Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Supporting Information

## An Energy-efficient Catalytic Process for the Tandem Removal of Formaldehyde and Aromatics by Metal/HZSM-5 Catalysts

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## Synthetic details of catalysts

The M/HZ (M = Pt, Pd, Ag) catalysts with nominal metal loading of 0.5 wt% were prepared via a conventional incipient wetness impregnation method using aqueous chloroplatinic acid, or palladium nitrate or silver nitrate solutions, and H-ZSM-5 ($SiO_2/Al_2O_3$ = 200, Nankai University, China). The impregnated samples were aged overnight at room temperature, dried at 120 $^oC$ for 6 h, and calcined at 500 $^oC$ for 4 h in air.

## Characterization methods

Surface areas were measured on an Autosorb-1 (Quantachrome, USA) surface area analyzer by nitrogen absorption at −196 $^oC$ using the Brunauer–Emmett–Teller (BET) method.

The loading of the M/HZSM-5 catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV, USA).

Transmission electron microscopy (TEM) images of the catalysts were obtained on a JEM-2000 microscope transmission electron microscope (JEOL, Japan).

The XPS spectrum of Pt/HZ catalyst was collected using Axis Ultra Imaging Photoelectron Spectrometer (Kratos Analytical Ltd.). 0.1 g powder of catalyst was made into a small tablet and held on the sample holder. The tablet of catalyst was firstly treated in the pretreatment chamber of XPS spectrometer under 20 ml/min flow of pure $N_2$ at 500 ºC for 2 h. The sample was then introduced into UHV chamber for XPS measurement at room temperatures. After measurement, the sample was transferred into pretreatment chamber and treated under simulated polluted air (70 ppm HCHO + 10 ppm $C_6H_6$ + 20 % $O_2$ + 80 % $N_2$, RH=50 %, 50 ml/min) for 2 hours. After consecutive measurement, the sample was further treated with 20 % $O_2$ + 80 % $N_2$ at 200 ºC for 10 min.

Infrared spectra were recorded on a Bruker Tensor 27 instrument (Bruker, Germany) equipped with a MCT detector using the DRIFT technique. Scans were collected from 4000 to 1000 $cm^{-1}$ (128 scans, resolution of 4 $cm^{-1}$).

TPO experiments were used to study the adsorption/regeneration behavior of the catalysts. HZ, Pt/HZ, Pd/HZ and Ag/HZ catalysts were saturated with a flow of 10 ppm $C_6H_6$/21% $O_2$/1.56% $H_2O/N_2$. Once the catalyst was saturated, the feed gas was switched to either 21% $O_2$/1.56% $H_2O/N_2$ or 21% $O_2/N_2$ (flow rate of 100 ml/min) and TPO was performed by increasing the temperature from room temperature to 600 $^oC$ at a rate of 10 $^oC$/min. The gas products were analyzed by an online mass spectrometer (MS, OmniStar$^{TM}$ Pfeiffer Vacuum, Germany) equipped with a fast-response inlet capillary/leak diaphragm system along with an infrared absorption spectrometer (IRAS, S710, SICK-MAIHAK, Germany). Concentrations of $C_6H_6$ (m/z = 78), and $H_2O$ (m/z = 18) were determined by MS, and the concentrations of CO and $CO_2$ in the gas phase were determined by IRAS.

## Catalytic evaluation

The evaluation of the catalyst was performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure. 0.10 g catalyst (20-40 mesh) was sandwiched between quartz wool layers in the tube reactor. Before performing the experiment, the catalysts were pretreated in flowing $N_2$ at 500 $^{o}$C for 2 h.

All the feed gases used in this work were of high-purity grade (99.99%). The gas flow rates were adjusted and controlled by mass flow controllers. Gaseous HCHO was generated by flowing $N_2$ over paraformaldehyde (99%, Aldrich) in a thermostated bath (the concentration of HCHO was controlled by adjusting the flow rate of $N_2$ and the temperature of thermostated bath). Gaseous $H_2O$ was carried into the gas stream by passing $N_2$ through a bubbler in a water bath at room temperature. The amount of water, expressed as the relative humidity (RH) at 25 $^{o}$C, was controlled by adjusting the flow rate of $N_2$, while keeping the total flow unchanged. The HCHO and $C_6H_6$ concentrations used in HCHO oxidation and $C_6H_6$ oxidation processes were 70 and 120 ppm, respectively. The $C_6H_6$ concentration used in $C_6H_6$ storage and TTPO process (with HCHO concentration of 70 ppm) was 10 ppm. The total flow rate was 100 ml/min, corresponding to a gas hourly space velocity (GHSV) of 30,000 $h^{-1}$. The concentrations of HCHO and $C_6H_6$ were measured by converting them to $CO_2$ in a homemade converter ($CuO\text{-}MnO_2/\gamma\text{-}Al_2O_3$ catalyst) at 500 $^{o}$C and determining the amount of $CO_2$ formed by IRAS.

