Supplementary Information

Improving the hydrothermal stability of Pd/SSZ-13 for the low-temperature NO adsorption: Promotional effect of Mg²⁺ co-cation

Jinhuang Cai [a], Huawang Zhao [a]*, Xiang Li [c], Guohua Jing [a], Johannes W. Schwank [b]

a. Department of Environmental Science & Engineering, College of Chemical Engineering, Huaqiao University, Xiamen, Fujian 361021, China

b. Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA.

c. Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo 02150, Finland

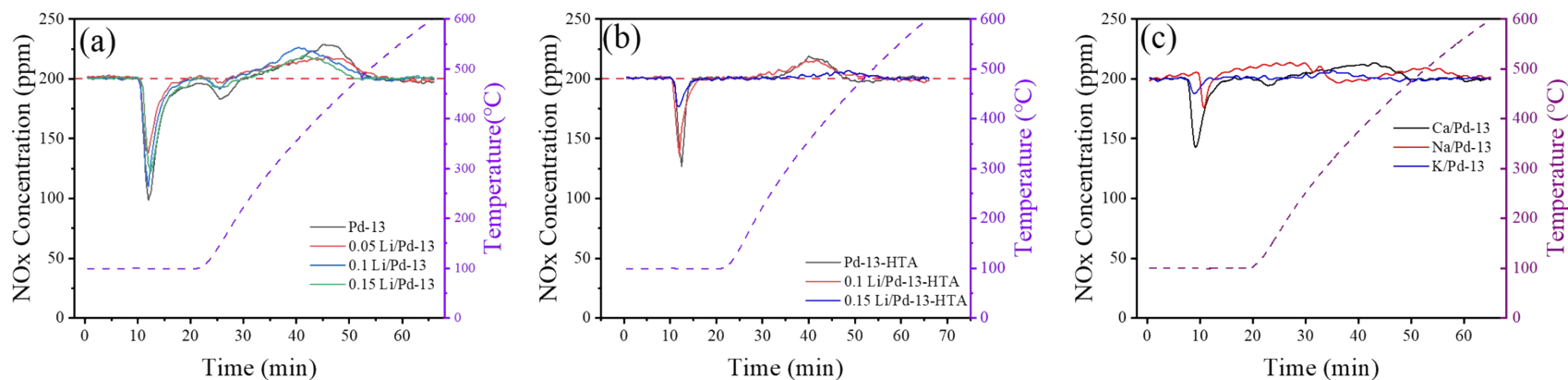* Corresponding author: hwzhao@hqu.edu.cn

Section S1

Fig. S1. The NO$_x$ profiles of Fresh (a) and HTA (b) Li/Pd-13 samples, (c) The NO$_x$ profiles of fresh alkaline (earth) metal doped Pd-13 samples.

Li/Pd/SSZ-13 and Na/Pd-SSZ-13 samples were prepared by a two-step incipient impregnation method. Firstly, Pd/SSZ-13 with a Pd loading of 1 wt.% were prepared by impregnating an appropriate amount of palladium nitrate solution. Li and Na loading were achieved by doping 1 mL LiNO$_3$ and NaNO$_3$ solution (0.07 mmol/L) on 1 g of Pd/SSZ-13, respectively. The catalysts were activated after calcination in a muffle furnace at 600 °C for 5 h. The ICP results show that the Na and Li loading in Na/Pd-SSZ-13 and Li/Pd-SSZ-13 is 83 and 75 μmol/g$_{cata}$, respectively.

