Hoveyda-Grubbs catalyst confined in nanocages of SBA-1: enhanced recyclability for olefin metathesis

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1. Experimental

1.1 Chemicals

The second generation Hoveyda-Grubbs catalyst (CAS No.: 301224-40-8) was purchased from Aldrich Co. The substrates for the RCM were also obtained for Aldrich Co.

1.2 Materials

Silica was achieved from Qidao Haiyang Chemical plant. Various mesoporous materials were synthesized according to the references.

materials	Templates	References
MCM-41	$C_{16}H_{33}N(CH_3)_3Br$	*J. Am. Chem. Soc.* **1992***,114,*10834
SBA-15	P123	*J. Am. Chem. Soc.* **1998**, *120*, 6024.
SBA-16	F127 +P123	*J. Phys. Chem. B*, **2004**, *108*, 11480.
FDU-1	F127	*J. Am. Chem. Soc.***2004,***127*,10794
SBA-1	$C_{12}H_{25}$ $N(CH_2CH_3)_3Br$	*Chem.Mater.* **1999**, *11*, 487
SBA-1(L)	$C_{16}H_{33}N(CH_2CH_3)_3Br$	*Chem.Mater*. **1999**, *11*, 487

1.3 Preparation of the solid catalyst

1.0 g of silica gel or mesoporous materials (evacuated at 398 K for 6 h) was dispersed in 17 mL of toluene containing 0.02 g the second generation Hoveyda-Grubbs catalyst (CAS No.: 301224-40-8); After stirring at room temperature for 6 h under N_2 atmosphere, the resulting solid was isolated by filtration, washed thoroughly with hexane and dried under vacuum, giving the greenish solid catalysts H-G/χ[χ=SiO_2, MCM-41, SBA-15, SBA-16, FDU-1 and SBA-1 and

SBA-1(L)].

1.4 A typical procedure for metathesis reaction

1 mL of dry hexane, 0.1 mmol of substrate and a given amount of solid catalyst with 0.0025 mmol Ru complex were mixed. The mixture was stirred at 25 ^{o}C under N_2 atmosphere for a given time. At the end of the reaction, the liquid was isolated by centrifugation and analyzed with GC. The obtained solid catalyst was recovered, washed thoroughly with hexane and dried directly for the next reaction cycle.

1.5 Characterization

Small-angle X-ray powder diffraction was performed on Rigaku (Cu Ka, 40 kV, 30 mA). N_2 physical adsorption was carried out on micrometritics ASAP2020 volumetric adsorption analyzer (before the measurements, samples were out gassed at 398 K for 8 h). The Brunauer–Emmett–Teller (BET) surface area was evaluated from data in the relative pressure range from 0.05 to 0.25. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P_0 (above 0.99). FT-IR spectra were collected on Thermo-Nicolet-Nexus 470 infrared spectrometer (under vacuum). Pd content was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). UV-vis spectra were recorded on the JASCOV-550 UV-vis spectrophotometer. Diffuse-reflectance UV-vis spectra were also recorded on the CARY300 spectrophotometer (Varian Co.)

1.6 Calculation

To more accurately estimate the size of the mono- and dinuclear Ruthenium complexes,

geometries of these complexes have been optimized at the DFT/B3LYP/ 3-21G* level using the Gaussian03[1] program package. Based on the optimized geometries, the cavity dimensions and volumes the mono- and di-nuclear Ruthenium chelates respectively, have been determined using the molecular graphics tool, Molekel [2-3], as displayed in Figs. **1** and **2**.

References

[1] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[2] Molekel 4.3, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000-2002.

[3] Stefan Portmann & Hans Peter Lüthi. Molekel: An Interactive Molecular Graphics Tool. ***Chimia***, **54**, 766-770, 2000.

Table S1 Textural parameters of the investigated materials and the loadings of Hoveyda-Grubbs catalyst on these materials

materials	Pore structures	S [a] (m^2/g)	V [b] (cm^3/g)	Pore size (nm)	[c] Loading of the Ru complex (wt%)
Silica	amorphous	346	0.92	12	1.35
MCM-41	channel-like	902	0.77	2.6	1.69
SBA-15	channel-like	667	0.93	7.5	1.61
SBA-16	cage-like	701	0.65	6.1	1.79
FDU-12	cage-like	788	0.77	14.7	1.38
SBA-1	cage-like	852	0.44	1.37	1.77
SBA-1(L)	cage-like	1231	0.56	1.85	1.76

[a] ET surface area.