Catalyst behavior for the oxidation of HCHO was studied at 20 $^{o}$C, while the oxidation of $C_6H_6$ was studied as a function of reaction temperature. $C_6H_6$ storage capacities were determined at 20 $^{o}$C. The examined parameters, HCHO conversion to $CO_2$ ($X_{HCHO\rightarrow CO2}$, %), $C_6H_6$ conversion to $CO_2$ ($X_{C6H6\rightarrow CO2}$, %), and $C_6H_6$ storage capacity ($N_{C6H6}$, mmol/$g_{cat}$) are defined as follows:

$$X_{\mathrm{HCHO}\rightarrow\mathrm{CO_2}}(\%)=\frac{C_{\mathrm{CO_2}}^{\mathrm{out}}}{C_{\mathrm{HCHO}}^{\mathrm{in}}}\times 100\% \qquad (1)$$

$$X_{\mathrm{C_6H_6}\rightarrow\mathrm{CO_2}}(\%)=\frac{C_{\mathrm{CO_2}}^{\mathrm{out}}}{6\times C_{\mathrm{C_6H_6}}^{\mathrm{in}}}\times 100\% \qquad (2)$$

$$N_{\mathrm{C_6H_6}}=\frac{C_{\mathrm{C_6H_6}}^{\mathrm{in}}F_1t_1}{W_{\mathrm{cat}}} \qquad (3)$$

where $C_{\mathrm{CO_2}}^{\mathrm{out}}$ is the $CO_2$ concentration in the products and $C_{\mathrm{HCHO}}^{\mathrm{in}}$ and $C_{\mathrm{C_6H_6}}^{\mathrm{in}}$ is the HCHO and $C_6H_6$ concentration in the feed gas, respectively. $F_1$ is the total flow rate, $t_1$ is the breakthrough time of benzene and $W_{cat.}$ is the catalyst weight. Breakthrough time was defined as the time when outlet $C_6H_6$ concentration reached 1% of feed concentration.

For TTPO process, the HCHO oxidation/benzene storage phase (gas composition: 70 ppm HCHO + 10 ppm $C_6H_6$/1.56 % water/21 % $O_2/N_2$, GSHV= 36,000 $h^{-1}$) was carried out at 20 ºC and the temperature was increased/flashed to a desired temperature and kept at that temperature for 10 mins to finish the oxidation of benzene. More specifically, at the moment of $C_6H_6$ breakthrough (the time at which the outlet $C_6H_6$ concentration reached 1% of the feed concentration, equivalent to 0.1 ppm), the HCHO and $C_6H_6$ gas flow was switched off, and replaced with dry air (the GSHV was kept unchanged). At this point the temperature was ramped to designated temperature at 20 ºC/min and held at that temperature for 1-10 min. During this oxidation phase the reactor effluent did not pass through the converter but was instead directly analyzed by MS and IRAS to detect CO, $CO_2$, $H_2O$ and $C_6H_6$. The examined parameters, i.e., the stored-$C_6H_6$ oxidation efficiency (stored-$C_6H_6$ to $CO_2$, %) and carbon balance ($B_c$, %) are defined as follows:

$$\text{Stored-C}_6\text{H}_6\ \text{to}\ \text{CO}_2(\%) = \frac{n_{\text{CO}_2}^{\text{out}}}{6 \times n_{\text{C}_6\text{H}_6}^{\text{stored}}} \times 100\% \tag{4}$$

$$B_{\text{c}}(\%) = \frac{n_{\text{CO}}^{\text{produced}} + n_{\text{CO}_2}^{\text{produced}} + 6 \times n_{\text{C}_6\text{H}_6}^{\text{desorption}}}{6 \times n_{\text{C}_6\text{H}_6}^{\text{stored}}} \times 100\% \tag{5}$$

