

Electronic Supplementary Information (ESI†)

Platinum Nanoparticles Supported on Ca(Mg)-Zeolites for Efficient Room-Temperature Alcohol Oxidation under Aqueous Condition

Yejiang Hong,^{a‡} Xiaoqing Yan,^{b‡} Xiaofeng Liao,^a Renhong Li,^{*b}
Shaodan Xu,^a Liping Xiao,^a Jie Fan^{*a}

Experimental section

Catalyst preparation: **PtNPs**: 100 mg Pt(acac)₂ was dissolved in 30 mL oleylamine at 110 °C for 10 mins, then cooled to 100 °C. The mixture was heated to 140 °C and kept for 4 h after the addition of 2 mL oleylamine containing 200 mg borane-tert-butylamine as the reducing agent. After cooling to room temperature, PtNPs were precipitated from the mixture by addition of 60 mL anhydrous ethanol, and then collected by centrifuge and ethanol washing, and drying in vacuum (60 °C) over night. **Ca-ZSM-5 and Mg-ZSM-5**: NaAlO₂ (0.08 g), tetrapropylammonium hydroxide (7 mL, 2 M in H₂O), and tetraethyl orthosilicate (7 mL) were mixed in water (20.0 mL), then 0.18 g Ca(NO₃)₂·4H₂O or 0.2 g Mg(NO₃)₂·6H₂O was added and aged at 100 °C for 2 h. After stirring for 12 h at room temperature, the mixture was transferred into an autoclave at 180 °C for 120 h for further crystallization. The product was collected by filtration,

dried in air, and calcined at 550 °C for 5 h to remove the residue template;

Supported PtNPs: PtNPs were loaded onto their support *via* a colloid deposition method, as shown in our previous work. The catalysts were calcined at 400 °C for 4 h prior to catalytic reactions.

Catalysis: The oxidation of alcohols was catalyzed by PtNPs loaded Ca(Mg)-Zeolites at room temperatures. Reaction conditions: 50 mg catalyst and 0.1 mmol alcohols were added into 5 ml H₂O, and then stirred for 20 h in open air. The catalytic performance was followed by measuring the values of alcohol and product concentration by GC-FID and calculating the substrate conversion and the selectivity toward aldehydes/ketones using ethanol as the solvent for both of water and alcohols.

EPR experiments: X-band EPR signals were recorded at room temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10 msec. A glass capillary tube containing calculated catalysts, alcohol and water suspension, and ice-cooled DMPO solution (0.08 M) was transferred and tested by EPR spectroscopy. No DMPO spin trapping signal was found in the absence of PtNPs. Other characterizations were all conventional techniques and not described here.

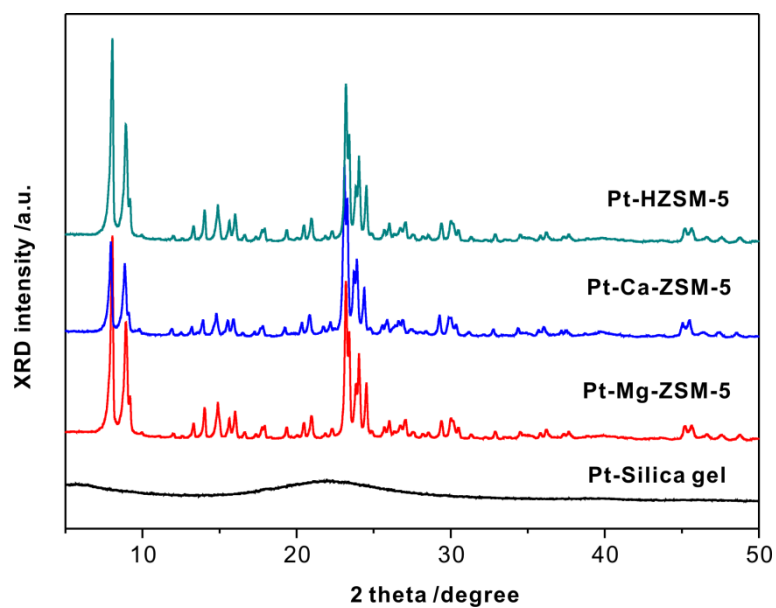


Fig. S1. XRD patterns of PtNPs supported on ZSM-5 and silica gel, where the Pt peak is difficult to discern because of its high dispersion and low loading amounts.

