Ultrasmall Amphiphilic Zeolitic Nanoreactors for Aerobic Oxidation of Alcohols in Water

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Chemicals and reagents

Tetrapropylammonium hydroxide (TPAOH, 25 wt. % aqueous solution), n-Hexadecane (>99.0%), and 3-Aminopropyltriethoxysilane (APTES, >98.0%) were purchased from Aladdin Chemicals, China. Tetraethyl orthosilicate (TEOS, AR), Sodium hydroxide (NaOH, AR), Aluminium isopropoxide (AR), Toluene (AR), Trichloromethane (AR), Ethanol (AR), Sodium chloride (NaCl, AR), Ethyl acetate (AR), and Sodium tetrachloropalladate (II) (Na_2PdCl_4) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Phenyltrimethoxysilane (PTMS, >98%) were purchased from Tokyo Chemical Industry Co., Ltd., China. All alcohols were purchased from Aladdin. All chemicals were used as received without further purification. The water (>18.2 MΩ cm) was obtained from a Millipore-Q water purification system (Millipore, USA) in this work.

Preparation of the lipophilic ZSM-5 (liZSM-5) zeolites.

The as-obtained ultrasmall ZSM-5 zeolites (1.0 g) were homogeneously dispersed into toluene (50.0 mL). Then, PTMS was added to the toluene suspension. After magnetic stirring at 80 ℃ for 4 h, the liZSM-5 zeolites were obtained through centrifugation and then washed three times with trichloromethane.

Preparation of the Pd@hyZSM-5 nanoreactors.

Pd@hyZSM-5 nanoreactors were prepared according to the above method by replacing amZSM-5 zeolites with hyZSM-5 zeolites.

Preparation of the Pd@liZSM-5 nanoreactors.

Pd@liZSM-5 nanoreactors were prepared according to the above method by replacing amZSM-5 zeolites with liZSM-5 zeolites.

Interfacial activity test

25 mg of the amZSM-5 zeolites were added into a 25 mL colorimetric tube with 10 mL of NaCl aqueous (1 M) and 10 mL of n-hexadecane. The emulsion was obtained by sonicating for 30 s and vigorously stirring.

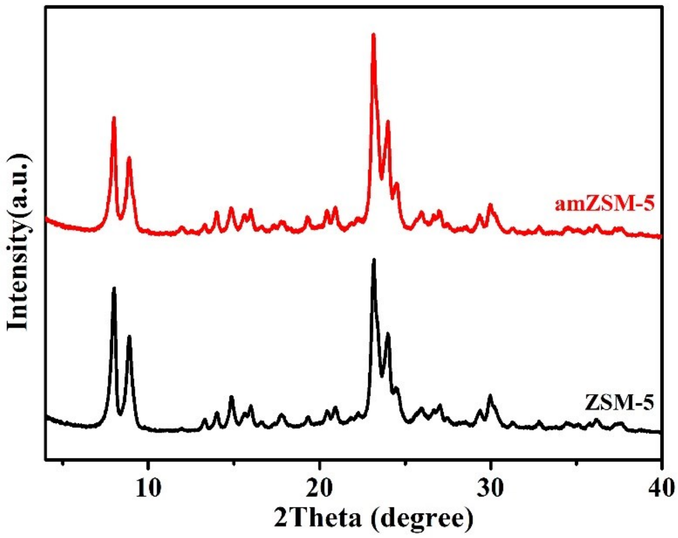


Figure S1. Wide-angle XRD patterns of ZSM-5 and amZSM-5 zeolites.

