Supporting Information

Mesoporous ZSM-5 Zeolite Supported Ru Nanoparticles as Highly Efficient Catalysts for Upgrading Phenolic Biomolecules

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Table S1. The textural parameters of various samples.

Catalyst	V_{total} (cm^3/g)[a]	V_{micro} (cm^3/g)[b]	Si/Al[c]	Ru (*wt*%)[c]	Ru NP size (nm)[d]	D_{Ru} (%)[e]	Acid density (mmol/g)[f]	
							Micropores	Mesopore and External surface
Ru/HZSM-5	0.13	0.12	39	1.1	4.1	32.5	0.22	0.04
Ru/HZSM-5-M	0.32	0.09	40	1.3	4.9	27.2	0.21	0.07
Ru/HZSM-5-OM	0.31	0.08	42	1.1	6.2	23.5	0.18	0.10

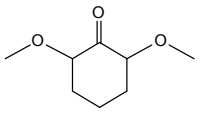
[a] Total pore volume; [b] Micropore volume; [c] By ICP analysis; [d] Average sizes by counting more than 120 particles in the TEM images, and the details of particle size distribution are shown in Figure S8; [e] The number of Ru atoms on the nanoparticle surface/Total Ru atoms, determined by particle size calculation; [f] The total density of acid sites is measured by the NH_3-TPD titration method, and the percentage of micropore or external/mesopore sites is calculated by the ^{31}P NMR spectra of adsorbed TMPO. The desired micropore or external/mesopore density is calculated as follows: The micropore acid density = (total acid density) * (percentage of micropore acid); The external/mesopore acid density = (total acid density) * (percentage of external/mesopore acid).

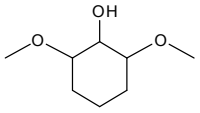
Table S2. Catalytic data under low conversion in the hydrodeoxygenation of 2,6-dimethoxyphenol over various catalysts.[a]

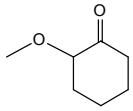
Catalyst	Conv. (%)	Product selectivity (%)[b]								
		P1	P2	P3	P4	P5	P6	P7	P8	P9
Ru/HZSM-5	7.9	8.7	1.2	8.6	35.2	26.3	7.5	4.5	--	--
Ru/HZSM-5-M	6.8	10.2	1.0	5.0	38.6	18.9	9.4	4.0	--	--
Ru/HZSM-5-OM	7.5	9.9	--	--	42.7	2.1	16.8	5.0	--	--

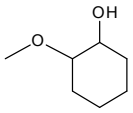
[a] Reaction conditions: 150 °C, 15 min, 4.0 MP of H_2, 50 mg of catalyst, 1 mmol of phenolic substrate, 8 ml of water; [b] (C atoms in each product/total C atoms in all products)*100%. The products are listed in the following.

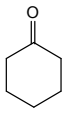
P1 MeOH

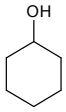
P2 

P3 

P4 

P5 

P6 

P7 

P8 

P9 

Table S2 shows the product selectivity at relatively low conversion (6.2-7.9%) in the hydrodeoxygenation of 2,6-dimethoxyphenol over Ru/HZSM-5, Ru/HZSM-5-M, and Ru/HZSM-5-OM. In these cases, the cyclohexane product was undetectable due to the short reaction time. However, these catalysts still exhibited significant difference in the selectivities to various intermediates. Notably, the Ru/HZSM-5

catalyst give higher selectivities to 2,6-dimethoxycyclohexanol (P3, 8.6%) and 2-methoxycyclohexanol (P5, 26.3%) than those over Ru/HZSM-5-OM (trace selectivity to P3, and 2.1% selectivity to P5). This phenomenon should be attributed to that the Ru/HZSM-5-OM with mesopores is favorable for the conversion of bulky alcohol substrates, compared with the Ru/HZSM-5 catalyst. These results clearly indicate the selectivity difference in the hydrodeoxygenation of 2,6-dimethoxyphenol over various catalysts with and without mesopores.

Table S3. Catalytic data in hydrodeoxygenation of 2,6-dimethoxyphenol over Ru catalysts supported on HZSM-5 zeolites with different crystal sizes.[a]

Catalyst	Zeolite crystal size	Conv. (%)	Product selectivity (%)	
			cyclohexane	Others[b]
Ru/HZSM-5	~300 nm	70.0	55.4	15.0
Ru/HZSM-5-L1	~3 μm	50.5	--	90.0
Ru/HZSM-5-L2	~5 μm	50.0	--	90.6

[a] The reaction conditions are the same to those in Table 2. [b] C_{6-8} oxygen containing molecules and some others.