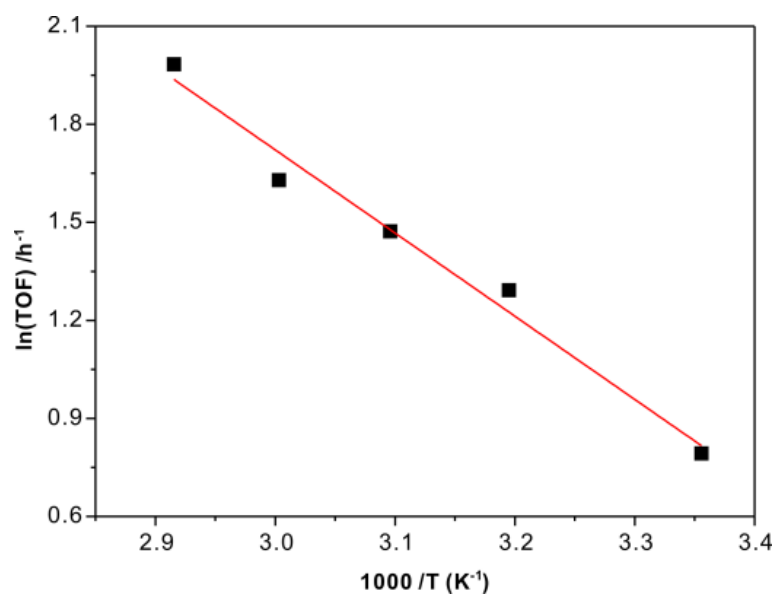


Fig. S2. Arrhenius plots for benzyl alcohol oxidation over Pt/Ca-ZSM-5 catalyst at different reaction temperatures; the apparent activation energy of the reaction is calculated to be 21.2 kJ/mol.

Table S1. Life cycle of Pt/Ca-ZSM-5 on benzyl alcohol oxidation at room temperature in aqueous system.^a

Recycling number	Conv. (%)	Sel. (%)	Pt loading (wt%)
1st	98.8	99	1.08
2nd	97	98	1.05
3rd	96.5	99	1.06
4th	96	99	1.08

^a Detailed experimental procedure: after each 20 h reaction with benzyl alcohol (20 mM) in water, the catalyst was centrifuged, the upper liquid was removed and the residual catalyst was regenerated by drying in air (60 °C).

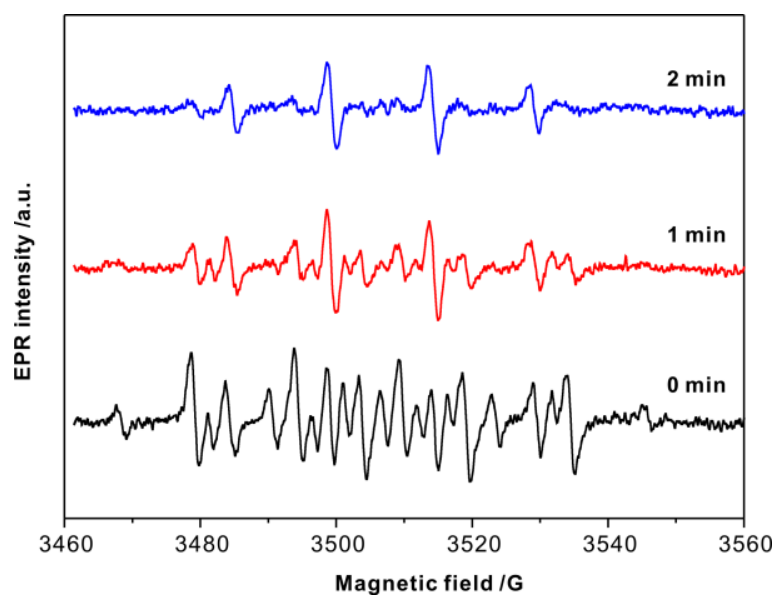


Fig. S3. *In situ* room temperature EPR spectra of the DMPO adducts recorded in the reaction system containing DMPO spin trapping reagent, cyclohexanol, water solvent and Pt/Ca-ZSM-5 catalyst from the beginning to the end of 2 min reaction time.

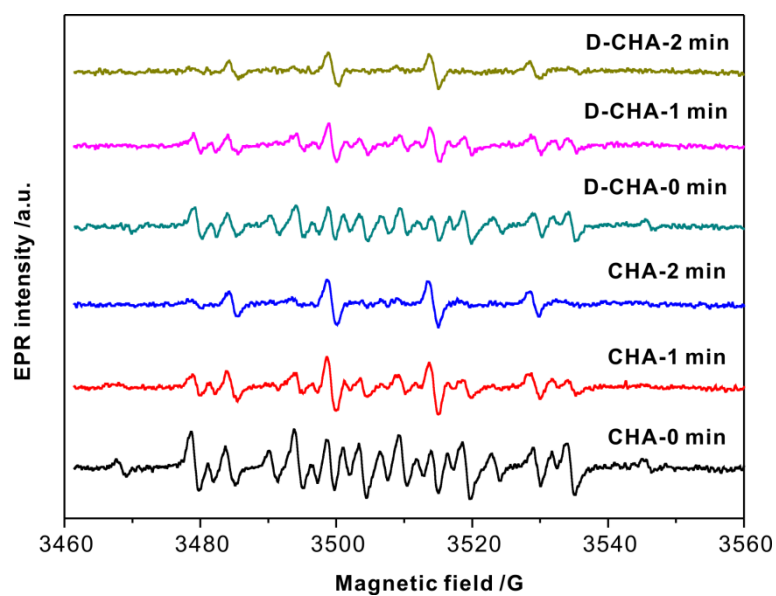


Fig. S4. *In situ* room temperature EPR spectra of the DMPO adducts recorded in the reaction system containing DMPO spin trapping reagent, cyclohexanol (C_6H_5-OH ; CHA) or deuterated cyclohexanol (C_6D_5-OH ; D-CHA), water solvent and Pt/Ca-ZSM-5 catalyst from the beginning to the end of 2 min reaction time.