Where $n_{\text{CO}_2}^{\text{produced}} = \int_0^{t_2} F_2 C_{\text{CO}_2} dt$ , $n_{\text{CO}}^{\text{produced}} = \int_0^{t_2} F_2 C_{\text{CO}} dt$ , $n_{\text{C}_6\text{H}_6}^{\text{desorption}} = \int_0^{t_2} F_2 C_{(\text{C}_6\text{H}_6)_\text{d}} dt$ , $n_{\text{C}_6\text{H}_6}^{\text{stored}} = C_{(C_6H_6)_\text{a}} F_1 t_1$ , $C_{(C6H6)a}$ and $C_{(C6H6)d}$ is the benzene concentration in the gas stream during the storage phase and in the gas stream of the oxidation phase, respectively. $C_{CO}$ and $C_{CO2}$ are the concentrations of CO and $CO_2$ in the gas stream of the oxidation phase; $F_1$ and $t_1$ are the total flow rate and the storage period of the storage phase, respectively; $F_2$ and $t_2$ are the total flow rate and oxidation period of the oxidation phase, respectively.

Moreover, during the TPO and TPD of the used catalysts, the concentration ($C_{CO2}$) and MS signal ($I_{44}$) of $CO_2$ were simultaneously obtained on-line by the $CO_x$ analyzer and the mass spectrometer, respectively. Therefore, the concentrations of benzene ($C_{C6H6}$) in the outlet gas are calculated according to the following method. The relationship of the mass signals at *m/z* = 44, 78, ($I_{44}$, $I_{78}$) and the concentrations ($C_{CO2}$, $C_{C6H6}$) is shown in Eq. (6)–(7).

$$I_{44} = \eta_{44} \sigma_{\text{CO}_2} \beta_{44}^{\text{CO}_2} C_{\text{CO}_2} \tag{6}$$

$$I_{78} = \eta_{78} \sigma_{\text{C}_6\text{H}_6} \beta_{78}^{\text{C}_6\text{H}_6} C_{\text{C}_6\text{H}_6} \tag{7}$$

where $\eta_{44}$ and $\eta_{78}$ are the detection constants of the mass spectrometer at *m/z* = 44 and 78, respectively; $\sigma_{CO2}$ and $\sigma_{C6H6}$ are the total ionization cross sections for $CO_2$ and $C_6H_6$; $\beta_{44}^{\text{CO}_2}$ and $\beta_{78}^{\text{C}_6\text{H}_6}$ are the ratios of the partial ionization cross section of $CO_2$ and $C_6H_6$ generating the ion fragment with *m/z* = 44 and 78 to their total ionization cross section. According to Eq. (6) and (7), $C_{C6H6}$ is obtained:

$$C_{\text{C}_6\text{H}_6} = \frac{\eta_{44} \sigma_{\text{CO}_2} \beta_{44}^{\text{CO}_2} I_{78}}{\eta_{78} \sigma_{\text{C}_6\text{H}_6} \beta_{78}^{\text{C}_6\text{H}_6} I_{44}} C_{\text{CO}_2} = k_1 \frac{I_{78}}{I_{44}} C_{\text{CO}_2} \tag{8}$$

where $k_1$ was calibrated to be 2.36 in this experiment.

**Table S1**. Textural properties of the HZ, Pt/HZ, Pd/HZ and Ag/HZ catalysts.

| Catalyst | Surface area [a], $m^2g^{-1}$ | Precious metal content [b], wt% | Average metal particle size [c], nm |
|---|---|---|---|
| HZ | 361 | - | - |
| Pt/HZ | 349 | 0.31 | 4.1 |
| Pd/HZ | 350 | 0.35 | 2.9 |
| Ag/HZ | 347 | 0.41 | 7.6 |

[a] BET specific surface areas determined from the linear part of the BET equation ($P/P_0$ = 0.05-0.25).

[b] Precious metal content measured by ICP-OES.