The Li doping decreased the NO$_x$ storage capacity of Pd-13 (Fig. S1a). The HTA stability also decreased in Li/Pd-13 compared to Pd-13 (Fig. S1b). The Na, K, Ca significantly decreased the NO$_x$ uptake ability (Fig. S1c).
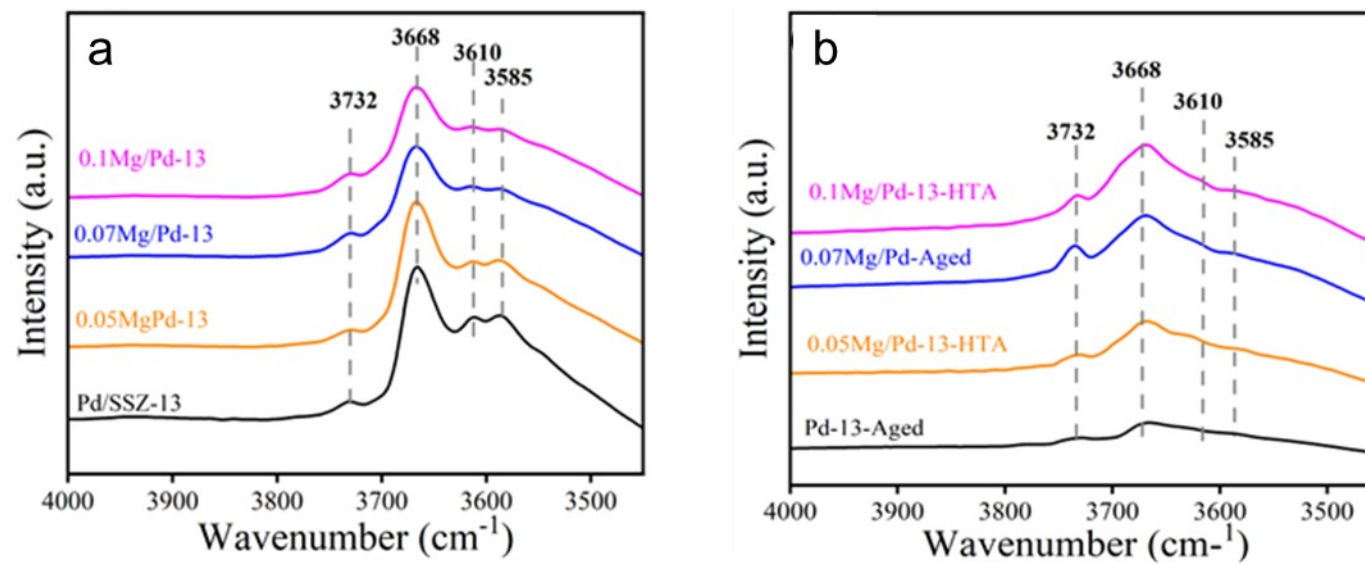
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Section S2

Fig S2. In situ DRIFTS spectra of fresh (a) and HTA (b) samples with a flow of 1000 ppm NH_3/N_2 measured at 30 °C. Total flow rate was 50 mL/min.
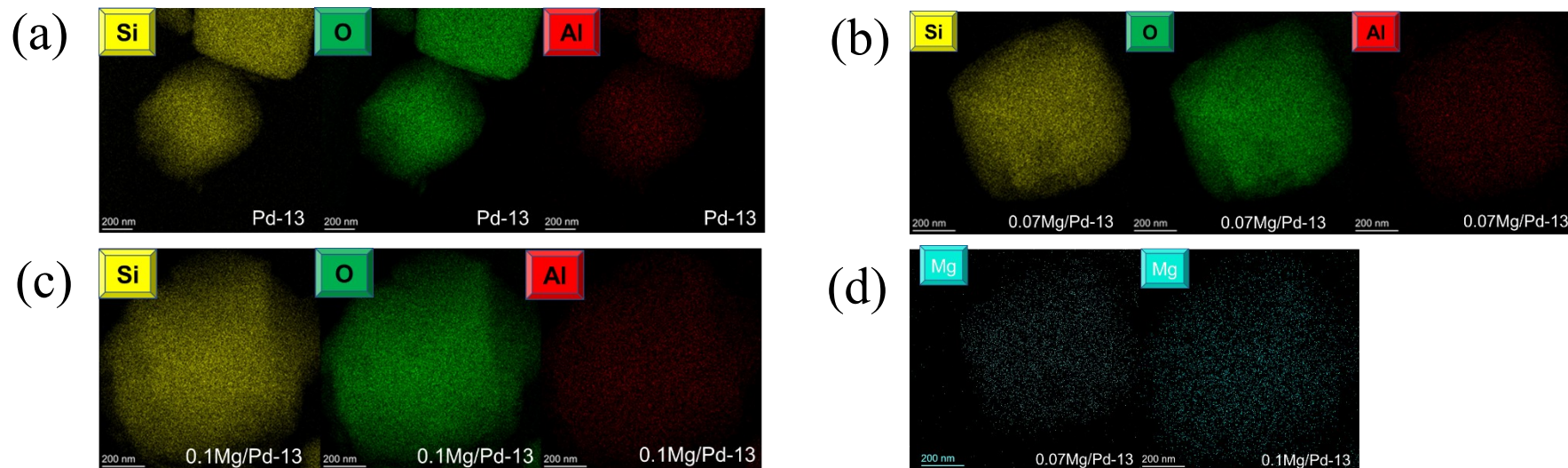
Section S3