Here, Ru catalyst supported on ZSM-5 zeolite with different crystal size at ~300 nm (Ru/HZSM-5, used as conventional microporous ZSM-5 in this work, Figure S7A), ~3 μm (Ru/HZSM-5-L1, Figure S9A), and ~5 μm (Ru/HZSM-5-L2, Figure S9B).

Table S3 shows the catalytic data in the hydrodeoxygenation of 2,6-dimethoxyphenol over these catalysts. Clearly, Ru/HZSM-5 exhibit 2,6-dimethoxyphenol conversion (70.0%) and cyclohexane selectivity (55.4%). In contrast, the cyclohexane product is undetectable over Ru/HZSM-5-L1 and Ru/HZSM-5-L2, because they have little exposed acid sites on their external surfaces. These results confirm the importance of catalytic activities to the ZSM-5 crystal sizes.

Table S4. Turnover frequencies (TOFs) of various catalysts in different reactions.

Steps	TOFs		
	Ru/HZSM-5	Ru/HZSM-5-M	Ru/HZSM-5-OM
Phenol hydrogenation (mol mol_{Ru}^{-1} h^{-1})	235.9	251.7	265.5
Cyclohexanone hydrogenation (mol mol_{Ru}^{-1} h^{-1})	376.7	399.9	455.0
Cyclohexanol dehydration (mol mol_{acid}^{-1} h^{-1})	102.7	135.8	147.6
Cyclohexene hydrogenation (mol mol_{Ru}^{-1} h^{-1})	956.9	898.8	1378.5
2,6-dimethoxyphenol hydrogenation (mol mol_{Ru}^{-1} h^{-1})	191.5	205.9	256.9
2-methoxycyclohexanol dehydration (mol mol_{acid}^{-1} h^{-1})	9.0	34.2	51.4

The turnover frequencies (TOFs) in the different reaction steps at the low conversions are calculated from the exposed Ru atoms and total acid sites. In the rate-controlling step (hydrogenation of phenol) of phenol hydrodeoxygenation, the Ru/HZSM-5, Ru/HZSM-5-M, and Ru/HZSM-5-OM catalyst exhibited TOF at 235.9, 251.7, and 265.5 h^{-1}. Particularly, the TOF of Ru/HZSM-5-OM is even higher than that of the Pd/C catalyst (240 h^{-1}), one of the most efficient catalysts in literature for the hydrogenation of phenol.[1]

In the hydrodeoxygenation of bulky phenolic molecule of 2,6-dimethoxyphenol, the rate-controlling step is the alcohol dehydration (*e.g.* dehydration of 2-methoxycyclohexanol). In this case, the TOFs are calculated from the acid sites on the external surface and/or in the mesopores of zeolite crystals. As presented in Table S4, the Ru/HZSM-5-OM catalyst exhibited TOF at 51.4 h^{-1}, which is much higher than that of Ru/HZSM-5 (9.0 h^{-1}), H_3PO_4 catalyst (1.1 h^{-1}), and Amberlyst-15 (2.5 h^{-1})

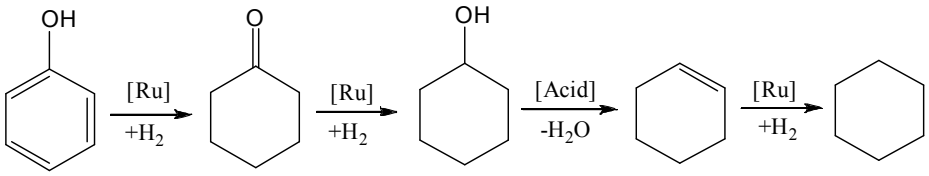
under the same reaction conditions.

These results indicate the superior catalytic activities of mesoporous zeolite Ru/HZSM-5-OM for the hydrodeoxygenation.

Table S5. Catalytic data in hydrodeoxygenation of phenol over Ru/HZSM-5-OM in various solvents.[a]

Solvent	Conv. (%)	Product selectivity (%)			Carbon balance (%)
		cyclohexane	cyclohexanol	cyclohexanone	
Water	>99.5	95.0	5.0	0.9	>99.5
Ethyl acetate	>99.5	96.4	<1.0	4.0	>99.5
Dodecane	60.0	96.0	<1.0	4.0	>99.5
Methanol[b]	90.0	65.1	3.0	1.0	97.9
Ethanol[b]	92.0	70.3	4.4	2.1	98.0

[a] The reaction conditions are the same to those in Table 2; [b] The by-products are ethers and some others.