[b] Single point pore volume calculated at relative pressure P/P_0 of 0.99.

[c] BJH method from adsorption branch.

Table S2 The percentages of the leached Ru in the first reaction cycle

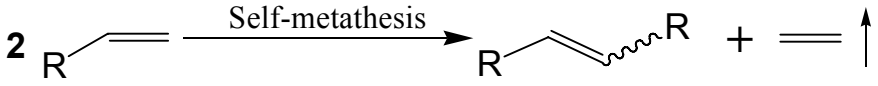
Solid catalyst	Leached Ru in the First reaction cycle (%) [a]
H-G/Silica	1.16
H-G/MCM-41	1.45
H-G/SBA-15	1.38
H-G/SBA-16	1.54
H-G/FDU-1	1.18
H-G/SBA-1	1.52
H-G/SBA-1(L)	1.51

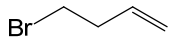
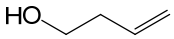
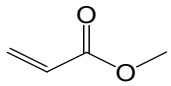
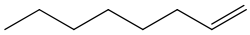
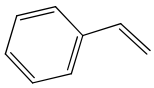
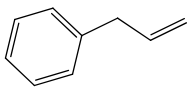
[a] (the amount of the leached Ru in the first reaction cycle)/(the amount of the Ru on the fresh solid catalyst)

Table S3 The recyclabilities of the immobilized Hoveyda-Grubbs catalysts in the references

References	Immobilization method	Ru complex loading	Cycle numbers
Organometallics **2002,** 671	polymer	5 mol%	4 th (3 h, 22% comversion)
Chem. Commun.,**2007**, 3771	Ionic liquid tagged	5 mol%	6 th (3 h, 98% conv.)
Adv. Synth. Catal. **2002**, *344,* 619.	polymer	2.5 mol%	4 th (40% conversion)
Adv. Synth. Catal. **2006**, *348, 751*	co-condensation	2 mol%	5 th (1.5 h, 66% conv.) 6 th (24 h, 98% conv.)
Adv. Synth. Catal. **2007,** *349*, 1066	Grafting	5 mol%	10 th (1 h, 77% conv.)
Chem. Commun.**2008,** 4312	Grafting	5 mol%	10 th (97% conv)
*Org. Lett.***2009**,5 1261	co-condensation	0.75 mol%	8 times (not complete conversion for each cycle)
ChemSusChem **2008**, *1,* 927	trimerization	2.5 mol%	8 th (98% conv.)
J.Am.Chem.Soc, **2004**,*126,* 74	polymer	2 mol%	5 th (96%, 50 ^{o}C)
*Angew.Chem.In.Ed.***2000**.*39 .3896*	polymer	5 mol%	8 th (98% conv.)
J. Am. Chem. Soc. **1999,** *121,* 791	polymer	5 mol%	3 rd (67-98% conv.)

Table S4 Olefin self metathesis over H-G/SBA-1[a]



Entry	Substrates	Solvents	Temperature /℃	Time/ h	Conv.[b]/%
1		hexane	40	4	93
2		hexane	40	4	99
3		hexane	40	5	85
4		Hexane	40	6	30
5		hexane	50	11	47
6		Hexane/CH_2Cl_2(1:1，V/V)	40	11	74
7		hexane	50	11	55
8		Hexane/CH_2Cl_2(1:1，V/V)	40	11	76

[a] Reaction conditions: 1 mmol (0.4 mmol/mL) and 2.5 mol% Ru with respect to substrates;

[b] Determined with GC.

The developed catalyst H-G/SBA-1 is also active towards the self-metatheses of the investigated olefins. For functionalized, short olefins, high conversions were achieved within 4-5 h in the presence of 2.5 mol% Ru (Table S4, entries 1-3). For long olefin, its activity is relatively low (Table S4, entry 4). For aryl-substituted olefins, moderate conversions were afforded using hexane as solvent ((Table S4, entries 5 and 7). Good conversions could be obtained by use of mixed solvents [Hexane/CH_2Cl_2(1:1,V/V)] (Table S4, entries 6 and 8).