Fig S3 Mapping diagram of Si, O, Al and (Mg) elements in fresh samples.

The transmission electron microscope (TEM) images were pictured by a Tecnai G2 20 at an acceleration voltage of 200 kV. Before taking the images, the powder catalyst was suspended in ethanol, dispersed by ultrasonication, and then dropped onto lacey formvar/carbon 200 mesh copper grids.
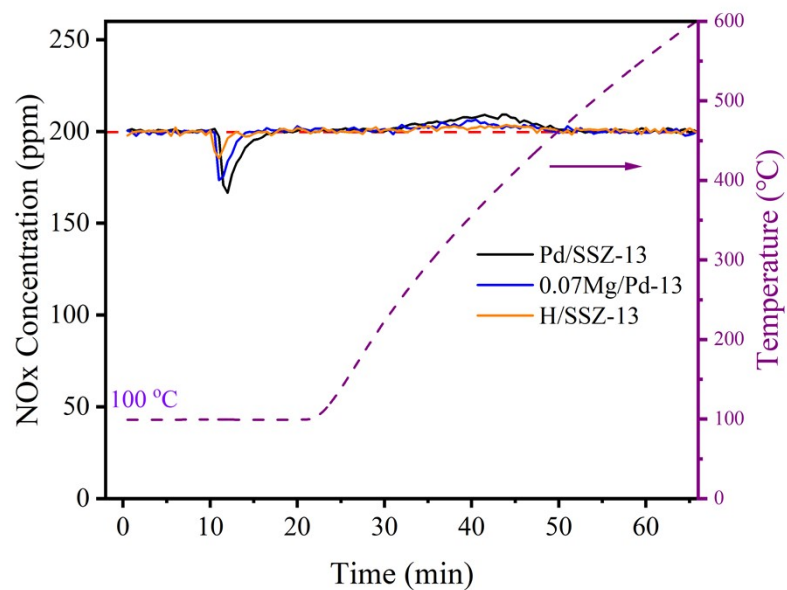
Section S4

Fig S4. The NO_x profiles of Fresh back-exchange Pd -13, 0.07Mg/Pd-13 and H/SSZ-13 samples for NO adsorption at 100 °C for 10 min followed with release (10 °C /min up to 600 °C). Reaction conditions: 200 mL min^{-1} (200 ppm NO, 5 %vol O_2, 5%vol H_2O and balanced with N_2). Note that during the first 10 min of data recording, the feed gas runs through the bypass line.