Scheme S1. The process of phenol hydrodeoxygenation to cyclohexane over combined Ru and acid sites.

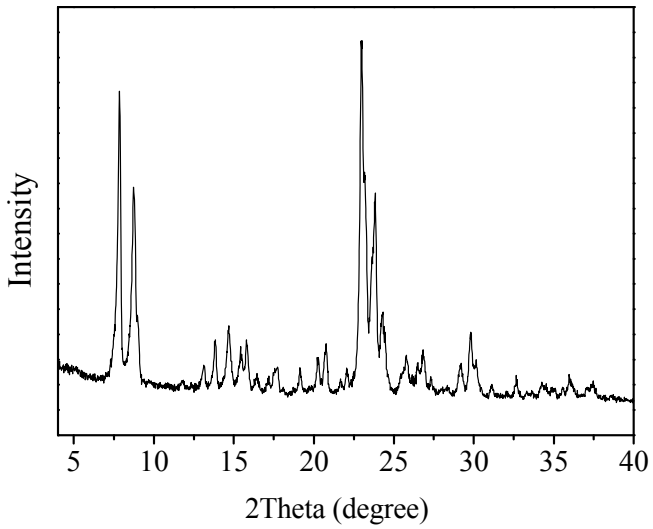


Figure S1. XRD pattern of HZSM-5-OM.

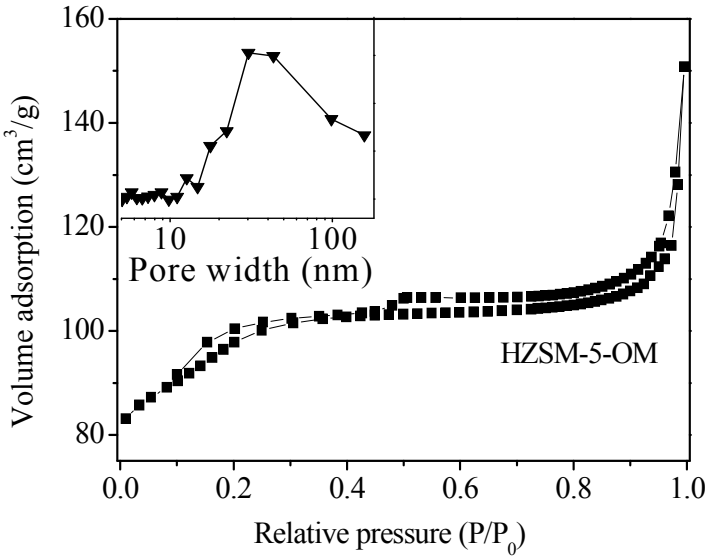


Figure S2. N_2 sorption isotherms of HZSM-5-OM (Insert: mesopore size distribution).

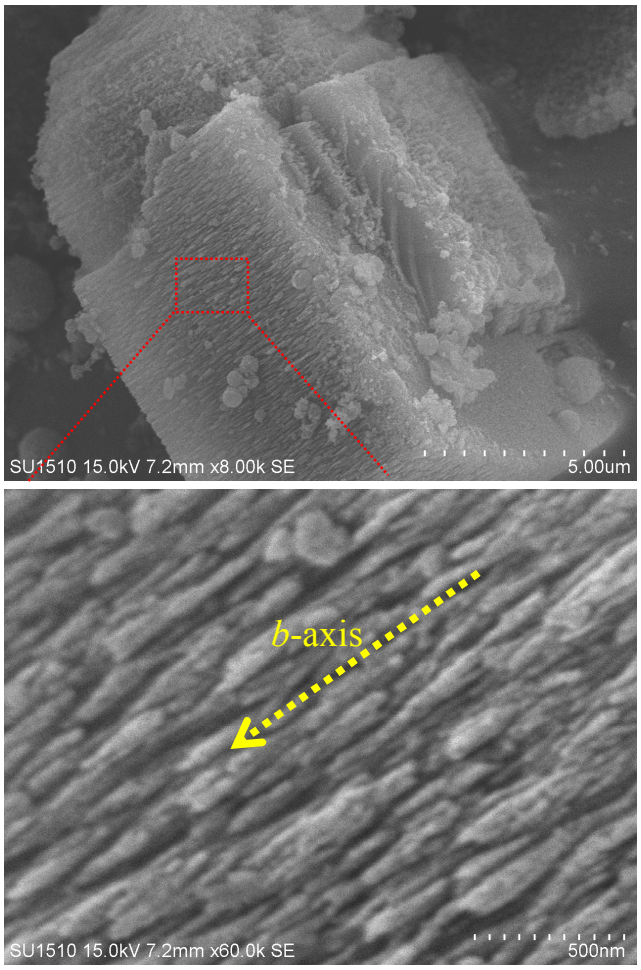


Figure S3. SEM images of HZSM-5-OM, giving a clear observation of the *b*-axis-aligned mesopores.