[c] From TEM

**Table S2.** Selectivities to $CO_2$, CO and desorbed-$C_6H_6$ during temperature program oxidation process over HZ, Pt/HZ, Pd/HZ and Ag/HZ catalysts.

| Catalyst | Gas composition | $S_{CO_2}$, % | $S_{CO}$, % | Desorbed-$C_6H_6$, % | Stored-$C_6H_6$ to $CO_2$, % | $B_c$, % |
|---|---|---|---|---|---|---|
| HZ | 21% $O_2$/1.56% $H_2O/N_2$ | 0.2 | 0.1 | 99.7 | 0.2 | 96.4 |
| | 21% $O_2/N_2$ | 0.1 | 0.1 | 99.8 | 0.1 | 93.5 |
| Ag/HZ | 21% $O_2$/1.56% $H_2O/N_2$ | 1.3 | 3.7 | 95.0 | 1.2 | 93.9 |
| | 21% $O_2/N_2$ | 5.4 | 4.1 | 90.5 | 5.0 | 92.4 |
| Pd/HZ | 21% $O_2$/1.56% $H_2O/N_2$ | 5.0 | 0.2 | 94.8 | 4.8 | 95.6 |
| | 21% $O_2/N_2$ | 85.3 | 0.2 | 14.5 | 79.9 | 93.7 |
| Pt/HZ | 21% $O_2$/1.56% $H_2O/N_2$ | 7.9 | 0.1 | 92.0 | 7.4 | 93.3 |
| | 21% $O_2/N_2$ | 99.7 | 0.1 | 0.2 | 97.4 | 97.7 |