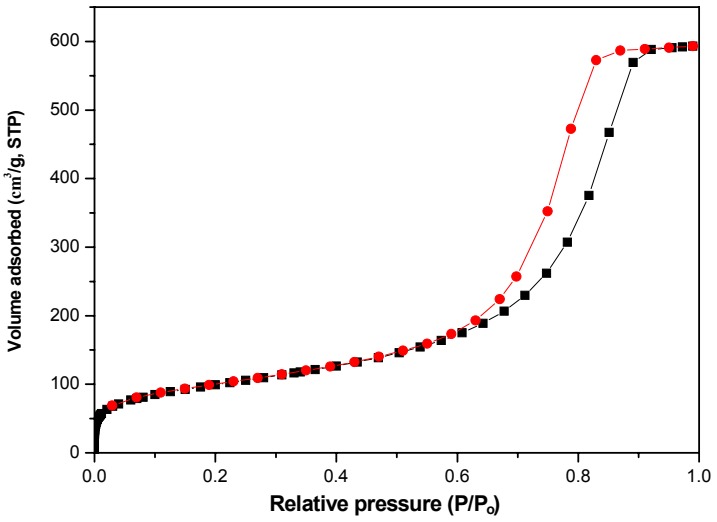


Fig. S1 N_2 adsorption/desorption isotherms of silica.

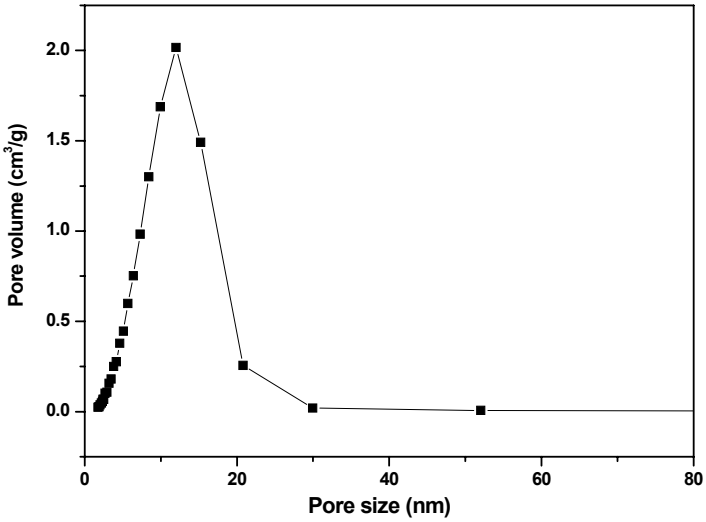


Fig. S2 Pore size distribution of silica.

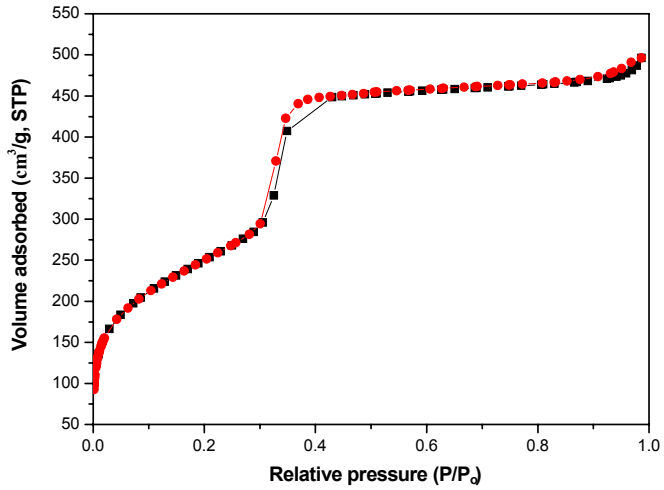


Fig. S3 N_2 adsorption/desorption isotherms of MCM-41.

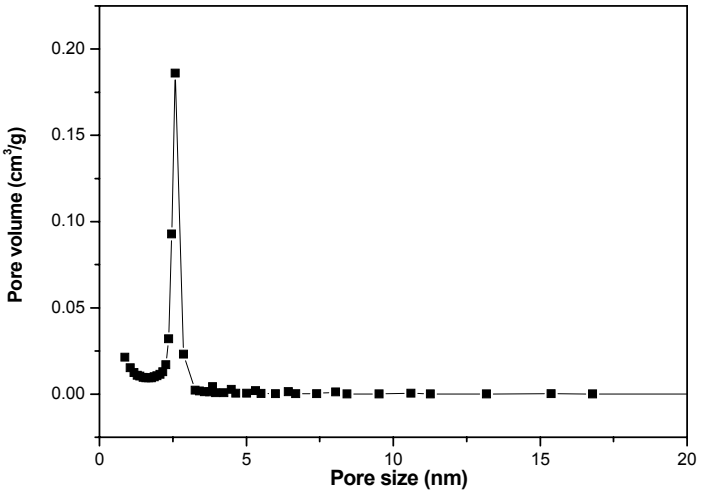


Fig. S4 Pore size distribution of MCM-41.