The NH_4^+-exchanged sample showed similar NO_x adsorption capacity to H-SSZ-13, indicating that the Pd^{2+} ions were almost completely removed.
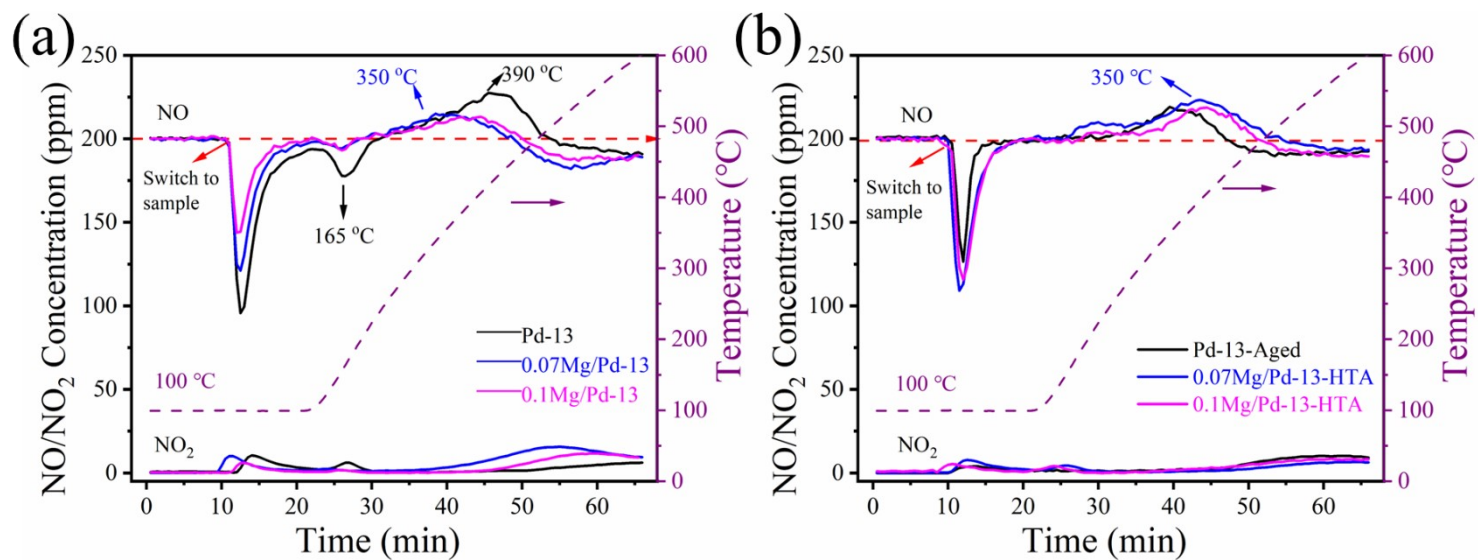
Section S5

Fig. S5. The concentrations of NO and NO2 of Fresh (a) and (b) Pd-13, 0.07Mg/Pd-13, 0.1Mg/Pd-13 samples during adsorption and release. Reaction conditions: 200 mL min^{-1} (200 ppm NO, 5 %vol O_2, 5%vol H_2O and balanced with N_2). Note that during the first 10 min of data recording, the feed gas runs through the bypass line.
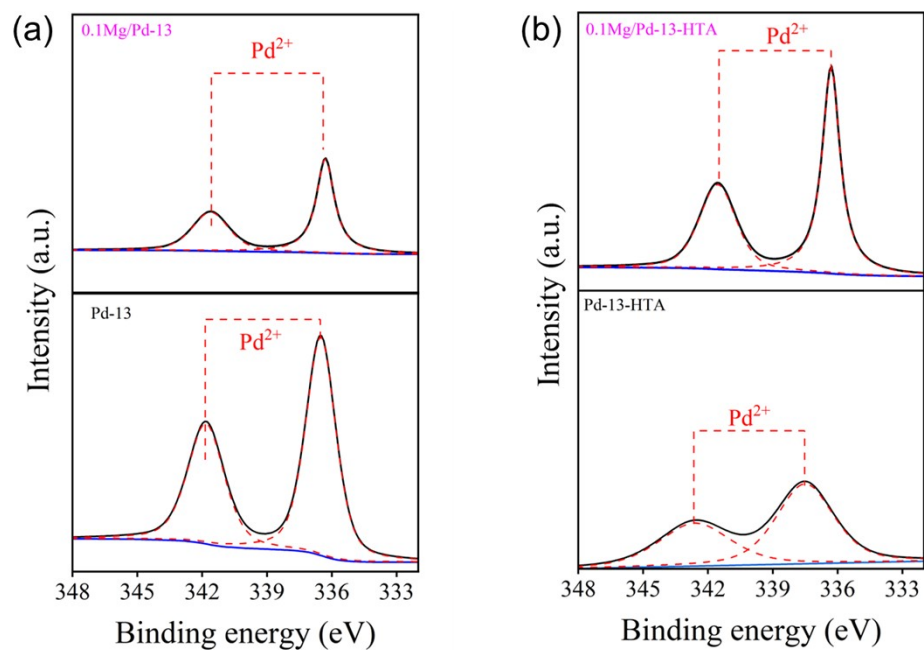
Section S6

Fig S6. XPS of Fresh (a) and HTA (b) samples.

