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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.

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 attractive 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

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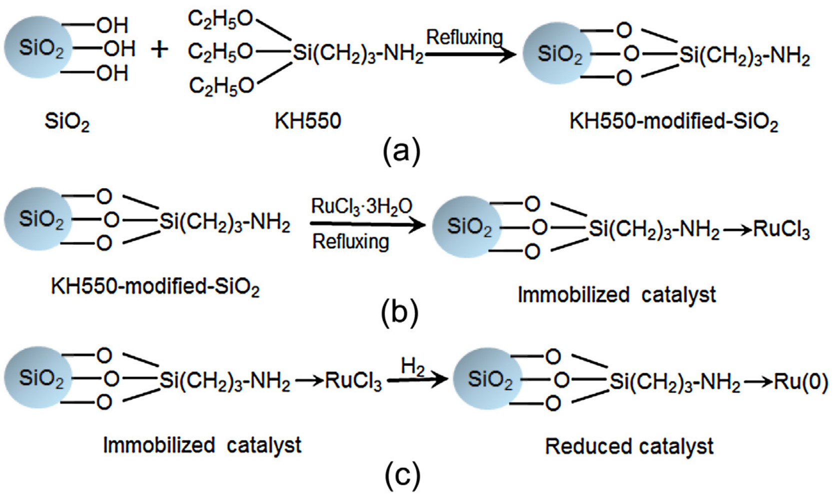

Scheme 1. (a) SiO_2 surface modification by KH550; (b) synthesis of the immobilized Ru-based catalyst; (c) reduction of immobilized Ru-based catalyst.

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_2O_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

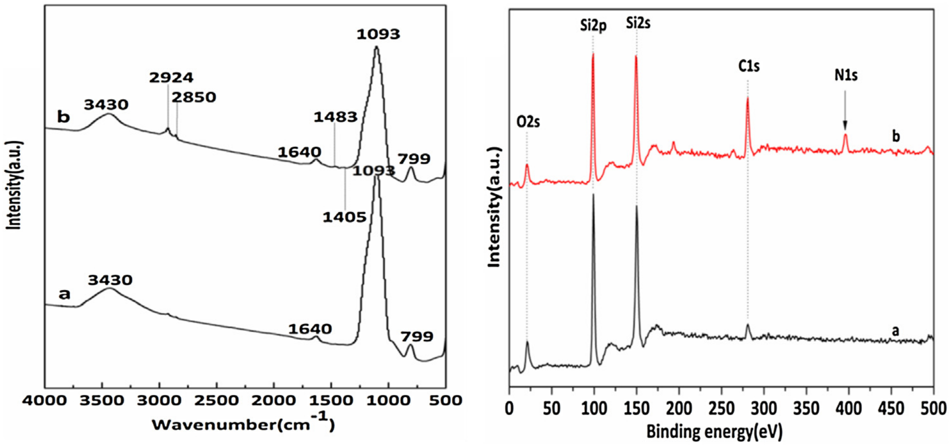

Fig. 1. (A) The FTIR spectra of (a) unmodified SiO_2 and (b) KH550-modified-SiO_2; (B) Full range XPS spectra of (a) SiO_2 and (b) KH550-modified-SiO_2.