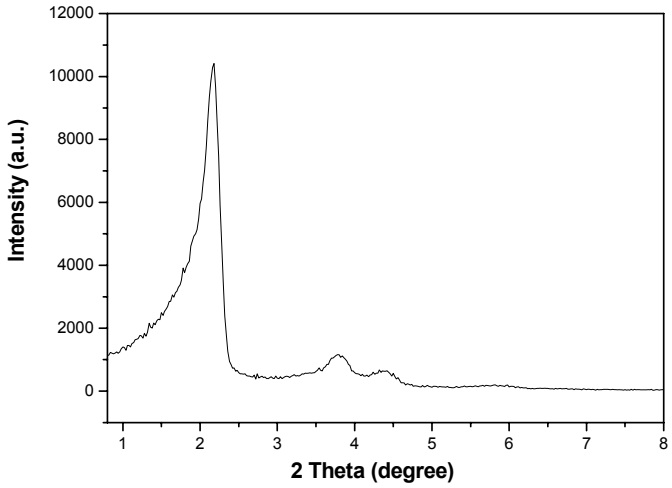


Fig. S5 XRD pattern of MCM-41.

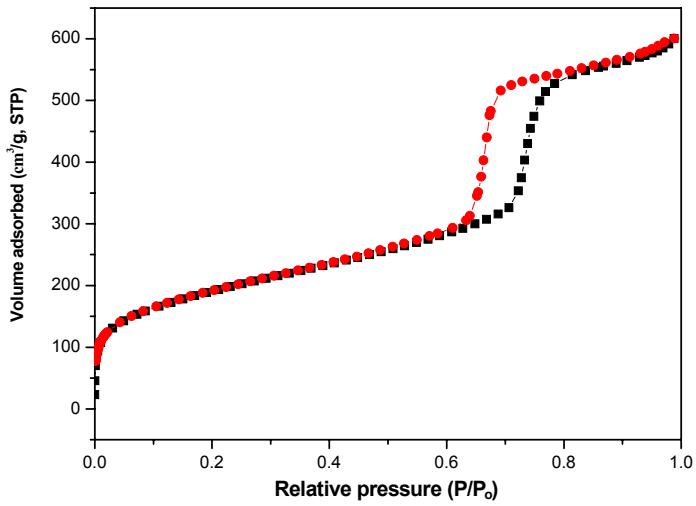


Fig. S6 N_2 adsorption/desorption isotherms of SBA-15.

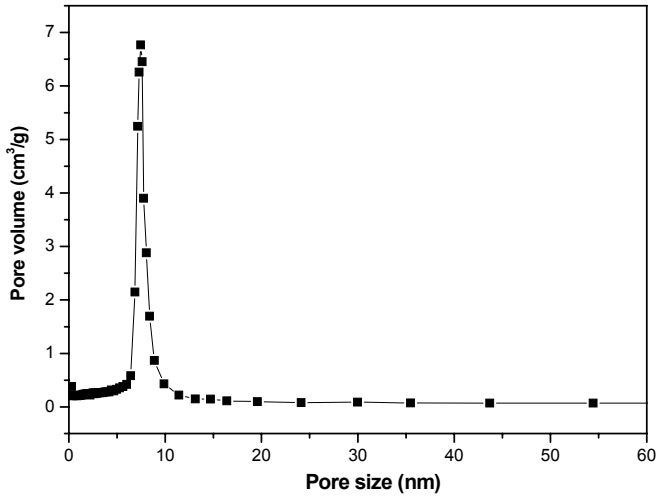


Fig. S7 Pore size distribution of SBA-15.

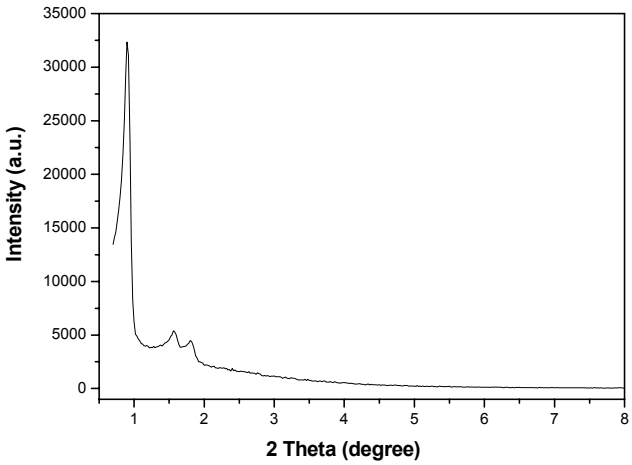


Fig. S8 XRD pattern of SBA-15.