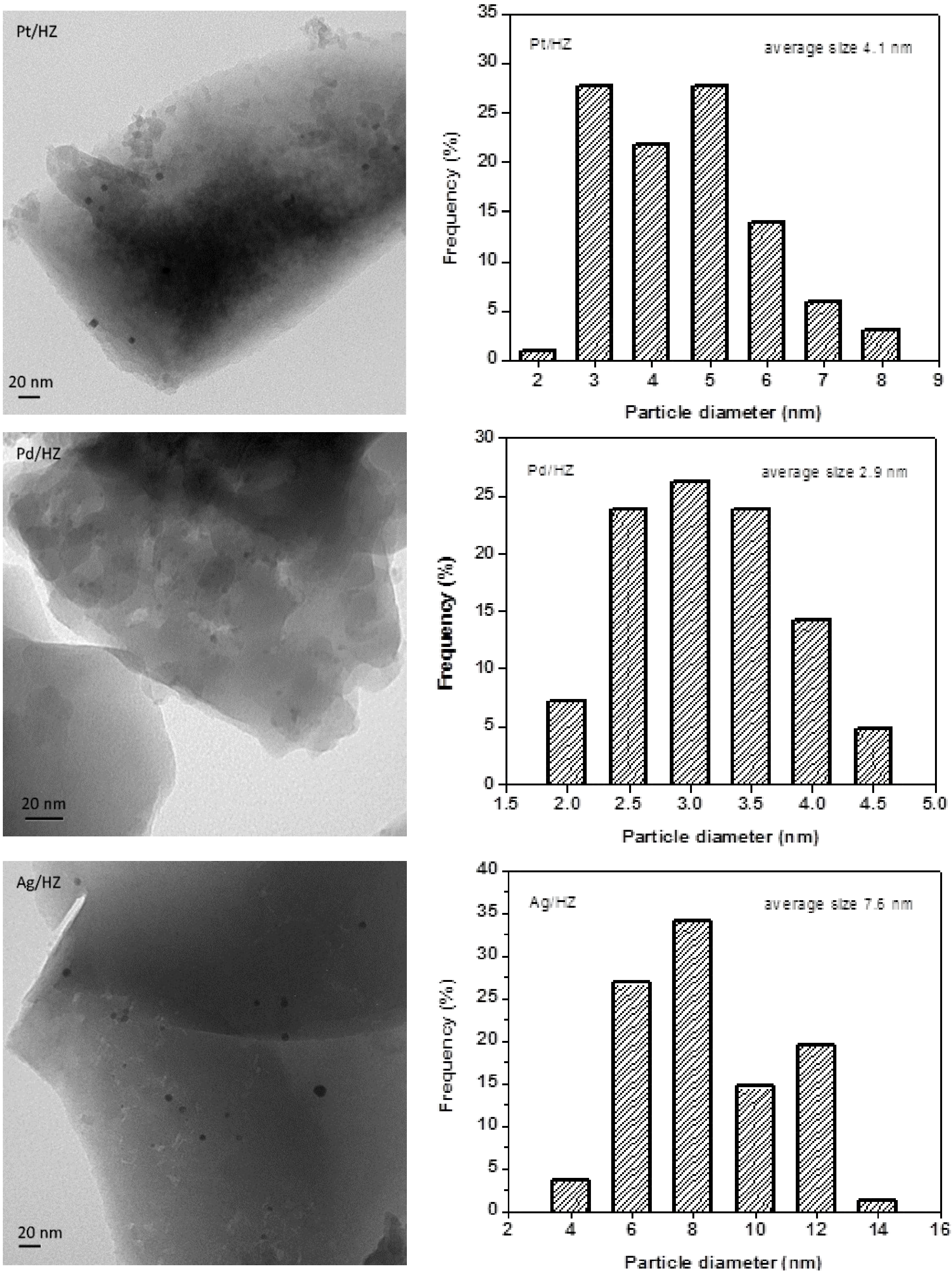

**Fig. S1.** TEM images and particle size histograms of Pt/HZ, Pd/HZ and Ag/HZ catalysts.

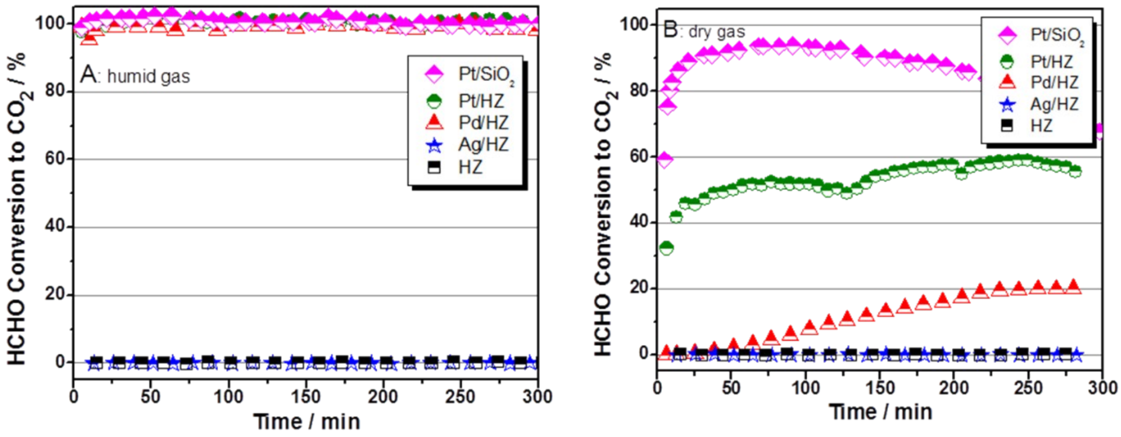

**Fig. S2.** Complete oxidation of HCHO to $CO_2$ over HZ, Pt/HZ, Pd/HZ, Ag/HZ and $Pt/SiO_2$ catalysts. A: humid air: 70 ppm HCHO/21% $O_2$/1.56% $H_2O/N_2$, B: dry air: 70 ppm HCHO/21% $O_2/N_2$.

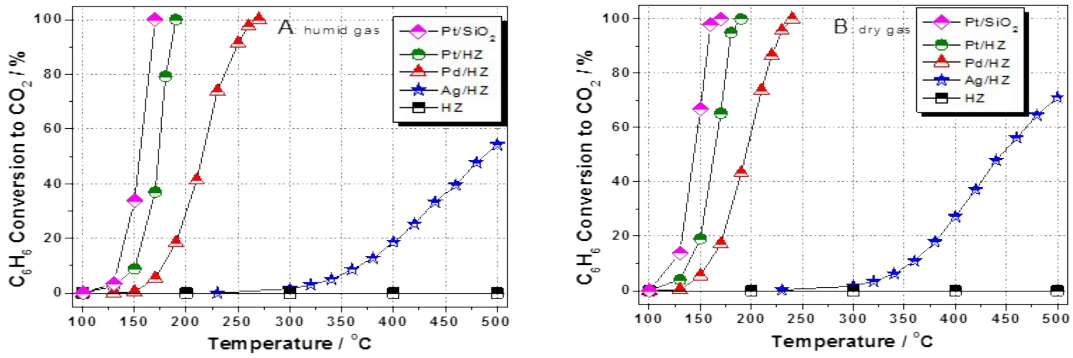

**Fig. S3.** Complete oxidation of $C_6H_6$ to $CO_2$ over HZ, Pt/HZ, Pd/HZ, Ag/HZ and $Pt/SiO_2$ catalysts. A: humid air: 120 ppm $C_6H_6$/21% $O_2$/1.56% $H_2O/N_2$, B: dry air: 120 ppm $C_6H_6$/21% $O_2/N_2$.

