Electronic Supplementary Information

Highly selective hydrogenation of dimethyl oxalate to methyl glycolate and ethylene glycol over an amino assisted Ru-based catalyst

1. Experimental

1.1 materials

RuCl₃·3H₂O and γ -aminopropyl triethoxy silane (APTES) were purchased from Aladdin Chemistry Co. Ltd. SiO₂, dimethyl oxalate and methanol were purchased from Chengdu Kelong Chemicals Co. Ltd. MCM-41 and SBA-15 were purchased from Nanjing Jicang Nano Technology Co. Ltd.

1.2 Preparation of Ru/NH₂-MCM-41

Functional NH₂-MCM-41 was prepared by mixing 6 g MCM-41 with 120 ml ethanol. Then APTES was slowly dropped with vigorous stirring. After refluxing at 373 K for 6 h, NH₂-MCM-41 was separated by vacuum filtration, and washed with ethanol for several times. Solid product was dried overnight at 343 K. Then the mixture of anhydrous ethanol solution of RuCl₃·3H₂O with NH₂-MCM-41 was refluxing for 6 h at 373 K. After cooling to ambient temperature, Ru/NH₂-MCM-41 was separated by vacuum filtration, washed with ethanol and dried in at 343 K overnight.

1.3 Preparation of Ru/MCM-41

Ru/MCM-41 was prepared by impregnation method. RuCl₃·3H₂O was dissolved in anhydrous ethanol. After fully mixing the ethanol solution and MCM-41, ethanol was removed by rotary evaporation at 323 K. The product was calcined in a muffle furnace at 773 K for 2 h.

1.4 Preparation of Ru/NH₂-SiO₂ and Ru/NH₂-SBA-15

 Ru/NH_2 -SiO₂ and Ru/NH_2 -SBA-15 were prepared in a similar way as Ru/NH_2 -MCM-41.

1.5 Catalyst characterization

X-ray photoelectron spectroscopy (XPS) was performed on Axis Ultra DLD

instrument, using Al Ka (1486.7 eV) as X-ray source, and power is 150 w. Calibrate all binding energies with C1s at 284.6 eV as the reference. Fourier transform infrared spectroscopy (FT-IR) was carried on Spectrum Two L1600300 Perkin Elmer. Test after fully mixing 120 mg KBr with 10 mg sample. The scanning range was from 4000-400 cm⁻¹. X-ray diffraction (XRD) was performed on PANalytical Empyrean diffractometer, using Cu Kα as radiation source at 40 kV, 30 mA, 2θ=10-90 °. Transmission electron microscope (TEM) was performed on Tecnai-G20 instrument at 200 kV accelerating voltage. The sample was evenly dispersed in ethanol, dropped on a copper grid, and tested after drying. N₂-physisorption was carried on Micrometrics Tristar \prod 3020 instrument. The sample was degassed at 120 °C for 8 h. ICP was performed on SPECTRO ARCOS instrument to test Ru content of the sample. Dissolve the sample in hydrofluoric acid, after heated and decomposed, cooling it to ambient temperature, and diluted with water to 100 ml for further tested. In situ DRIFT spectra of CO adsorption was performed on Thermal Fisher infrared spectroscopy. The sample was pretreated for 30 minutes in helium atmosphere. After cooling to 30 °C, switch to CO until the sample was fully adsorbed CO. Then switch to helium and started timing and collect spectra. The spectrum was collected every 30 seconds for the first five minutes and every 5 minutes for 5 to 30 minutes.

The H₂ temperature-programmed reduction (H₂-TPR) of catalyst was carried on a ChemStar TPx chemisorption analyzer. The sample was pretreated for one hour at 150 °C in argon atmosphere. After cooling to 50 °C, switch to 10 vol% H₂-Ar mixed gas to perform reduction from 50 °C-900 °C. Record detection signals with TCD. Pulse CO-Chemisorption was also performed on a ChemStar TPx chemisorption analyzer.

1.6 Catalyst performance test

Prior to the reactions, the products were reduced by H_2 at 773 K for 2 h in a quartz tube furnace. Catalyst performance test was carried out in a 100 ml stainless autoclave reactor. Typically, 3.5 mmol DMO was dissolved in 30 ml methanol, and 0.5 g catalyst was loaded into the reactor. After the reactor sealed, 1 MPa H_2 was filled for ten times to purge out the air. Then injected H_2 till the pressure was 5 MPa, and raised the temperature to the reaction temperature. After reacted for 24 h, catalyst was separated by centrifugation. The liquid phase product was detected by gas chromatography. The recycled Ru/NH_2 -MCM-41 catalyst obtained by centrifugation was used for the next test as described above.

DMO conversion, selectivity and yields of product, and turnover frequency (TOF) were calculated by:

 $Conversion = \frac{Mole \ of \ DMO \ charged - mole \ of \ DMO \ left}{Mole \ of \ DMO \ charged} \times 100\%$ $Selectivity = \frac{Mole \ of \ a \ product \ generated}{Total \ mole \ of \ all \ products} \times 100\%$ $Yield = Conversion \times Selectivity \times 100\%$ $TOF = \frac{Mole \ of \ DMO \ reacted}{Mole \ of \ surface \ Ru \ atoms \times reaction \ time}$



Fig.S1 (a) N₂ adsorption-desorption isotherms and (b) pore size distributions of Ru/NH₂-SiO₂, Ru/MCM-41, fresh Ru/NH₂-MCM-41 and Ru/NH₂-MCM-41 after reaction.