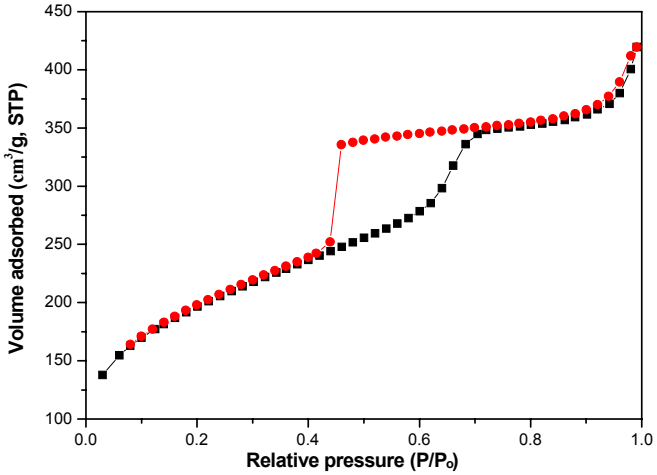


Fig. S9 N_2 adsorption/desorption isotherms of SBA-16.

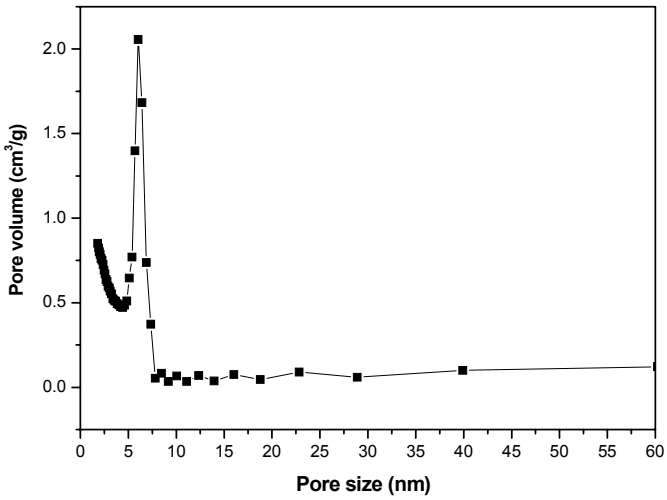


Fig. S10 Pore size distribution of SBA-16

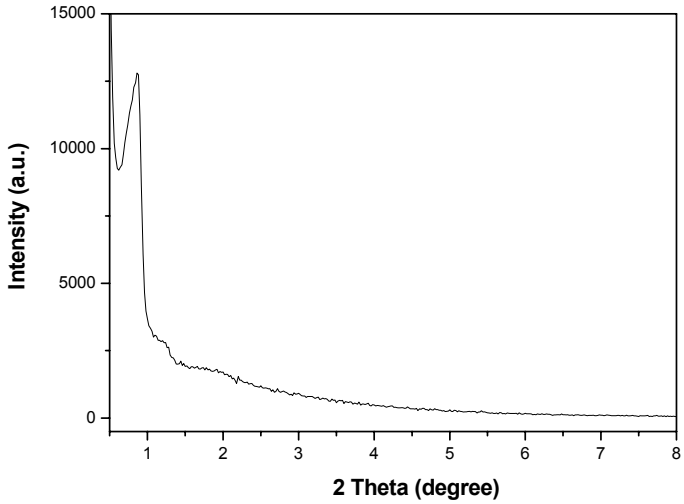


Fig. S11 XRD pattern of SBA-16.

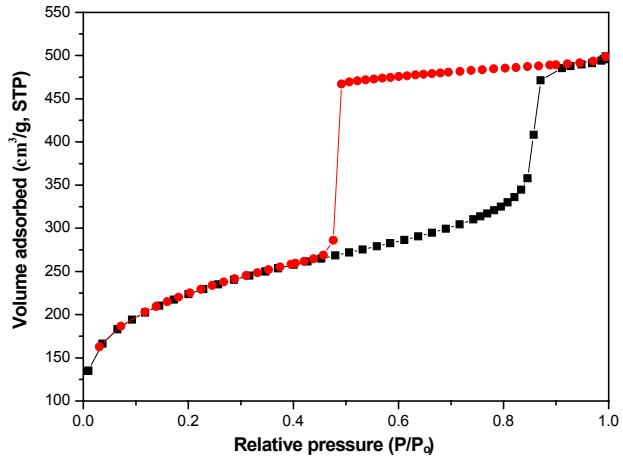


Fig. S12 N_2 adsorption/desorption isotherms of FDU-1.