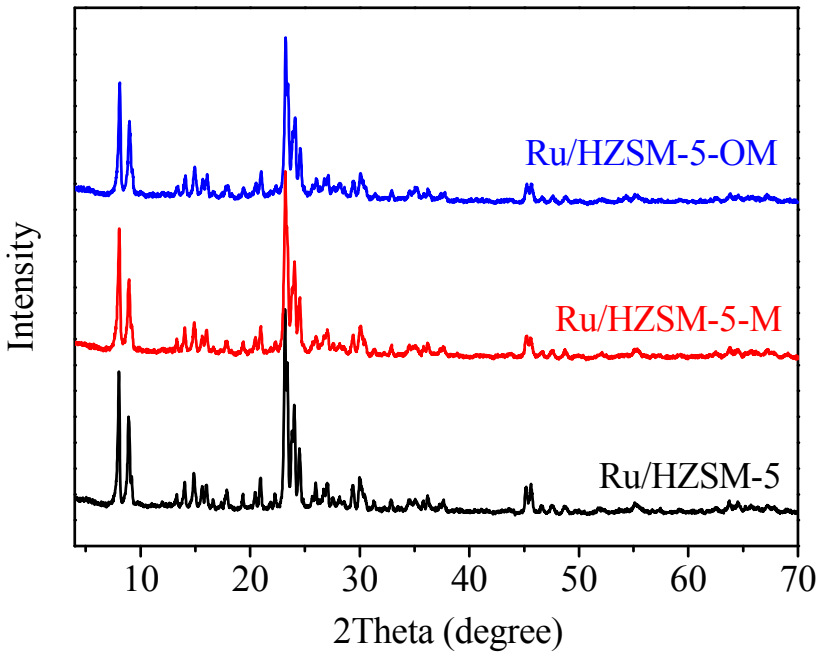


Figure S4. XRD patterns of Ru/HZSM-5-OM, Ru/HZSM-5-M, and Ru/HZSM-5 samples. The peaks associated with Ru species could not be found in these XRD patterns, indicating the small sizes of the Ru nanoparticles.