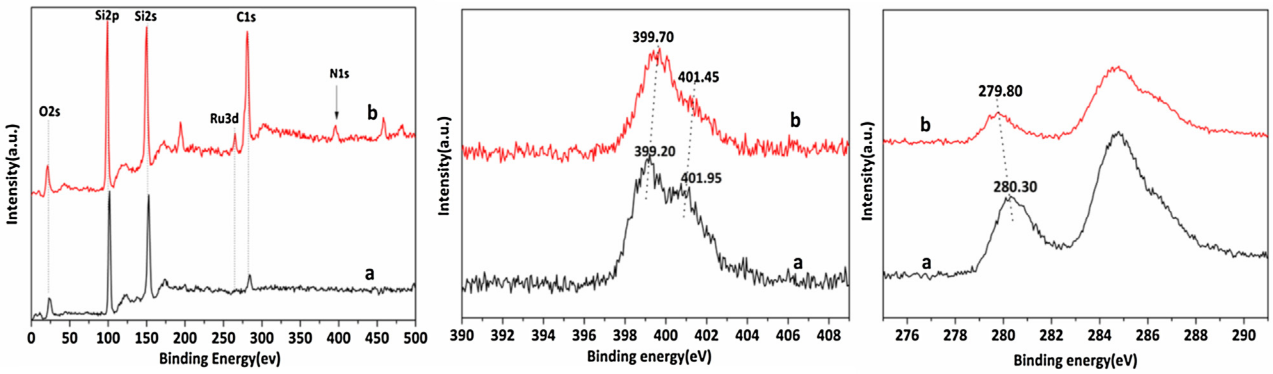

Fig. 2. (A) full range XPS spectra of (a) Ru/SiO_2, (b) Ru-NH_2-SiO_2; (B) XPS spectra of N 1s in (a) KH550-midified-SiO_2, (b) Ru-NH_2-SiO_2; (C) XPS spectra of Ru3$d_{5/2}$ in (a) reduced Ru/SiO_2, (b) reduced Ru-NH_2-SiO_2.

ligands. The reduced Ru-NH_2-SiO_2 catalyst exhibits a superior low-temperature activity and high stability. A high yield of 86.8% for MG was obtained at the temperature as low as 80 °C. The activity of the Ru-NH_2-SiO_2 catalyst did not decrease after being reused more than five times, indicating the great potential of the Ru-NH_2-SiO_2 catalyst in the hydrogenation of DMO in industrial.

2. Experimental section

2.1. Chemicals

Dimethyl oxalate, 3-aminopropyltriethoxysilane (KH550, 99%) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). SiO_2 was purchased from the Silicon Co., Ltd, of China. $RuCl_3{\cdot}3H_2O$, methanol, anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Methods

2.2.1. Preparation of Ru/SiO_2 catalyst

The catalyst containing 2.0 wt.% Ru was prepared by wet impregnation method as follows. SiO_2 was dried at 100 °C overnight before using. An aqueous solution containing $RuCl_3{\cdot}3H_2O$ was prepared, the dried support was impregnated with this solution at room temperature(25 °C) for 24 h, then dried at 100 °C for 24 h. In order to remove the chloride, Ru/SiO_2 was calcined at 300 °C for 3 h. Ahead of the reaction, the catalyst was reduced at 500 °C for 2 h in H_2 atmosphere.

2.2.2. Surface modification of SiO_2

3-aminopropyltriethoxysilane (KH550) was used as silanization agent to modify the surface of SiO_2. The modification procedure is depicted as follows: 0.1 mol SiO_2 was fetched and mixed with 120 ml anhydrous ethanol in a 500 ml flask. 0.02 mol KH550 was slowly dropped into it under stirring. Then the mixture was refluxed at 100 °C for 48 h. After cooling down to ambient temperature, the mixture was centrifuged and washed three times with anhydrous ethanol to wipe off unreacted KH550, then dried at 80 °C for 24 h.

2.2.3. Preparation of Ru-NH_2-SiO_2 catalyst

0.467 g $RuCl_3{\cdot}3H_2O$ was dissolved completely in 180 ml anhydrous ethanol, and then added 8.62 g KH550-modified-SiO_2 support. The mixture was refluxing under stirring at 100 °Cfor 24 h. After cooling down to ambient temperature, the catalyst was centrifuged and washed for three times with anhydrous ethanol, and dried at 80 °C for 24 h. Ahead of the reaction, the catalyst was reduced at 500 °C for 2 h in H_2 atmosphere.

2.2.4. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded on a D/Max-RA X-Ray diffractometer (Germany) with Cu Kαradiation operated at 30 KV and 10 mA, with a scanning rate of 4 °C/min ranging from 5° to 80°.

BET surface area was tested via N_2 physical adsorption at −196 °C on a Micromeritics ASAP 2420 instrument. All samples were degassed at 100 °C for 8 h to remove physically adsorbed impurities in vacuum.

