandings, we prepared the Ru/SiO$_2$ catalyst by immobilization method. Organic silicon was introduced to modify the surface of support in order to provide ligands for the loading of the metal complexes, then through coordination bonds between the amino groups and the ruthenium metallic centers to produce the high dispersed Ru based catalyst. As typical surface modification additives, organic silicon coupling agents have being usually applied in modulating the performance of composite materials and improving interfacial adhesion accomplished via chemical reaction [22,23]. Because of its special structure, the silane coupling agent 3-aminopropyltriethoxysilane (KH550), which has two different functional groups, that is, triethoxy groups and electron-donating groups (-NH$_2$) situated at two ends [24], was attractive in modifying the support. By modification, the abundant Si-OH groups on the surface of SiO$_2$ could react with the triethoxy groups to form a firm Si-O-Si structure (Scheme 1a). More significantly, the introduced —NH$_2$ groups could anchor Ru species due to the existence of isolated electron pairs, and tremendously improved the dispersion of Ru NPs on the surface of SiO$_2$ (Scheme 1b). Particularlly, as good electron donors, the —NH$_2$ groups could endow Ru with an electron-rich state, leading to a superior catalytic performance in the hydrogenation of carbonyl groups (—C=O) as the sufficient electrons on Ru sites are in favor of π-back bonding to C=O groups [25].

In this paper, we selected KH550 as the modification reagent to modify the SiO$_2$ support to introduce the ligands —NH$_2$ for the loading of the metal complexes, and then an immobilized Ru-NH$_2$-SiO$_2$ catalyst was synthesized by bonding ruthenium active sites on the surface of KH550-modified-SiO$_2$ through coordination with amino