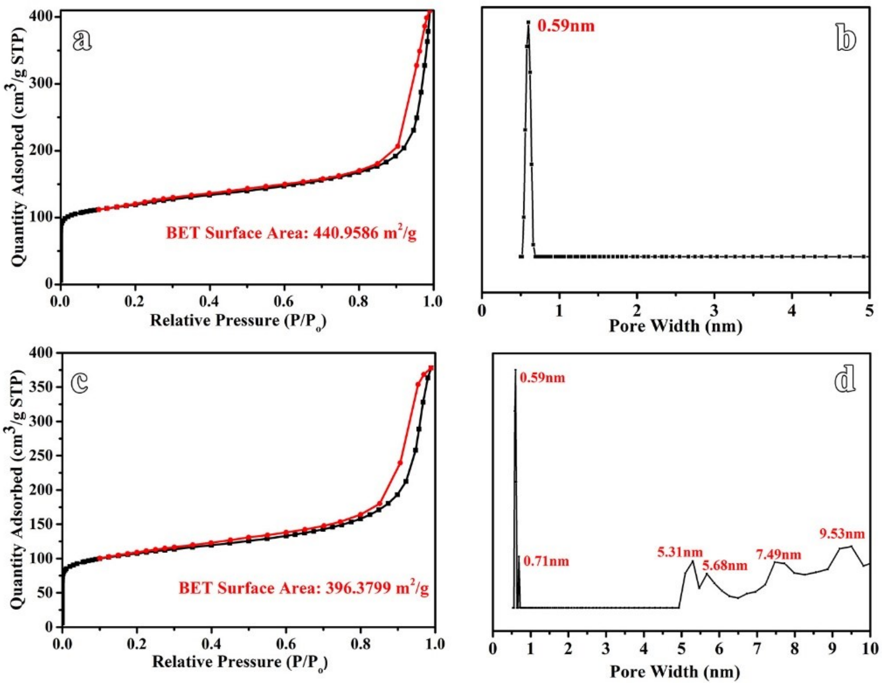


Figure S2. N_2 sorption isotherms (a, c), and the pore size distributions (b, d) of the ZSM-5 zeolites (a, b) and amZSM-5 zeolites (c, d).

Table S1. Physical properties of the ultrasmall ZSM-5 zeolites, and amZSM-5 zeolites.

Sample	**BET Surface Area (m^2/g)**	**Micropore Area (m^2/g)**	**Extermal Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Micropore Size (nm)**	**Mesopore Size (nm)**
Ultrasmall ZSM-5 zeolites	440.9586	263.8625	177.0960	0.635260	0.59	-
amZSM-5 zeolites	396.3799	229.9724	166.4075	0.585909	0.59	5.31