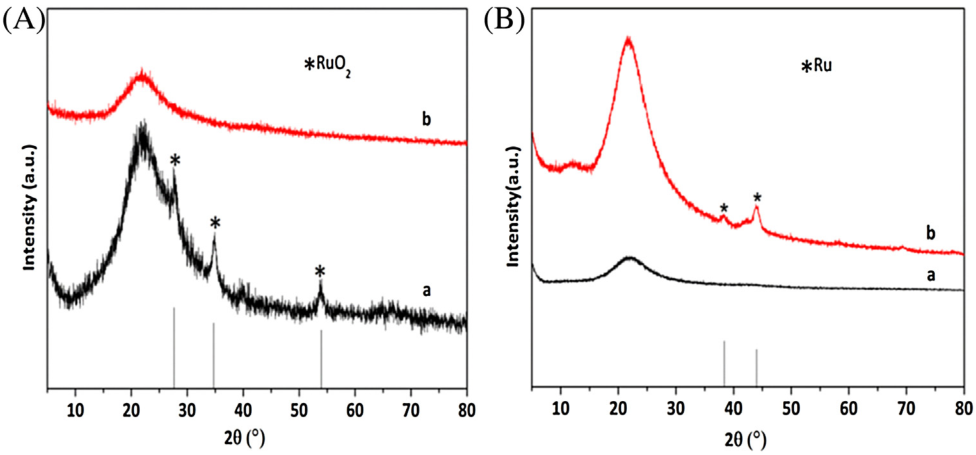

Fig. 3. (A) XRD of (a) fresh Ru/SiO_2, (b) fresh Ru-NH_2-SiO_2; (B) XRD of (a) reduced Ru-NH_2-SiO_2, (b) reduced Ru/SiO_2.