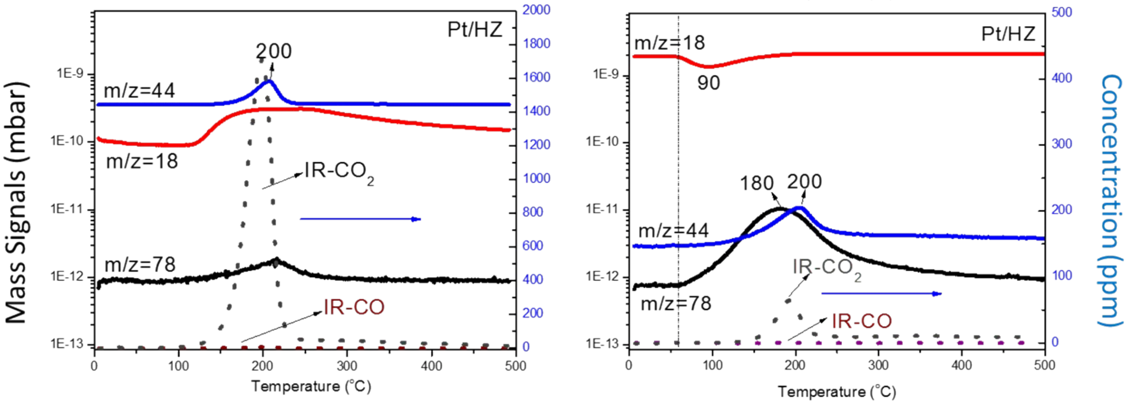

**Fig. S4.** Temperature programmed oxidation of adsorbed $C_6H_6$ under dry and humid conditions over Pt/HZ catalyst and the concentration of gas phase CO and CO2 determined by IRAS method. TPO conditions: (left) dry air: 21% $O_2/N_2$; (right) humid air: 21% $O_2$/1.56% $H_2O/N_2$.