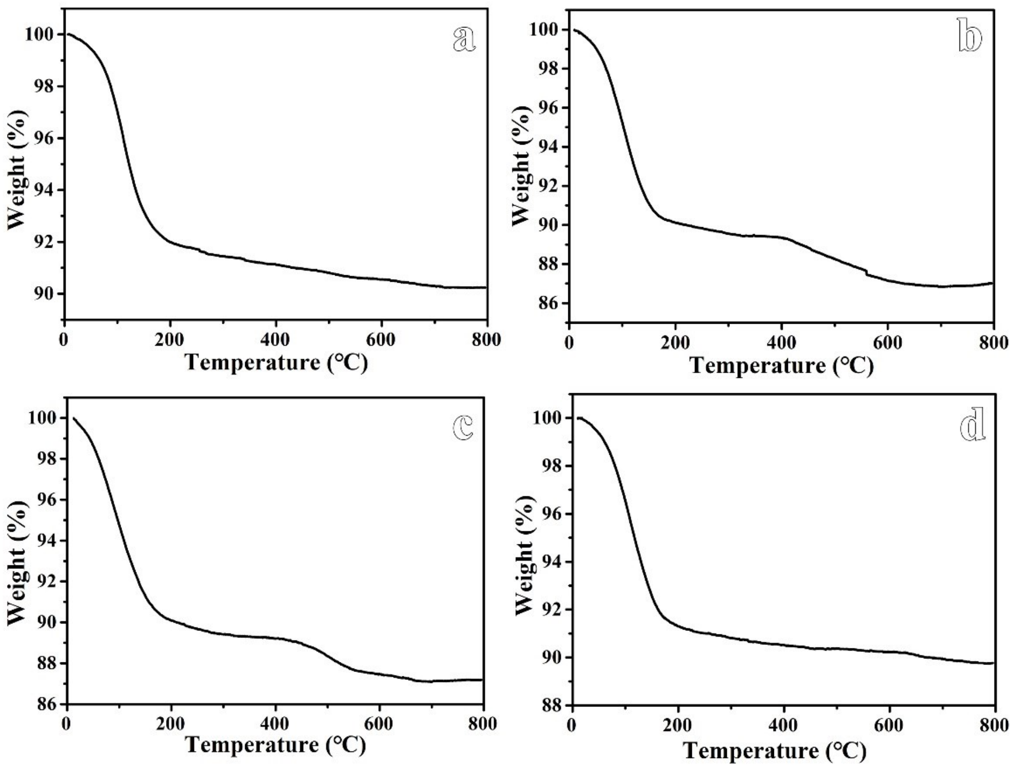


Figure S3. TGA curves of hyZSM-5 zeolites after low concentration alkali etching (a), amZSM-5 (b), hyZSM-5 (c), and liZSM-5 nanoreactors (d).

Table S2. Thermogravimetric analysis results of the amZSM-5 zeolites, hyZSM-5 zeolites, and liZSM-5 zeolites.

	aminopropyl groups (mmol/g)	**phenyl groups (mmol/g)**
amZSM-5 zeolites	0.1219	0.1158
hyZSM-5 zeolites	0.1947	-
liZSM-5 zeolites	-	0.1167

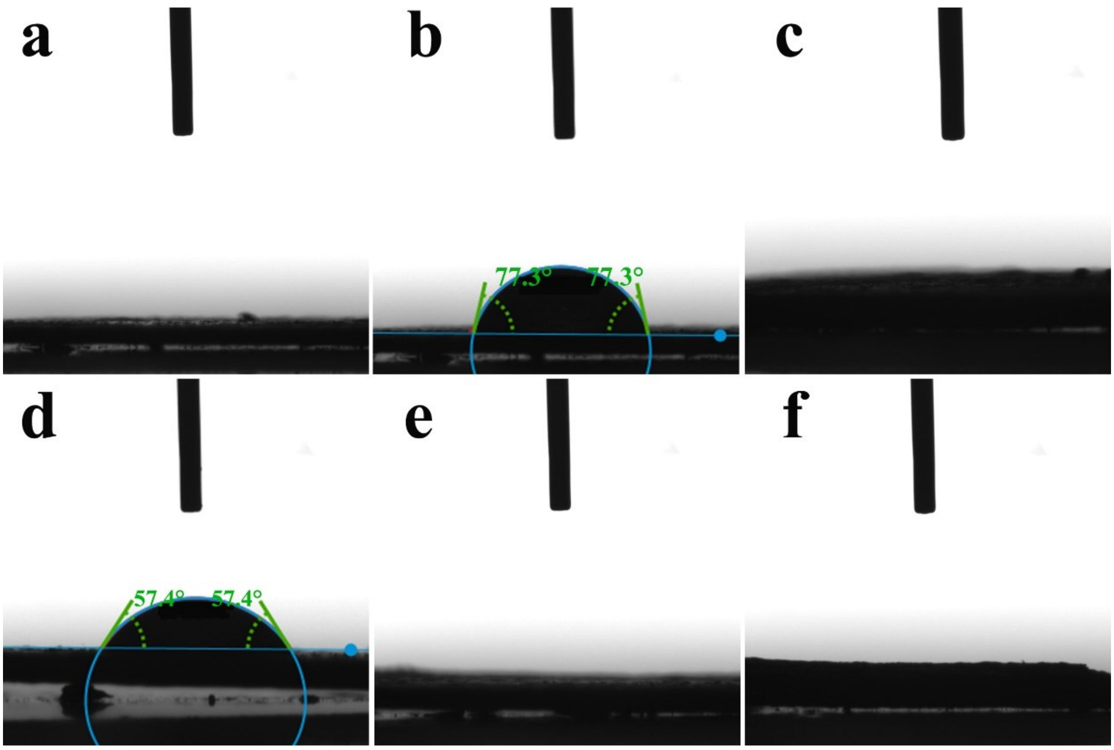


Figure S4. Water-solid-air three phase contact angles (a, b, c) and oil-solid-air three phase contact angles (d, e, f) of the hyZSM-5 (a, d), liZSM-5 (b, e), and amZSM-5 (c, f) zeolites. The oil phase is hexadecane.