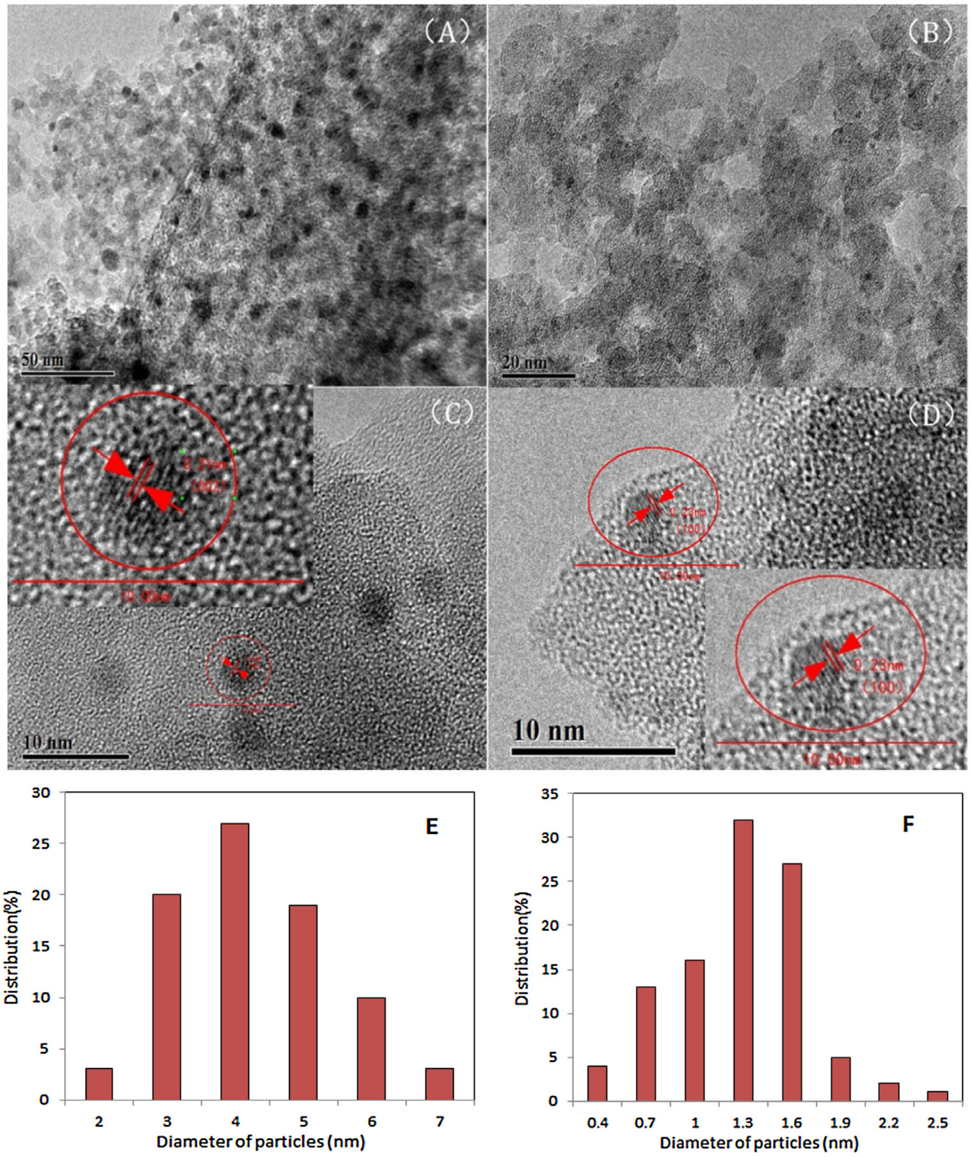

Fig. 4. HRTEM and particle size distribution histograms of reduced Ru/SiO_2 **(A,C,E)** and Ru-NH_2-SiO_2 **(B,D,F)**.

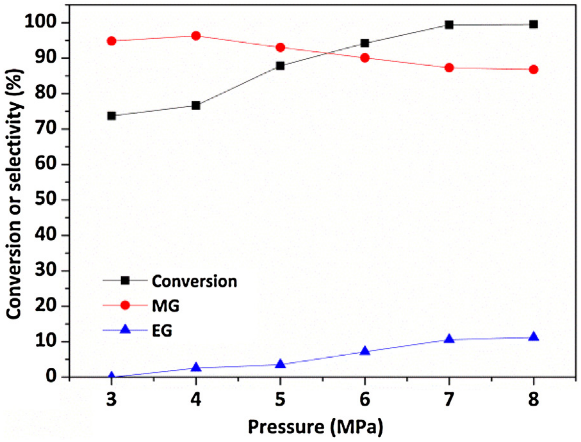

Fig. 5. The effect of hydrogen pressure on the catalytic performance of Ru-NH_2-SiO_2 Reaction conditions: 0.5 g of 2 wt.% reduced Ru-NH_2-SiO_2, 10 ml methanol, 0.4 g DMO, 80 °C, t = 24 h.

The FTIR spectra were recorded by a BRUKER TENSOR27 FTIR spectrophotometer (Bruker, Germany) equipped with a DTGS detector. The samples were grinded to fine powder and mixed carefully with KBr, then pressed into translucent disks. The spectra were recorded from 400 cm^{-1} to 4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) was measured on a VG MiltiLab 2000 spectrometer with Al Kαradiation and a multichannel detector. Prior to the test, the samples were reduced at 500 °C in 1 atm H_2 for 2 h. The obtained binding energies were calibrated using the C1s peak at 284.6 eV as the reference. The experiment error was given with ±0.1 eV.

TEM and HRTEM measurements were determined by a field-emission transmission electron microscopy (FETEM, JEM-2011F) operated at 200 kV voltages. Prior to test, the reduced catalysts were suspended in ethanol with an ultrasonic dispersion for 15 min, and deposited on copper grids coated with amorphous carbon films.

The content of Ru in the samples was ascertained by ICP optical emission spectroscopy (Perkin Elmer Optima 2100DV).

2.2.5. *Catalyst performance tests*

The catalytic tests were performed in a batch reactor (50 ml) with magnetic stirring. For a specific procedure, the reactor was fed with DMO (0.4 g), methyl alcohol (10 ml), catalyst (0.5 g), then sealed and purged by H_2 to exclude the air for several times. After that, the reactor was fulfilled with H_2 to reaction pressure and heated to object temperature. When reaction was over, the reactor was quenched in cool water. The products were separated from catalyst by centrifuging and analyzed by a GC instrument with a FID detector. The catalyst was recycled as following procedure: after each run, the catalyst was separated by centrifuging and thoroughly washed with methyl alcohol for three times, then reused for another run under the identical conditions. The conversion and selectivity of products were calculated based on the following equations:

$$Conversion\,(\%) = 100 - \frac{Amount\ of\ DMO\ after\ reaction\,(mol)}{Total\ amount\ DMO\ in\ the\ feed\,(mol)} \times 100$$

$$Selectivity\,(\%) = \frac{Amount\ of\ a\ product\,(mol)}{Total\ amount\ of\ all\ products\,(mol)} \times 100$$

Turnover frequency (TOF) was calculated to explore the intrinsic catalytic activity. It was estimated by the total Ru loadings:

$$TOF = \frac{Number\ of\ DMO\ molecular\ converted}{(Number\ of\ surface\ Ruatoms\ ) \times (reaction\ time, h)}$$