The X-ray photoelectron spectroscopy (XPS) was performed on a on a Thermo Scientific K-Alpha XPS instrument, using Mg Kα as X-ray source (1253.6 eV) under a residual pressure of 5×10^{-6} Pa. The error of the binding energy is ± 0.2 eV using C 1 s at 284.6 eV as the standard.
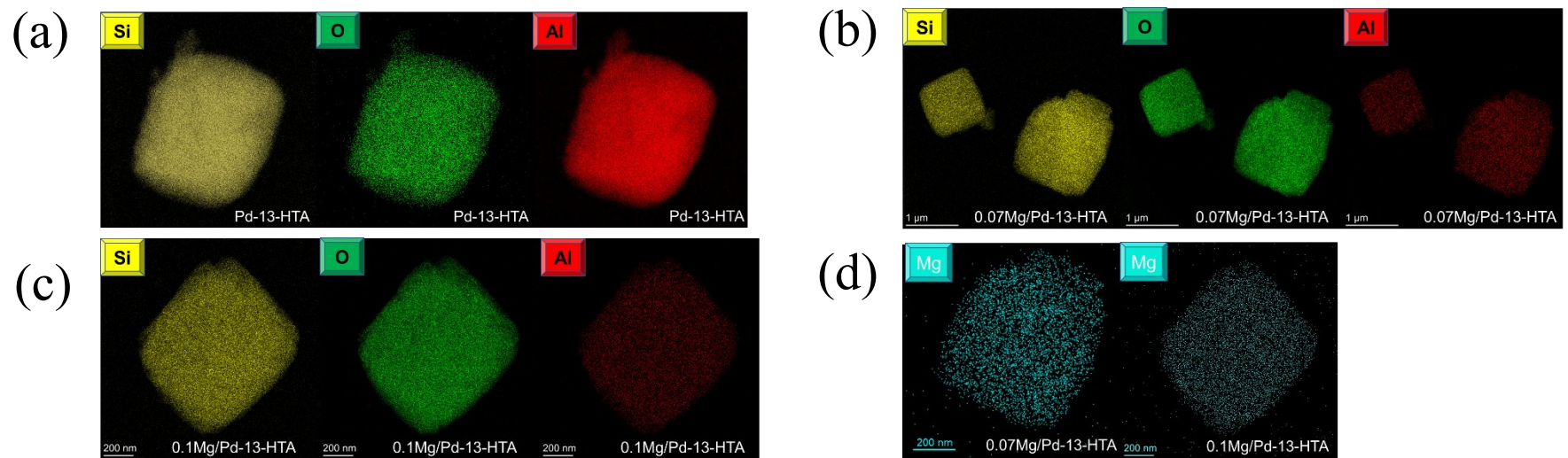
Section S7