Fig.S2 H₂-TPR profiles of Ru/NH₂-SiO₂, Ru/MCM-41and Ru/NH₂-MCM-41.



Fig.S3 (a) XRD patterns of the fresh Ru/NH₂-SiO₂, Ru/MCM-41 and Ru/NH₂-MCM-41. (b) XRD patterns of fresh Ru/NH₂-MCM-41, and Ru/NH₂-MCM-41 used for five times at 433 K and 343 K. (c) XRD spectrums of the fresh Ru/MCM-41 and Ru/NH₂-MCM-41 catalysts. (d) low angle XRD patterns of MCM-41, Ru/MCM-41 and Ru/NH₂-MCM-41 catalysts

The particle size of Ru on the Ru/NH₂-MCM-41 is quite small, beyond the detection limit of the XRD instrument (< 5 nm), so that we cannot observe the diffraction peaks corresponding to Ru.

The pore sizes of MCM-41, Ru/MCM-41 and Ru/NH₂-MCM-41 are 4.26 nm, 3.49 nm, 3.70 nm respectively. After the loading of Ru, the (100) peak of Ru/MCM-41, and Ru/NH₂-MCM-41 shifted to the direction of high angle. According to the Bragg's Law (2dsin θ =n λ), when the diffraction angle (θ) increases, the crystal plane spacing (d) decreases, which indicates the loading of Ru may slightly block the channel. The Ru nanoparticles over the reduced Ru/NH₂-MCM-41 and Ru/MCM-41 samples are 1.08 nm and 13.69 nm, respectively. For the Ru/MCM-41 sample, most of the Ru nanoparticles are too large to enter the pores of MCM-41. Therefore, the (100) peak of the PXRD of Ru/NH₂-MCM-41 shifted more obviously than that of Ru/MCM-41 sample.



Fig.S4 Full range spectrum of used and fresh Ru/NH₂-MCM-41, Ru/MCM-41 and

NH₂-MCM-41



Fig.S5 Catalytic performances of the RuCl₃, Ru³⁺/NH₂-MCM-41 and Ru/NH₂-MCM-41 at 343 K, 5 MPa.

The reaction solvent is methanol, and the reaction is carried out at high pressure, which exactly satisfies the condition of alcohol thermal reduction. During the reaction process, both of RuCl₃ and RuCl₃/NH₂-MCM-41 are reduced. Without the constrains of amino and supports, RuCl₃ has no catalytic activity. RuCl₃/NH₂-MCM-41 has a certain catalytic activity (63.43% MG yield) after alcohol thermal reduction. However, the catalytic activity of RuCl₃/NH₂-MCM-41 was worse than that reduced by H₂ (89.6% MG yield).



Fig.S6 FT-IR spectrum of SiO₂, MCM-41, NH₂-SiO₂, and NH₂-MCM-41 samples.

The peaks at 2930 cm⁻¹ and 2854 cm⁻¹ are attributed to symmetric and antisymmetric vibrations of -CH₂. The peaks at 1554 cm⁻¹ and 695 cm⁻¹ are assigned to in-plane bending vibration and out -plane bending vibration of -NH₂. The appearance of -CH₂ and -NH₂ indicates the successful grafting of APTES. After grafting of APTES, the vibration strength of Si-OH at 960 cm⁻¹ decreases, which is the other evidence that APTES has successfully grafted. The broad peak at 3450 cm⁻¹ is attributed to the vibration of Si–OH and adsorbed water molecules. The peaks at 1095 cm⁻¹ and 798 cm⁻¹ are assigned to antisymmetric and symmetric vibrations of Si–O-Si. The bending vibration peak of H₂O appears at 1635 cm⁻¹.



Fig.S7 (a) MCM-41 (b) NH₂-MCM-41 (c) Ru/NH₂-MCM-41 before reduction (d) used Ru/NH₂-MCM-41 collected at different stages of the preparation process.



Fig. S8 Catalytic performance of the Ru/NH_2 -MCM-41 catalyst in catalytic hydrogenation of MG.

MCM-41.				
	Ν	С	Н	
NH ₂ -MCM-41	3.19	8.42	3.49	
Ru ³⁺ /NH ₂ -MCM-41	2.98	9.21	3.76	
Ru/NH ₂ -MCM-41	2.20	8.60	2.75	

Tab.S1 Elemental analysis of NH₂-MCM-41, Ru³⁺/NH₂-MCM-41 and Ru/NH₂-MCM-41.

Catalysts	$S_{BET} \left(m^2/g\right)$	$V_{pore} (m^3/g)$	D _{pore} (nm)
Ru/NH_2 -SiO ₂	127.9	0.96	33.8
Ru/MCM-41	912.9	0.95	3.70
Ru/NH ₂ -MCM-41	702.7	0.53	3.49
Used Ru/NH ₂ -MCM-41	980.8	0.69	3.53

Tab.S2 Textural and physicochemical characteristics of Ru/NH_2 -SiO₂, Ru/MCM-41,

 $Ru/NH_2\mbox{-}MCM\mbox{-}41$ and $Ru/NH_2\mbox{-}MCM\mbox{-}41$ after reaction.