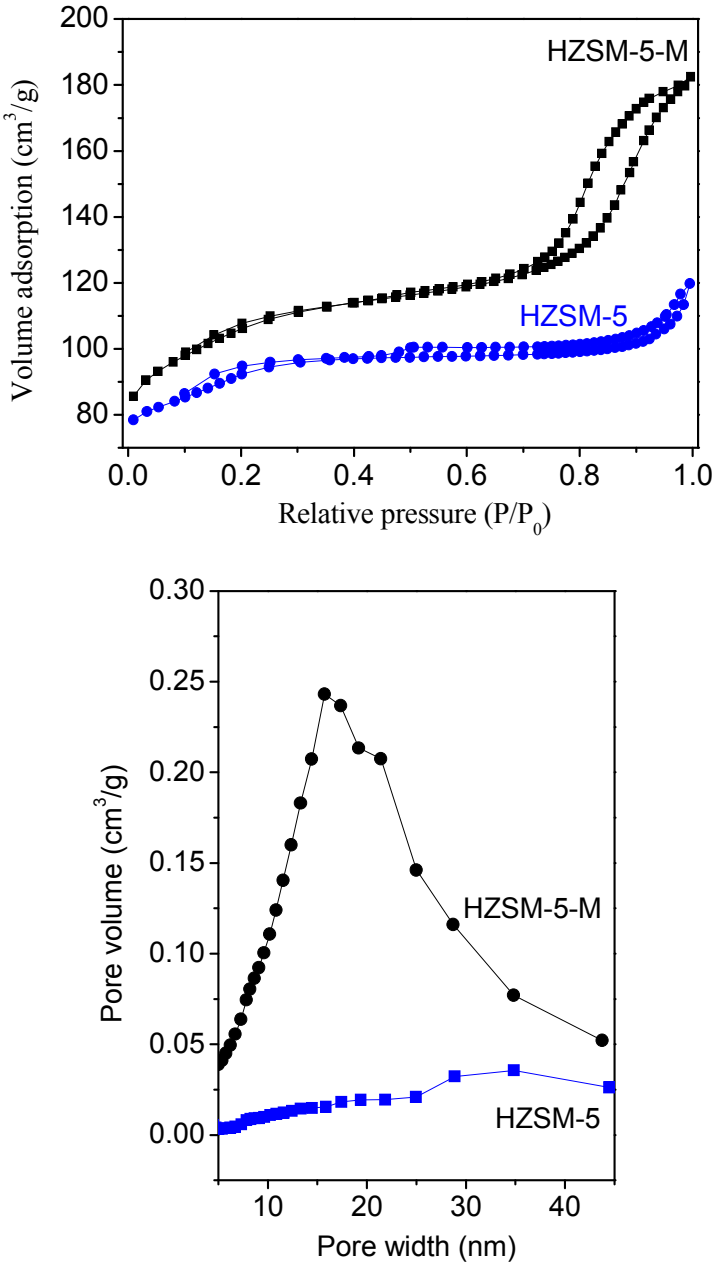


Figure S5. (Top) N_2 sorption isotherms and (bottom) mesopore size distribution of the HZSM-5 and HZSM-5-M. The ZSM-5-M exhibits N_2 sorption isotherms with a hysteresis loop at a relative pressure of $0.72 < P/P_0 < 0.90$, indicating the presence of the mesoporosity in the sample. In contrast, no obvious mesoporosity could be observed in the HZSM-5.

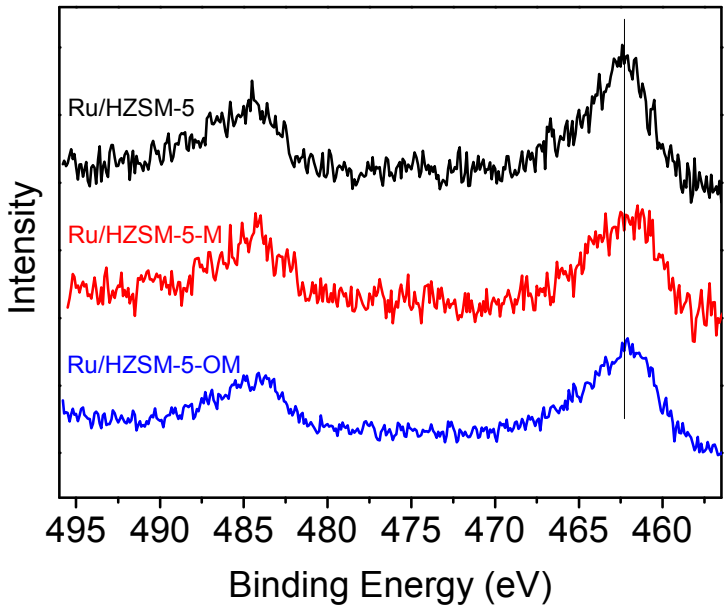


Figure S6. Ru3p XPS spectra of Ru/HZSM-5, Ru/HZSM-5-M, and Ru/HZSM-5-OM.

The strongest Ru3d peak was not employed to determine the chemical state of Ru due to overlapping with the C1s peaks. In Figure S6, the Ru 3p XPS spectra exhibit $3p_{3/2}$ binding energy at 462.2 eV and the $3p_{3/2}$-$3p_{1/2}$ doublet separation of 22.3 eV, indicating that most of the Ru species are presented as metallic state. However, it is worth noting that there might be Ru^{n+} ($0 < n \leq 4$) species, which is difficult to distinguish in the XPS spectra.[2] In order to eliminate/reduce the Ru^{n+} species, the Ru/HZSM-5-OM sample was treated in H_2 at 350 °C for 2 h, denoted as Reuced-Ru/HZSM-5-OM. Interestingly, Ru/HZSM-5-OM and Reuced-Ru/HZSM-5-OM exhibited very similar reaction rate (6.2 and 5.9 mmol g^{-1} h^{-1}) in the hydrogenation of phenol. These results suggest that the Ru^{3+} in the catalysts could be completely ignored if these species in the catalysts could not be detected by the XPS technique.