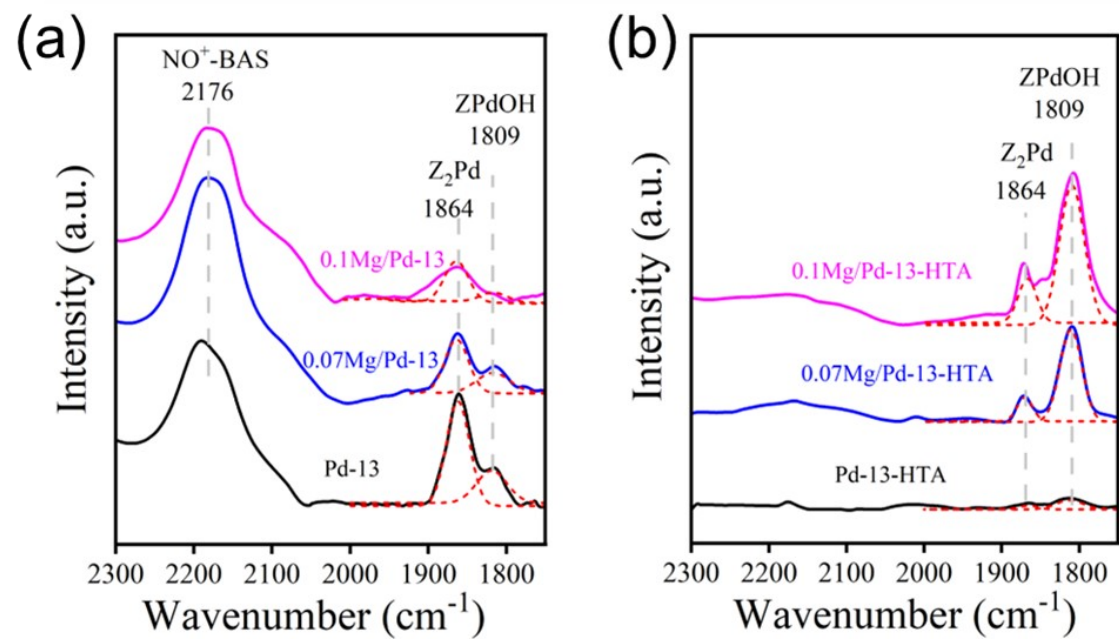Fig S7. Mapping diagram of Si, O, Al and Mg elements in HTA samples.

Section S8

Fig. S8. The deconvolution peaks of NO adsorption curves in Fig.7.

For the IR spectra in Fig.7, the peaks are deconvoluted via Lorentzian/Gaussian fitting using Peakfit software, with the peak position not fixed for the best fit. All samples allow the fitting parameters in the deconvolution to be optimized.
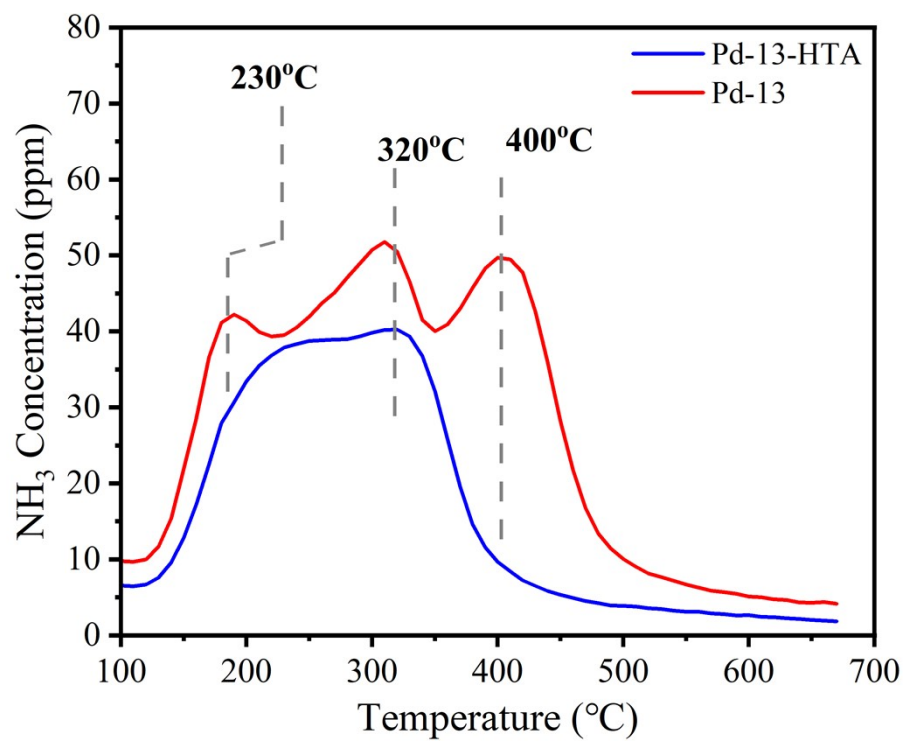
Section S9