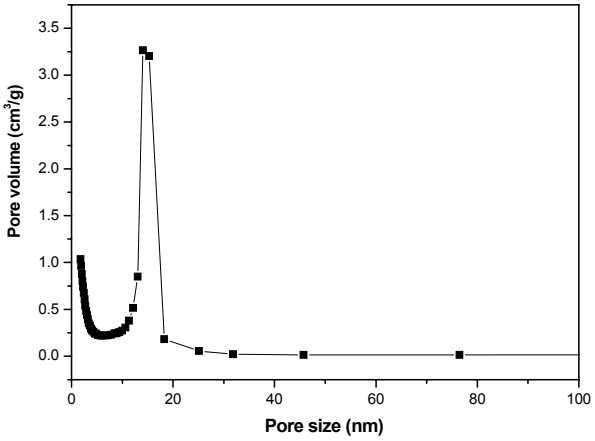


Fig. S13 Pore size distribution of FDU-1.

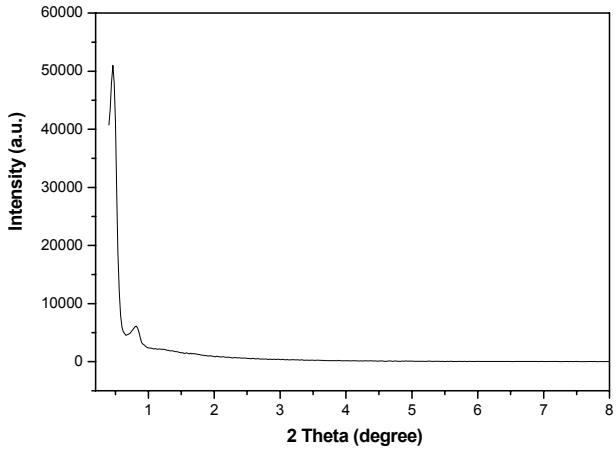


Fig. S14 XRD pattern of FDU-1.

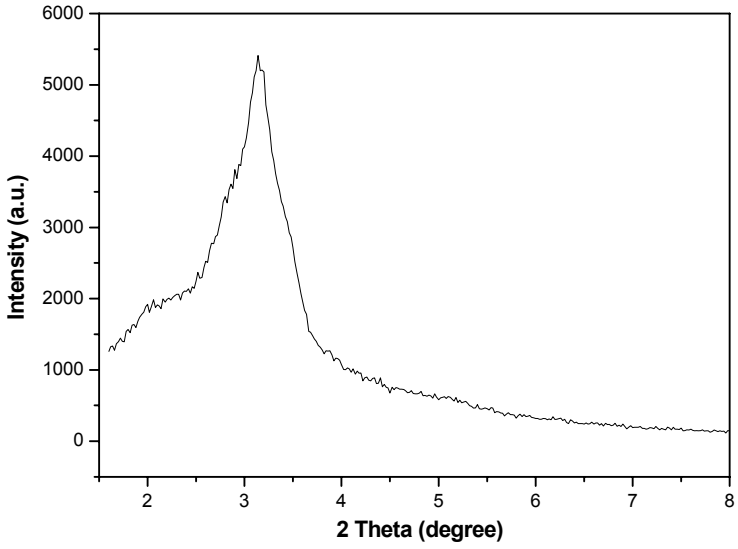


Fig. S15 XRD pattern of SBA-1.

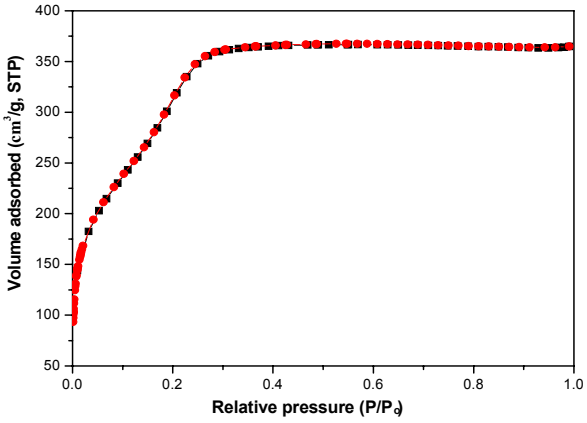


Fig. S16 N_2 adsorption/desorption isotherms of SBA-1(L).