3. Results and discussion

3.1. *Characterization of KH550-modified-SiO_2*

To introduce ligands for the loading of the metal complexes, SiO_2 was primarily modified via a silylation reaction between the surface hydroxyl groups on SiO_2 and $-C_2H_5O$ groups in KH550. The typical Fourier transform infrared spectroscopy (FTIR) absorption peaks of SiO_2 and KH550-modified-SiO_2 can be observed in Fig. 1 (as shown in Fig. 1A). As observed in the spectrum of KH550-modified-SiO_2, 2924 cm^{-1} and 2850 cm^{-1} were the characteristic bands of the symmetric and antisymmetric vibrations of $-CH_2$ connected to the silane chains, while two bands at 1483 cm^{-1} and 1405 cm^{-1} were assigned to the bending vibrations of $-CH_2$. These results verified the successful incorporation of organic carbon chain, existing in KH550, onto the surface of SiO_2. The typical vibrations of N—H and C—N were not obvious in the spectrum as the great influence by antisymmetric stretching vibration at 1093 cm^{-1} of Si-O-Si bonds generated from the abundant Si-OH groups on the surface of SiO_2 and the triethoxy groups in KH550. However, the existence of N element in KH550-modified-SiO_2 was corroborated by X-ray photoelectron spectroscopy (XPS) (as seen in Fig. 1B). Additional signals of N were clearly observed in the XPS spectrum of KH550-modified-SiO_2. These results indicated the successful bonding of aminosilane onto the surface of SiO_2 through the silylation reaction. The remaining bands at 799 cm^{-1}, 3430 cm^{-1} and 1640 cm^{-1} were ascribed to the systematic stretching vibration of Si-O and the antisymmetric stretching and bending vibrations of water molecular, respectively.

3.2. *Characterization of Ru–NH_2-SiO_2 catalyst*

As their isolated electron pairs, the introduced $-NH_2$ groups can strongly bond with Ru sites though coordination. Therefore they act as anchoring sites for Ru complexes and highly improve the dispersion of Ru sites on the surface of SiO_2 (as shown in Scheme 1b). The physicochemical properties of catalysts are listed in Table 1.

3.2.1. *Physicochemical properties Ru–NH_2-SiO_2 catalyst*

Compared to SiO_2, the BET area, pore size and pore volume of Ru/SiO_2 and Ru-NH_2-SiO_2 had slightly changed. The particles size of Ru species was much smaller on Ru-NH_2-SiO_2 than those on Ru/SiO_2.

3.2.2. *XPS analysis of Ru–NH_2-SiO_2 catalyst*

To study the structure and chemical environment of the Ru-NH_2-SiO_2, the catalysts were characterized by XPS. As shown in Fig. 2A, the N signal appeared in the spectrum of Ru-NH_2-SiO_2 catalyst, while absent in the spectrum of Ru/SiO_2. It could also be observed that a positive shift of 0.50 eV for N 1s appeared in the spectrum of Ru-NH_2-SiO_2 compared with that in KH550-midified-SiO_2 (as shown in Fig. 2B). These results indicated the formation of NH_2-Si-O-Si structure and the coordination of Ru^{3+} sites and $-NH_2$ groups [17][17a]. The chemical state of Ru^0 on the Ru/SiO_2 and Ru-NH_2-SiO_2 catalysts was also studied. As previously reported, the $Ru3d_{5/2}$ XPS peak for Ru^0 is at 280.2 eV. In this work, the BE value of Ru^0 on Ru/SiO_2 catalyst is 280.30 eV, while a negative shift of 0.50 eV was obtained on Ru-NH_2-SiO_2 catalyst, which was 279.80 eV. This result reflected that some electrons were transferred from amino ligands to Ru^0, leading to an electron-rich state of Ru^0 (as shown in Fig. 2C). The electron-rich state of Ru^0 could effectively activate $-C{=}O$ bonds as the adequate electrons on Ru^0 sites are readily to yield electronic feedback to anti π orbitals of the $-C{=}O$ [25].