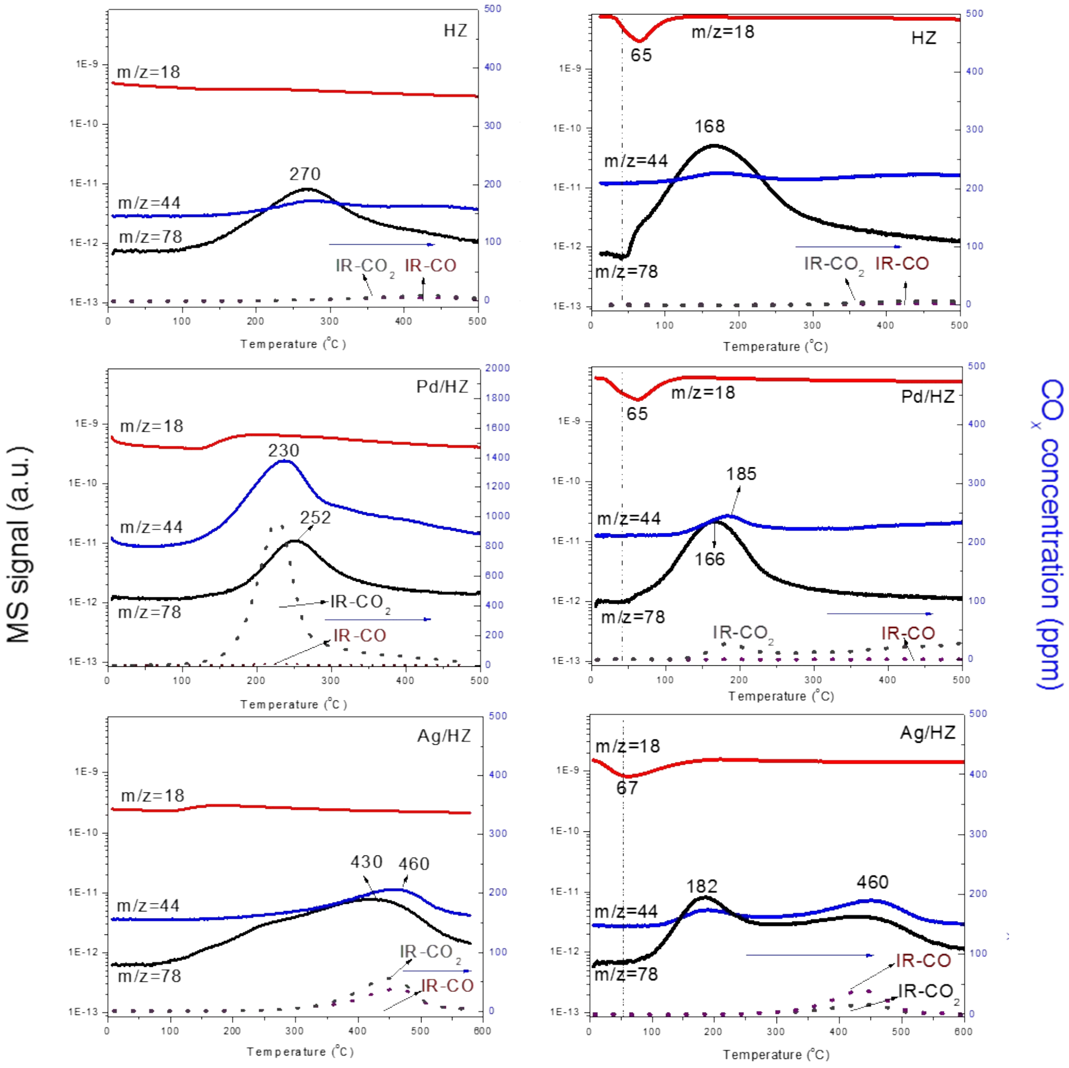

**Fig. S5.** Temperature programmed oxidation of adsorbed $C_6H_6$ under dry and humid conditions over HZ, Pd/HZ and Ag/HZ catalysts and the concentration of gas phase CO and CO2 determined by IRAS method. TPO conditions: (left) dry air: 21% $O_2/N_2$; (right) humid air: 21% $O_2$/1.56% $H_2O/N_2$.

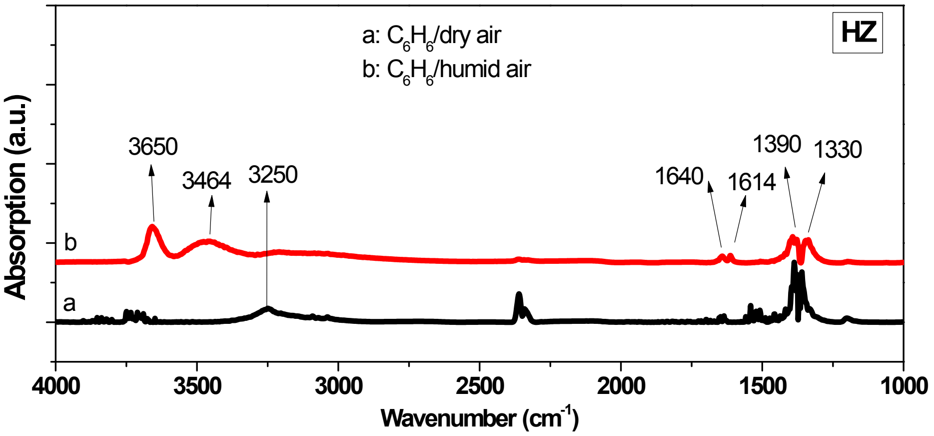

**Figure S6**. DRIFTS spectra of benzene adsorption over HZSM-5 zeolite under dry and humid conditions

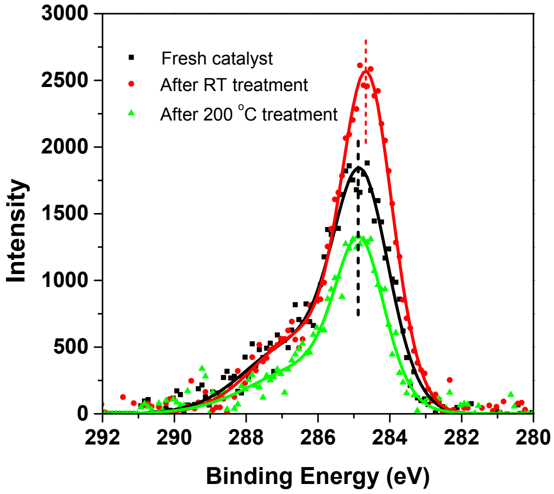

**Fig. S7.** C 1*s* XPS spectra of Pt/HZ catalyst during different treatment processes.