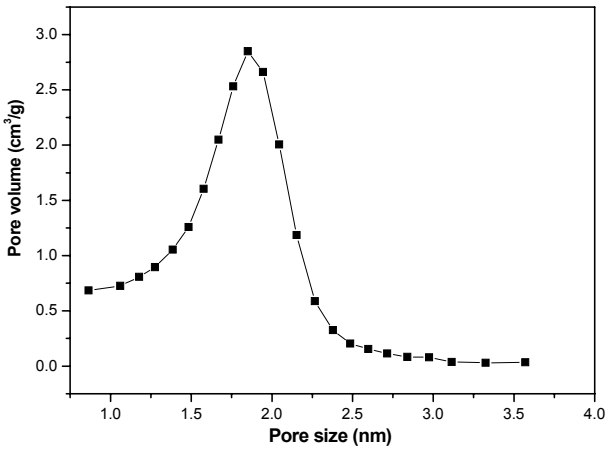


Fig. S17 Pore size distribution of SBA-1(L).

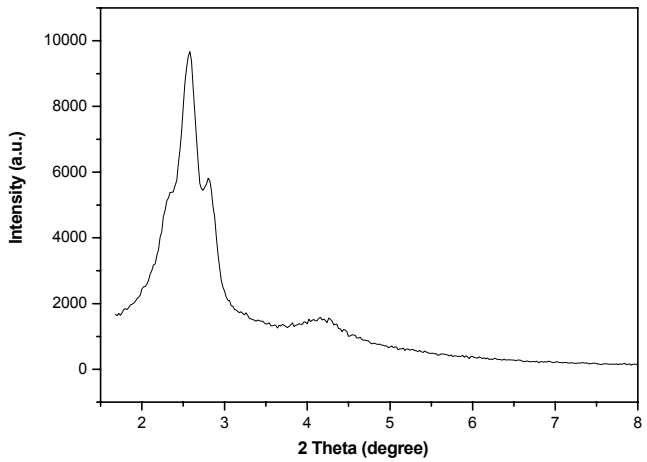


Fig. S18 XRD pattern of SBA-1(L).

(A) (B)

Fig.S19 Images of SBA-1 (A) and H-G/SBA-1 (B).

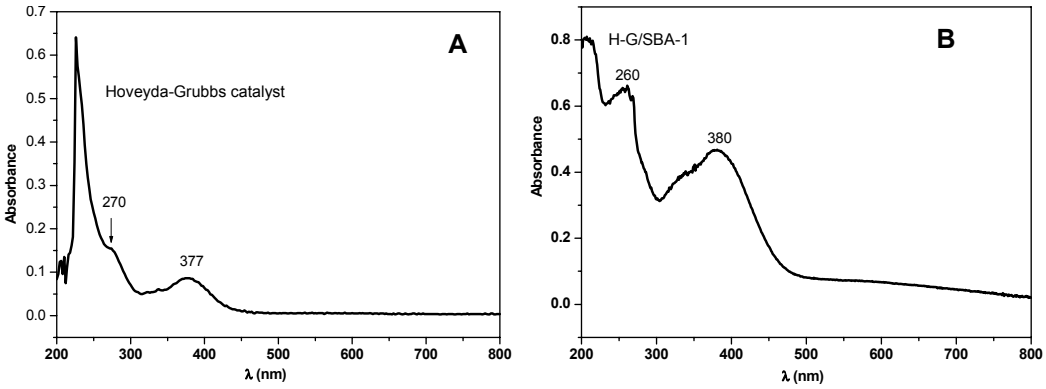


Fig.S20 (A) UV-vis spectrum of Hoveyda-Grubbs catalysts in a dichloromethane solution and (B) Diffusion reflectance UV-vis spectrum of H-G/SBA-1.