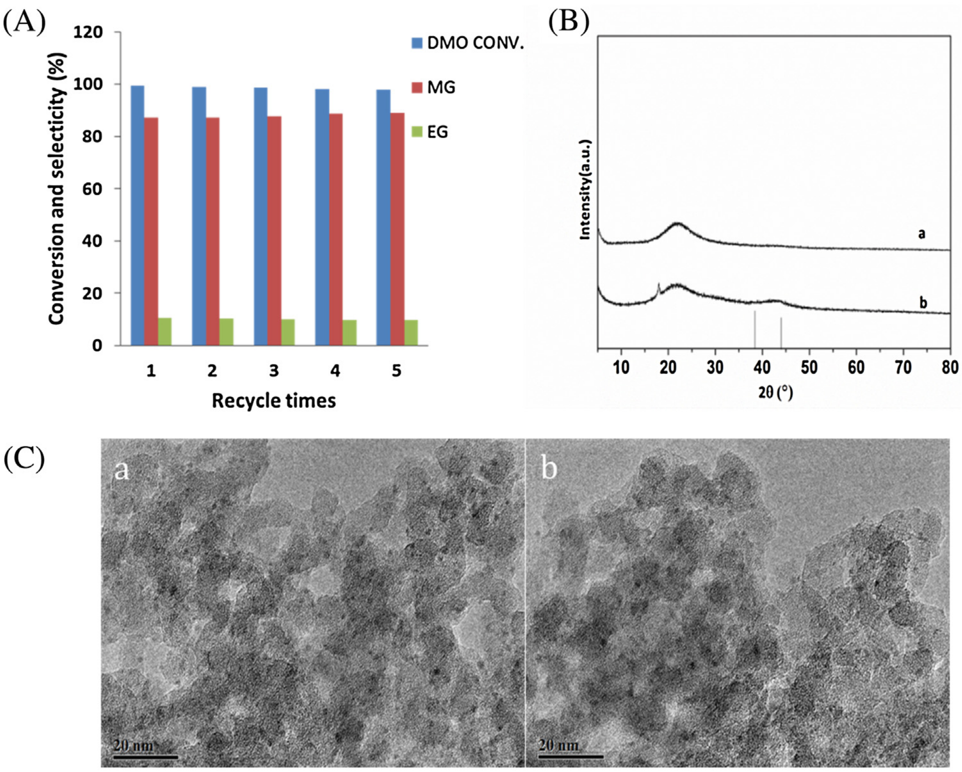

Fig. 6. (A) Recycle experiments of the Ru-NH_2-SiO_2, reaction conditions: Cat.0.5 g, DMO 0.4 g, methanol 10 ml, H_2 = 7 MPa, T = 80 °C, t = 24 h; (B) XRD of (a) fresh Ru-NH_2-SiO_2, (b) Ru-NH_2-SiO_2 spent for 5 runs; (C) HRTEM of (a) fresh Ru-NH_2-SiO_2, (b) Ru-NH_2-SiO_2 spent for 5 runs.

Table 1
Physicochemical properties of catalysts.

Entry	Catalyst	Ru (wt.%)[a]	S_{BET} (m^2/g)[b]	V_p (cm^3/g)[b]	d_p (nm)[b]	d_{Ru} (nm)[c]
1	SiO_2	–	352.73	0.92	8.73	–
2	Ru/SiO_2	1.92	352.07	0.90	8.80	4.5
3	Ru-NH_2-SiO_2	1.95	327.16	0.88	8.91	1.3

[a] Ru loading were determined by ICP-OES analysis.
[b] The BET surface area and pore volume and pore size were measured by N_2 physical adsorption.
[c] The size of Ru particles were calculated by HRTEM.

3.2.3. *XRD diffraction*

To study the dispersion of Ru species on Ru/SiO_2 and Ru-NH_2-SiO_2 catalysts, the diffraction patterns of fresh and reduced samples were recorded. As illustrated in Fig. 3, the peaks at 28.0°, 35.1°, 40.4° and 54.3° assigned to RuO_2 and the peaks at 38.4° and 44.0° ascribed to Ru NPs were observed in the fresh Ru/SiO_2 and reduced Ru/SiO_2 catalyst, respectively. However, the diffraction peaks of RuO_2 or Ru NPs were not detected in fresh or reduced Ru-NH_2-SiO_2 catalyst, reflecting that the sizes of Ru species are below the detection limit of XRD. This result demonstrated the higher dispersion of Ru species in Ru-NH_2-SiO_2 than those in Ru/SiO_2.