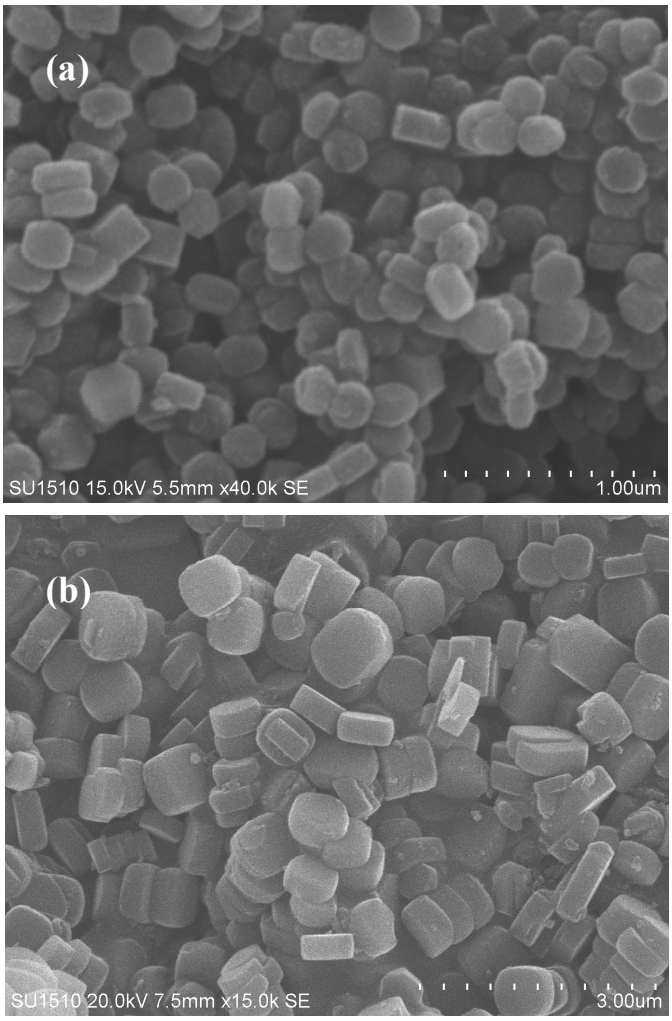


Figure S7. SEM images of (a) Ru/HZSM-5 and (b) Ru/HZSM-5-M.