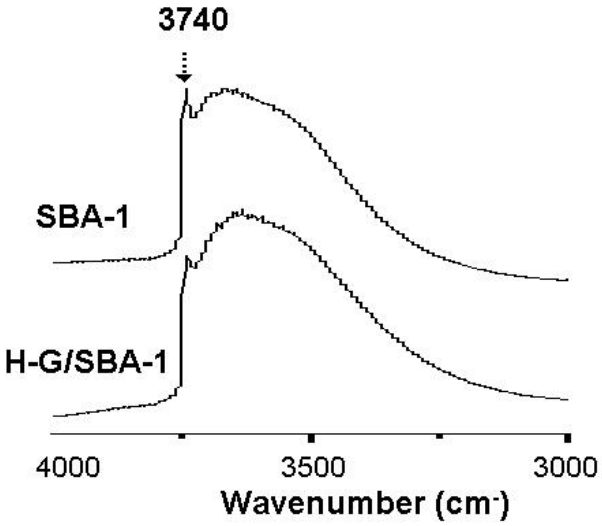
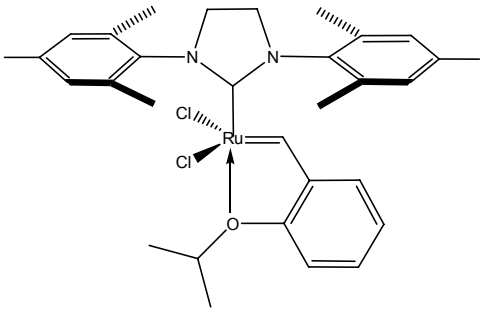
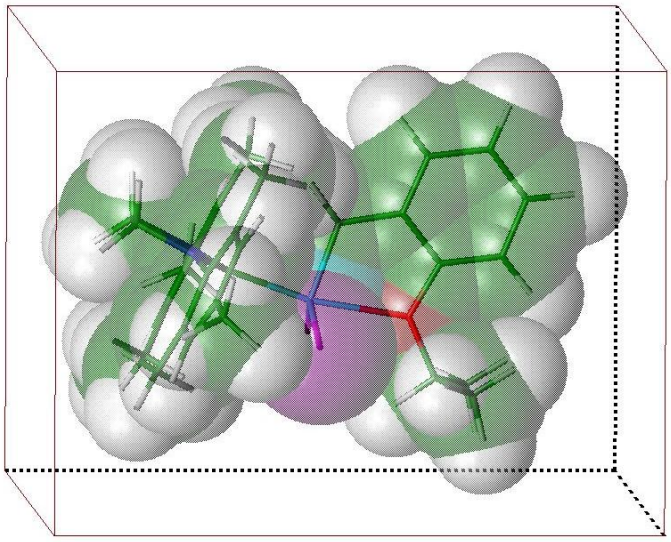


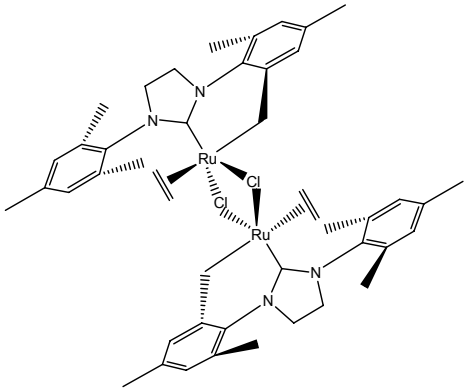
Fig.S21 FT-IP spectra of SBA-1 and H-G/SBA-1.

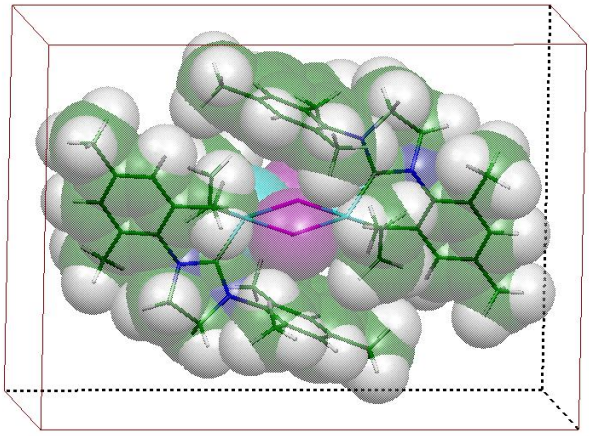




1.7644162 nm×1.3698322 nm×1.0474243 nm

Fig.S22 The molecular structure and size of Hoveyda-Grubbs catalyst (the mononuclear Ru complex).





2.0157542 nm×1.4496200 nm×0.9687726 nm

Fig.S23 The molecular structure and size of the dinuclear Ru complex.