3.2.4. *TEM and HRTEM*

TEM and HRTEM were adopted to identify the dispersion of Ru species and morphology of the Ru/SiO_2 and Ru-NH_2-SiO_2 catalysts. HRTEM analysis obviously exhibited the much higher dispersion and smaller size of Ru NPs on the surface of Ru-NH_2-SiO_2 compared with those on Ru/SiO_2. The size of Ru NPs on Ru-NH_2-SiO_2 catalyst was around at 1.3 nm, while a large average size of 4.5 nm was observed on Ru/SiO_2 catalyst. This result indicated that the introduced $-NH_2$ groups significantly enhanced the dispersion of Ru species on the surface of KH550-modified-SiO_2 (Fig. 4A and B) which was well consistent with the XRD results. Primo et al. reported that the activity of smaller size of Ru NPs was much higher than those of larger ones in the hydrogenation of $-C{=}O$ [26]. It is hence inferred that the activity of Ru-NH_2-SiO_2 catalyst was higher than Ru/SiO_2 catalyst.

3.3. *Catalytic performance in DMO hydrogenation*

The hydrogenation of DMO was investigated to testify the catalytic performance of Ru/SiO_2 and Ru-NH_2-SiO_2 catalyst (as seen in Table 2). The conversion of DMO was 54.7% over Ru-NH_2-SiO_2 catalyst, which was as twice as that on Ru/SiO_2 catalyst at 50 °C(entries 1–2). As temperature increased to 70 °C(entries 3–4), a high conversion of 94.7% for DMO was achieved on Ru-NH_2-SiO_2 catalyst, whereas the conversion of DMO was only 30.1% on Ru/SiO_2 catalyst. A nearly complete conversion of DMO was obtained at 80 °C on the Ru-NH_2-SiO_2 catalyst, however, the Ru/SiO_2 catalyst still maintained lower catalytic performance even when the temperatures rose to 100 °C (entries 8). Moreover, it can be found that the attained TOF values (50 °C–100 °C) over Ru-NH_2-SiO_2 catalyst were about ten times of the values over Ru/SiO_2. This result clearly revealed the higher intrinsic activity of Ru-NH_2-SiO_2 catalyst compared with Ru/SiO_2 catalyst.

The hydrogenation of DMO is a tandem reaction that partially hydrogenated to MG firstly, then deep hydrogenation of MG to produce EG. The predominant product could be obtained through

Table 2
Catalytic hydrogenation of DMO to MG and EG[a].

Entry	Catalyst	T (°C)	t/h	DMO conv. (%)	MG sel. (%)	EG sel. (%)	TOFs (h^{-1})[b]
1	Ru-NH_2-SiO_2	50	24	54.7	97.1	–	1.14
2	Ru/SiO_2	50	24	26.2	100	–	0.17
3	Ru-NH_2-SiO_2	70	24	94.7	86.8	9.38	5.45
4	Ru/SiO_2	70	24	30.1	98.9	–	0.41
5	Ru-NH_2-SiO_2	80	24	99.4	87.3	10.6	6.66
6	Ru/SiO_2	80	24	34.8	99.1	–	0.63
7	Ru-NH_2-SiO_2	100	24	99.8	59.0	38.2	9.0
8	Ru/SiO_2	100	24	48.8	97.1	1.18	1.07

[a] Reaction conditions: 0.5 g of 2 wt% reduced Ru catalyst, 10 ml methanol, 0.4 g DMO, H_2:7 MPa.
[b] Reaction conditions: the DMO conversion was kept below 30%.

tuning the reaction conditions, especially for temperature. In our work, the Ru/SiO_2 catalyst showed an excellent selectivity to MG when the reaction temperature was below 100 °C, but the poor catalytic activity leaded to a low yield of MG. By contrast, the Ru-NH_2-SiO_2 catalyst displayed both high catalytic activity and high selectivity of MG at 80 °C, the attained yield of MG is 86.8%, which is about 3 times than those over Ru/SiO_2 at the same conditions.

Furthermore, the effect of pressure on the catalytic activity of the Ru-NH_2-SiO_2 catalyst was investigated at 80 °C. As showed in Fig. 5, it could be observed that the conversion of DMO rose from 73.7% to 99.4% while the selectivity of MG decreased from 94.8% to 87.3% with the pressure increasing from 3 MPa to 7 MPa. Additionally, it was found that the catalytic activity of Ru-NH_2-SiO_2 was kept unchangeable as the pressure increased from 7 MPa to 8 MPa. It is hence that the optimum reaction pressure was 7 MPa.