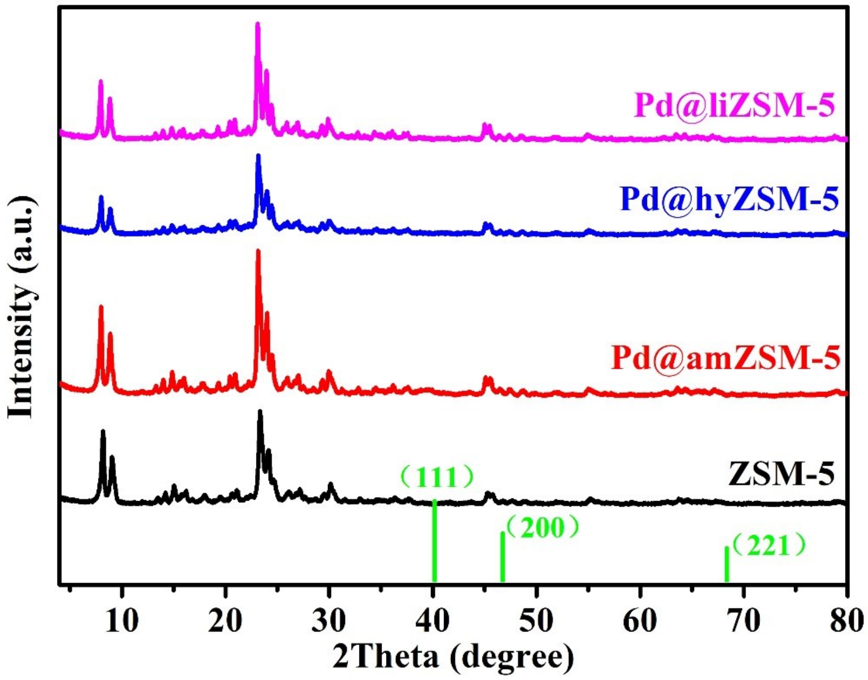


Figure S5. Wide-angle XRD patterns of ultrasmall ZSM-5, Pd@hyZSM-5, Pd@liZSM-5, and Pd@amZSM-5 composites.

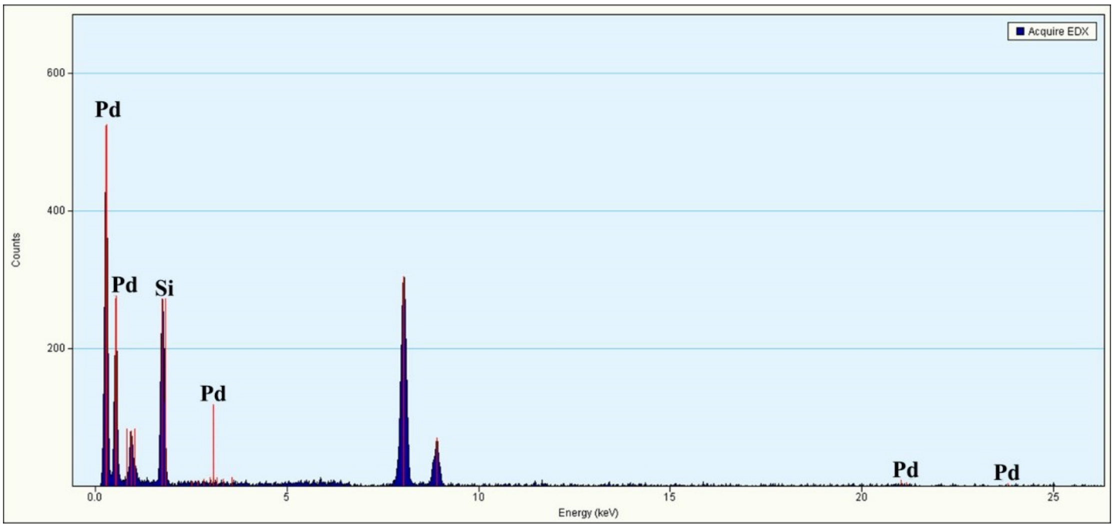


Figure S6. Energy dispersive X-ray Spectroscopy (EDX) results of Pd@amZSM-5 nanoreactors.