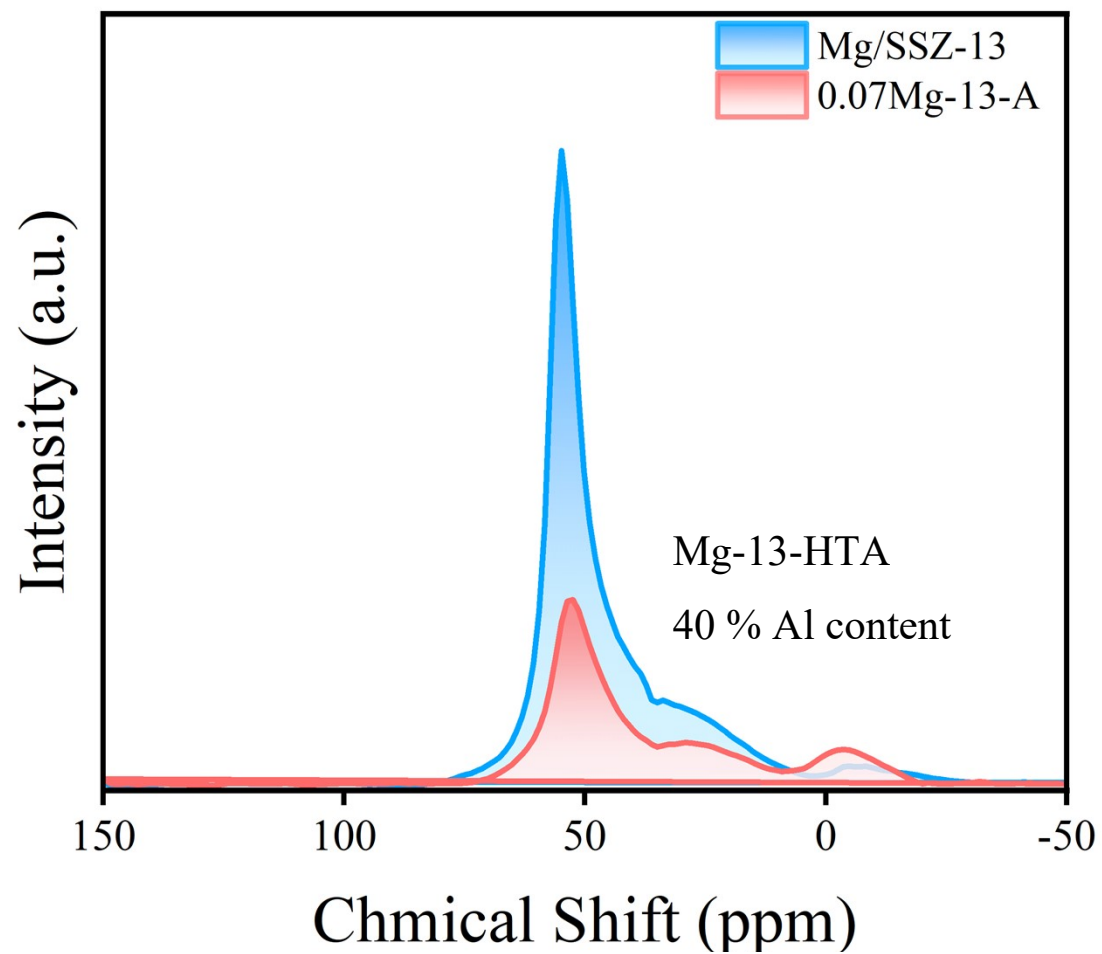Fig S9. NH$_3$-TPD (a) profiles for H/zeolites, fresh Pd/SSZ-13, Mg/Pd-13 samples.

Fig. S10. ^{27}Al MAS NMR spectra of Fresh and Aged 0.07Mg/SSZ-13 samples.