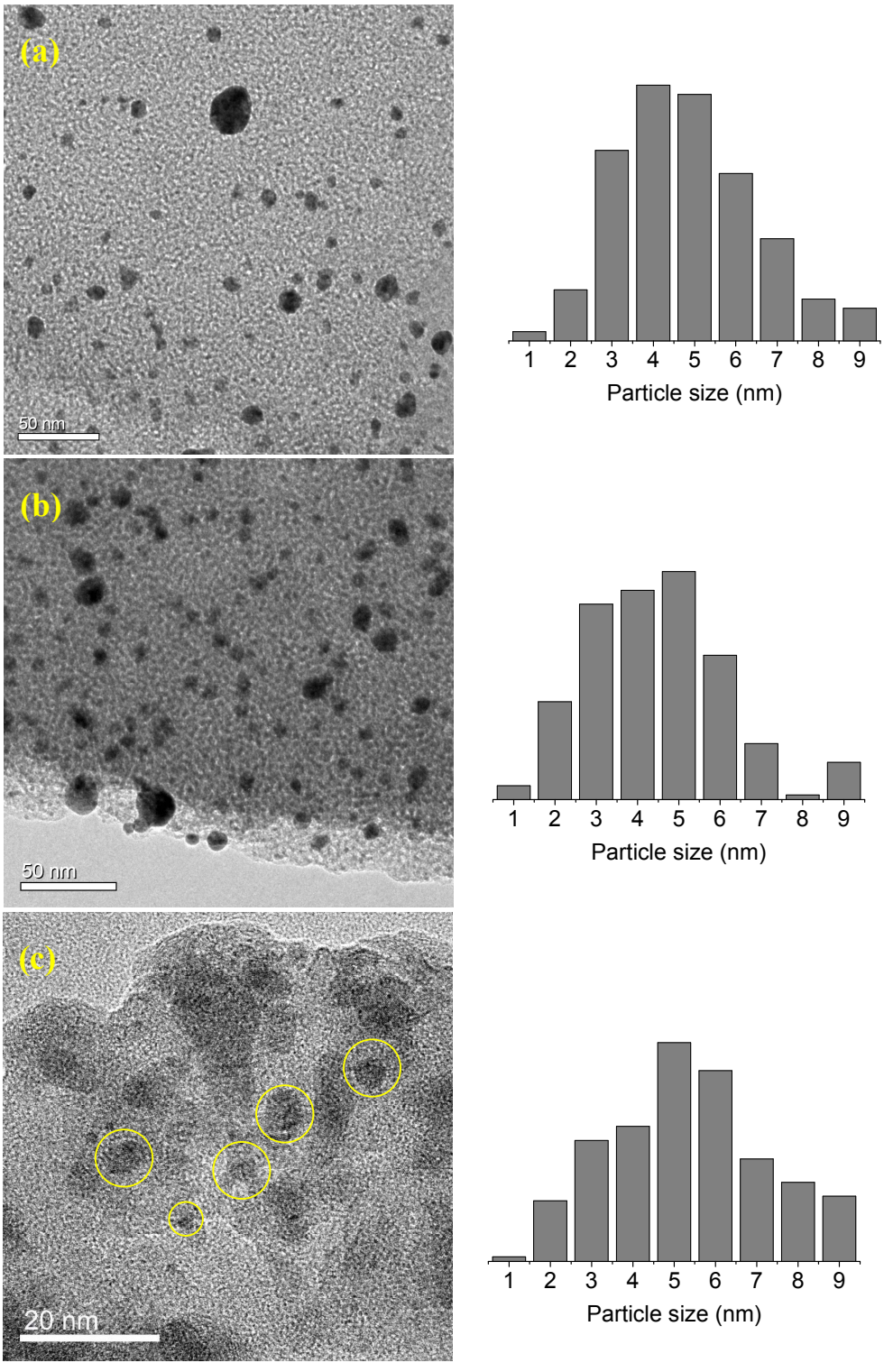


Figure S8. TEM images the corresponding Ru nanoparticle size distribution of (a) Ru/HZSM-5, (b) Ru/HZSM-5-M, and (c) Ru/HZSM-5-OM.