Typically, the thermodynamic equilibrium constant for the first hydrogenation step to MG is 2 orders of magnitude smaller than that of the subsequent hydrogenation step, so it is hard to obtain high yield of MG without further hydrogenation [27]. However, in our case, a high yield of MG (86.8%) was achieved at 80 °C over Ru-NH_2-SiO_2 catalyst, which is the lowest temperature that has been reported for the hydrogenation of DMO to MG in literature. The superior catalytic performance of the Ru-NH_2-SiO_2 catalyst was largely attributed to the excellent dispersion of Ru NPs on the surface of KH550-modified-SiO_2. XRD (Fig. 3) and HRTEM (Fig. 4) characterizations verified that the dispersion of Ru^0 on the surface of Ru-NH_2-SiO_2 catalyst was much better than those on the Ru/SiO_2 catalyst. By modification, the introduced $-NH_2$ groups on the support of SiO_2 greatly facilitated the dispersion of Ru^0 sites via covalent bonding. The Ru^0 particles size decreased from 4.5 nm to 1.3 nm, about one third smaller than that on impregnation prepared Ru/SiO_2 catalyst. More importantly, it is noticed that the presence of amino ligands might promote the catalytic behavior by increasing the electron cloud density of Ru^0 centers. As confirmed by the characterization of XPS, the BE value of Ru^0 on the Ru-NH_2-SiO_2 catalyst shifted toward lower binding energy than that on Ru/SiO_2 catalyst, which means that the active Ru^0 center was in rich-electronic state on the catalyst of Ru-NH_2-SiO_2 catalyst. The electron-rich state of Ru^0 could effectively activate $-C{=}O$ bonds as the sufficient electrons on Ru^0 sites are favorable to produce electronic feedback to anti π orbitals of the $-C{=}O$ groups.

3.4. *The stability of the Ru-NH_2-SiO_2 catalyst*

Finally, the reusability and stability of Ru-NH_2-SiO_2 catalyst was investigated for the conversion of DMO into MG under the optimal conditions (80 °C, H_2 7 MPa, 24 h) (Fig. 6A). After each reaction, the catalyst was separated from the reaction mixture by filtration and washed with the solvent of methanol for 3 times. Then, the recycled catalyst was reused for the next run. It was found that the Ru-NH_2-SiO_2 catalyst exhibited an excellent stability and the activity was maintained at a high level after five consecutive reuses. The conversion of DMO only decreased from 99.4% to 98.0%. In addition, no obviously variation was observed for the selectivity of MG, which was maintained at the level of 87%. Furthermore, a comparison of the XRD patterns and the TEM of the catalyst used for five runs (Ru-NH_2-SiO_2) with that of the fresh one suggested that the variation of Ru^0 NPs size and the morphology of the catalyst was negligible (Fig. 6B and C). It is hence concluded that the Ru-NH_2-SiO_2 catalyst is a more outstanding hydrogenation catalyst in terms of its reactivity and reusability.

4. Conclusion

In conclusion, we have discovered that a new catalyst of Ru-NH_2-SiO_2 synthesized by modification and immobilization was a valuable and promising catalyst in the hydrogenation of DMO to MG at low temperatures. Compared with the catalyst of Ru/SiO_2 prepared by impregnation method, the Ru-NH_2-SiO_2 catalyst exhibited a superior low temperature catalytic activity in the hydrogenation of DMO to MG, and realized the effective synthesis of MG with a high yield of 86.8% at the temperature as low as 80 °C,which was the lowest temperature for the hydrogenation of DMO to MG in literature. The excellent catalytic performance for Ru-NH_2-SiO_2 catalyst was attributed to the introduction of NH_2 functional groups on the support of SiO_2. The introduced $-NH_2$ groups not only facilitated the dispersion of Ru species, but also modulated their electronic properties. In consequence, the nanoscale sized Ru centers with high dispersion and electron-rich state were formed in the catalyst of Ru-NH_2-SiO_2, which owned high activity in the hydrogenation of $-C{=}O$ groups. In addition to the high activity, the Ru-NH_2-SiO_2 catalyst displayed a high stability in the hydrogenation of DMO to MG, its catalytic activity was maintained at a high level after five runs. It is hence that the coupling agents modification would provide an novel way for the catalysts synthesis and the as-synthesized Ru-NH_2-SiO_2 would be a promising catalyst applied in the hydrogenation of DMO or other catalytic reactions for the green ways of coal resources utilization.

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