Section S11

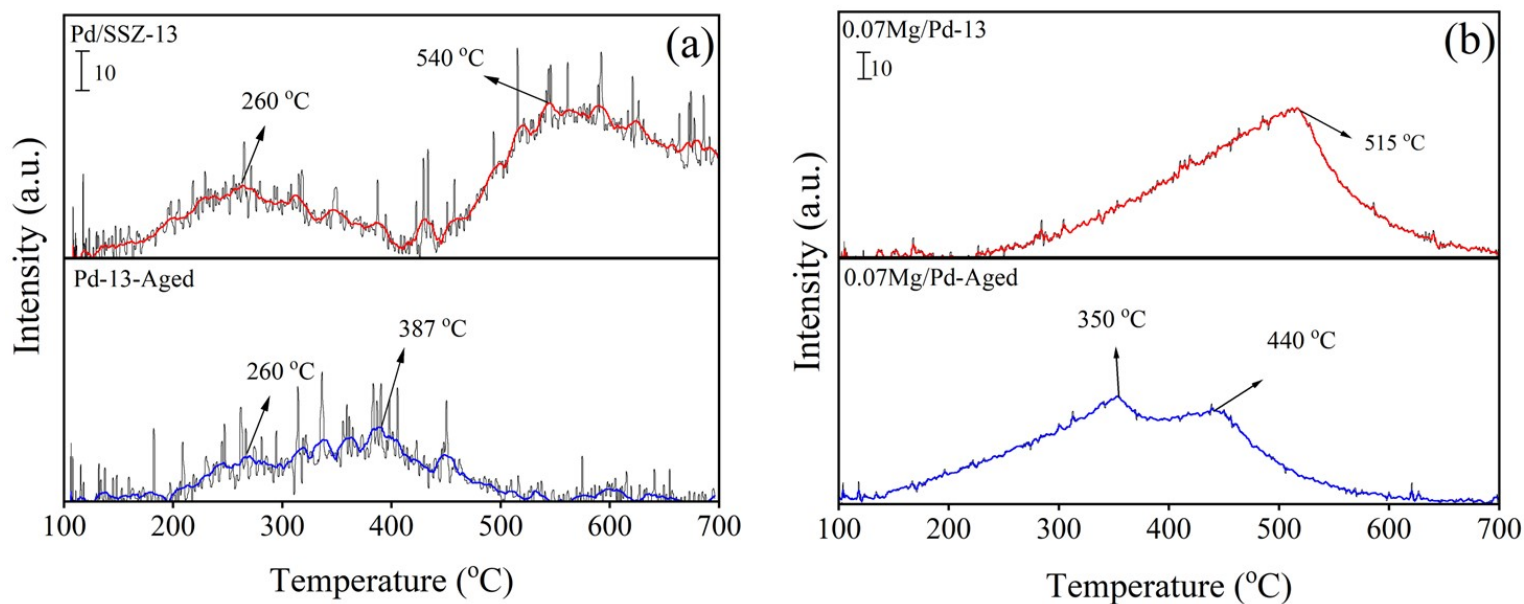Fig. S11. (a) The H_2O-TPD profiles of Pd/SSZ-13 and Pd-13-HTA, and (b) corresponding to 0.07Mg/Pd-13 and 0.07Mg/Pd-13-HTA.

H_2O-TPD test procedure:

1, To remove adsorbed species, 50mg of sample was heated to 500 °C, pretreated with 50 ml/min 10% O_2/He for 30 min, and cooled to 100 °C;

2. Then, turn off O_2 and absorb H_2O gas at the flow rate of 50 mL/min (5% H_2O+10% O_2/He) for 1 hour;

3. After the adsorption, purging the pipeline with airflow (10% O_2/He) with a flow rate of 50 ml/min for 1 hour;

4. After purging, release the H_2O at 100 °C to 600 °C at a flow rate of 50 ml/min (5% H_2O+10% O_2/He). The heating rate was 10 °C/min.

Section 12

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [1-2]. The Perdew-Burke-Ernzerhof (PBE) functional for the exchange correlation term was used with the projector augmented wave (PAW) potentials and a cutoff energy of 400 eV [3]. The convergence of energy and forces were set to 1×10^{-5} eV and 0.02 eV/Å, respectively. The binding energy (ΔEb) was calculated as: $\Delta Eb = E(CHA\text{-}M) - E(M) - E(CHA)$, where $E(CHA\text{-}M)$, $E(M)$, and $E(CHA)$ are the energies of the CHA with doping atom Pd or Mg, doping atom Pd or Mg and the CHA, respectively.

(1). G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169-11186.
(2). G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758-1775.
(3). J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865-3868