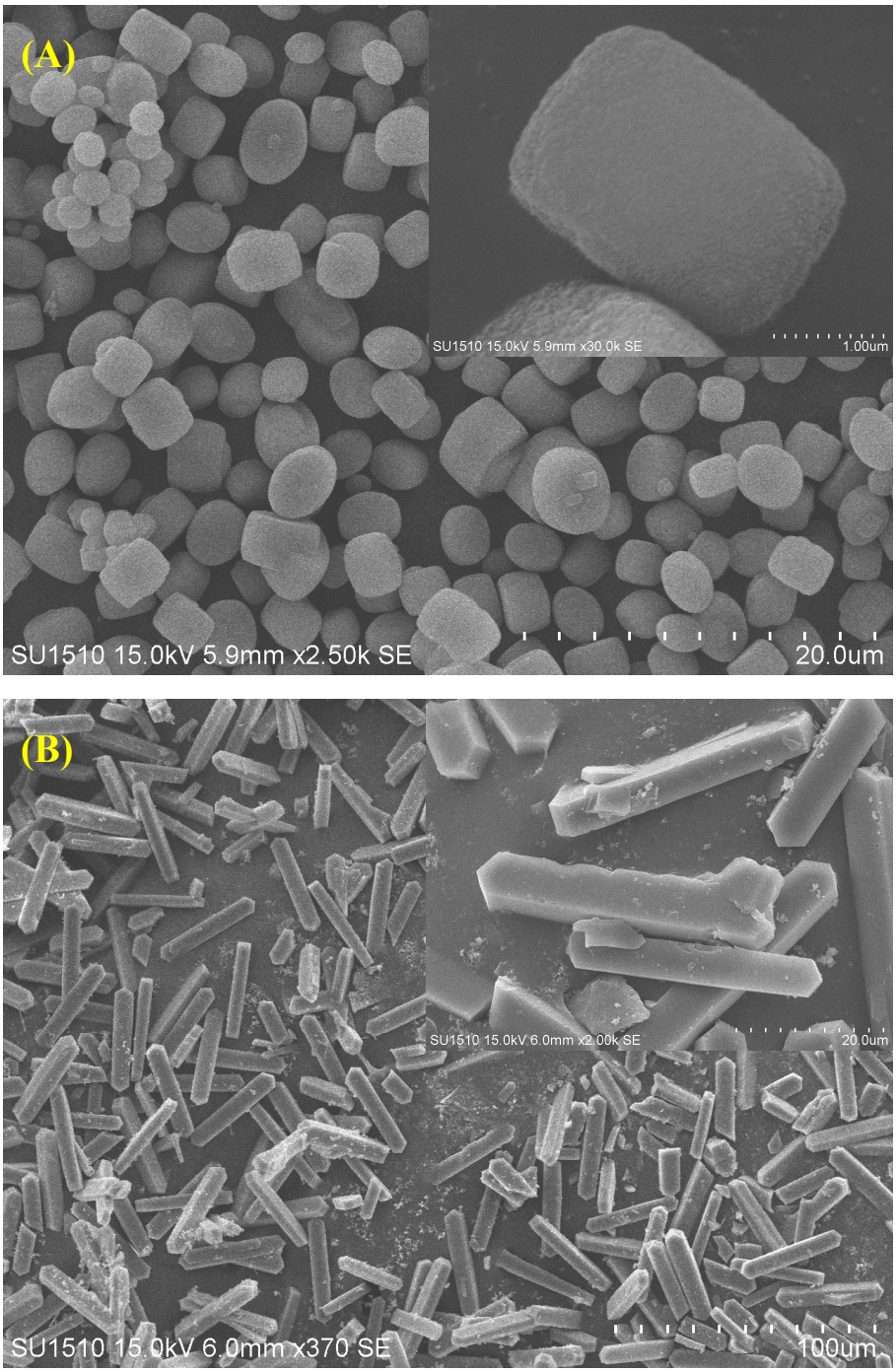


Figure S9. SEM images of (A) Ru/HZSM-5-L1 and (B) Ru/HZSM-5-L2.

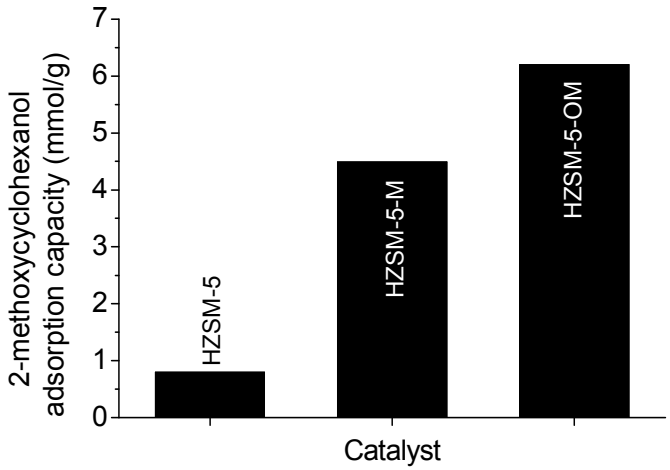


Figure S10. The adsorption capacity of 2-methoxycyclohexanol over various samples. HZSM-5-OM exhibits higher adsorption capacity (6.2 mmol/g) of 2-methoxycyclohexanol than HZSM-5-M and HZSM-5 (0.8-4.4 mmol/g), confirming the importance of open mesopores in the zeolite for access of the bulky molecules.

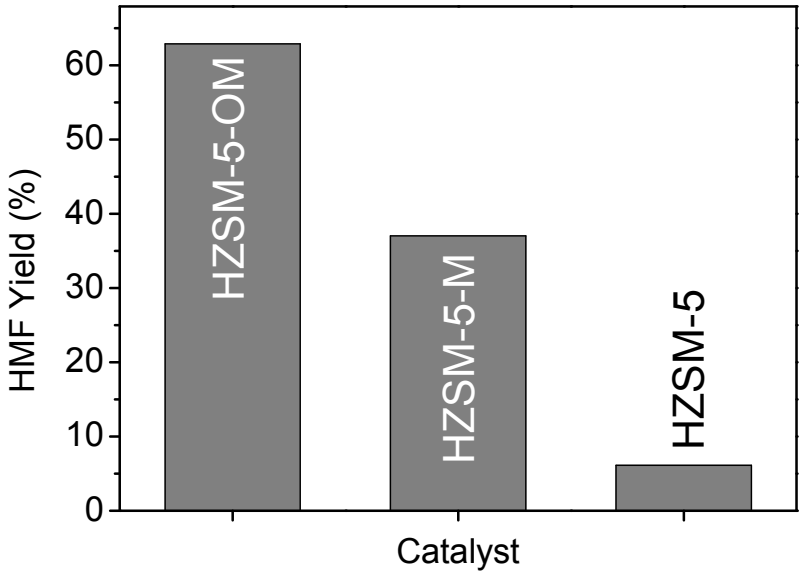


Figure S11. The yields of 5-hydroxymethylfurfural (HMF) from conversion of glucose over various catalysts. Reaction conditions: 20 mg of catalyst, 1 mmol of glucose, 2.5 g of [Emim]Cl ionic liquid, 80 ℃, 2 h.

References

(1) Zhao, C.; Kou, Y.; Lemonidou, A. A.; Li, X.; Lercher, J. A. *Angew. Chem. Int. Ed.* **2009**, *48*, 3987.

(2) Qadir, K.; Joo, S. H.; Mun, B. S.; Butcher, D. R.; Renzas, J. R.; Aksoy, F.; Liu, A.; Somorjai, G. A.; Park, J. Y. *Nano Lett.* **2012,** *12,* 5761.