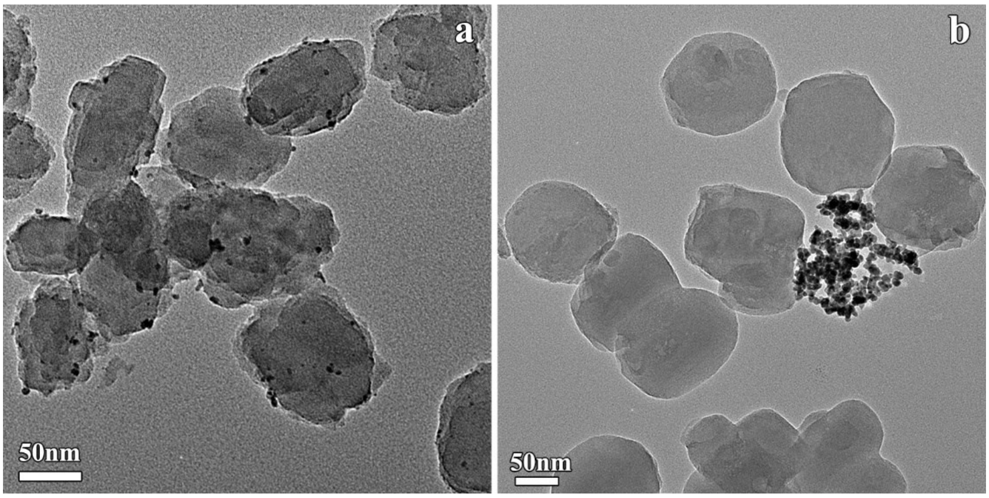
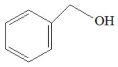
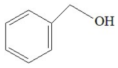
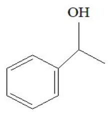
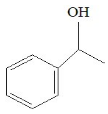
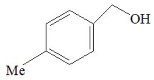
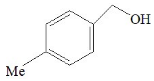
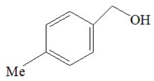
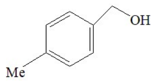
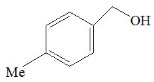
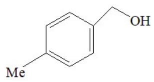


Figure S7. TEM images of Pd@hyZSM-5, and Pd@liZSM-5 nanoreactors.

Table S3. Catalytic results of various nanoparticle catalysts for the selective oxidation of alcohols.

Entry	Reactant	Catalyst	Reaction conditions	Conv. /Sel. (%)	TOF[h^{-1}]	Ref
1		AuCl	4 mL H_2O, 90℃, air	100/99	0.67	1
2		Ru/CNT–TiO_2	5 mL H_2O, 10 mL toluene, 85℃, 0.1 MPa O_2	95/99	10.8	2
3		PS/$Au_{1.25}Pt_1$	H_2O, air, 40℃	99/-	1.4	3
4		Au@P_0PD-supported	K_2CO_3 (3 equiv), room temperature, air, H_2O	90/-	6.1	4
5		Au@Pd@Ph-PMO	K_2CO_3 (0.5 mmol, 1 equiv.), 4 mL H_2O, open air, 80℃	100/96	13.5	5
6		Fe_3O_4@SiO_2@Pd/HS-PMO	K_2CO_3 (0.5 mmol, 1 equiv.), 4 mL H_2O, open air, 80℃	>99/>98	16.9	6
7		Pt/N_xC@mSiO_2	K_2CO_3 (0.5 mmol, 1 equiv.), 4 mL H_2O, open air, 80℃	>99/>99	26.7	7
8		$RuCl_3$@MIL-101(Cr)–tpy	H_2O (5 mL), 100 ℃, H_2O_2 (0.75 mmol)	>99/>99	16.7	8
9		Pd@amZSM-5	4 mL H_2O, open air, 80℃	>99/>99	42.9	This work
10		Pd1Au_{24}/CNT	K_2CO_3 (80mol%), 10 mL H_2O, 0.1 MPa O_2, 30℃	74/	57.1	9

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