Electronic Supplementary Information (ESI)

Importance of platinum particle size for complete oxidation of toluene over Pt/ZSM-5 catalysts

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1. Experimental details

Materials

$H_2PtCl_6 \cdot 6H_2O$, ethylene glycol (EG), tetrapropylammonium hydroxide solution (TPAOH, 1.0 M in H_2O), and KCl were purchased from Aladdin. Polyvinylpyrrolidone (PVP, M_w=29000) was purchased from Sigma-Aldrich. NaOH, HCl, $NaAlO_2$, tetraethyl orthosilicate (TEOS), ethanol, and toluene were purchased from Sinopharm Chemical Reagent. All these were analytical grade and used without further purification.

Catalyst preparation

Pt nanoparticles. Pt nanoparticles with mean diameters from 1.3 to 2.3 nm were synthesized by polyol reduction method according to the literature.[1,2] Typically, a EG solution of NaOH (0.22 g, 20 mL) was added into a EG solution of $H_2PtCl_6 \cdot 6H_2O$ (20 mL) with stirring. After stirring at room temperature for 1 h, a transparent yellow suspension was obtained. The mixture was heated at 90°C for 2 h with a N_2 flow passing through the reaction system, then a transparent dark-brown homogeneous colloidal solution of the Pt nanoparticles was obtained without any precipitate. The Pt nanoparticles were precipitated by addition of 0.3 M HCl solution, collected by centrifugation, and dispersed in ethanol containing 40 mg PVP.[3] A series of size-controllable Pt nanoparticles were denoted as Pt-*x*, where *x* stands for the Pt nanoparticles mean diameter. The preparation parameters for the Pt nanoparticles and their corresponding mean diameters determined from TEM measurements (Fig. S1) are shown in Table S1.

ZSM-5 zeolite. As a typical run, 0.22 g $NaAlO_2$ was dissolved in 94 mL water, followed by addition of 38 mL TPAOH. After stirring at room temperature for 15 min, 35.5 mL TEOS were added into the mixture. After stirring at room temperature for 5-6 h, the mixture was transferred into an autoclave at 180°C for 4 days for crystallization. The product was collected by centrifugation, washing with water, dryness in air, and calcination at 550°C for 5 h to remove the organic templates. KZSM-5 was prepared from K^+-exchange of NaZSM-5.[4] Typically, the as-calcined

NaZSM-5 was added into a KCl solution (1 M), stirring at room temperature for 3 h. This ion-exchange procedure was repeated for one time. After centrifugation, washing with water, and dryness in air, the KZSM-5 was finally obtained. The Si/Al ratio in the ZSM-5 zeolite was 62.

Pt-*x*/ZSM-5 catalysts. A certain amount of ZSM-5 was added into 50 mL ethanol containing an appropriate amount of size-controllable Pt nanoparticles, stirring at room temperature for 12 h. After centrifugation, washing with ethanol, dryness in air, calcination in air at 350°C for 12 h, and reduction with a H_2 flow at 300°C for 2 h, size-controllable Pt nanoparticles loaded ZSM-5 catalysts designated as Pt-x/ZSM-5 catalysts, were finally obtained, where x stands for mean diameter of Pt nanoparticles. The Pt loadings in the samples determined from ICP-OES measurements are presented in Table S2. In addition, the dispersions of Pt (D_{Pt}) in the catalysts are calculated from the mean diameters (x) of the Pt nanoparticles based on spherical geometry,[5,6] giving the formula in the following: $D_{Pt}=(1.132/x)\times 100\%$.

Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a RIGAKU Ultimate IV diffractometer using Cu $K\alpha$ radiation. Nitrogen sorption isotherms at -196°C were measured using a Micromeritics ASAP 2020M system. The surface areas were calculated from using the Brunauer-Emmett-Teller (BET) method. The Si/Al ratio of ZSM-5 and the Pt content in the catalysts were determined by inductively coupled plasma with a Perkin-Elmer plasma 8000 optical emission spectrometer (ICP-OES). X-ray photoelectron spectra (XPS) of the catalysts were recorded using a Thermo ESCALAB 250 with Al $K\alpha$ X-ray radiation for the X-ray source. Prior to XPS measurements, the samples were reduced with a H_2 flow at 300°C for 2 h, and then exposed to air at room temperature in order to obtain real Pt species information under catalytic conditions, because the feed gas in the toluene catalytic oxidation reaction contain 21% O_2 and this concentration is the same as that of air. Transmission electron microscopy (TEM) images were performed at 100 kV on a Hitachi HT-7700 electron microscope. High-resolution TEM (HR-TEM) images were performed at 200 kV on a JEOL 2100F electron microscope. The H_2 and CO chemisorption of the samples were performed using a Finetec Finesorb-3010 instrument equipped with a TCD. Typically, 0.1 g of the sample was pre-treated in a pure Ar or He flow (20 mL/min) at 200 °C for 0.5 h and then cooled down to 25 °C. Pulse chemisorption measurements were performed at this temperature with 10% H_2/Ar or 20% CO/He (20 mL/min).

Catalytic evaluation

Completely catalytic oxidation of 1000 ppm toluene experiments were performed in a continuous flow fixed-bed microreactor at the atmospheric pressure, consisting of a quartz tube (6 mm i.d.) that was filled with catalysts. A typical experiment was performed using a catalytic bed of 100 mg of catalyst (0.45-0.90 mm size) with total flow rate of feed gases (79% N_2 + 21% O_2) at 100 mL/min, giving a space velocity (SV) at 60,000 mL/(g·h). The relative humidity (RH) of the feed gases was determined by a high accuracy thermo-hygrometer with a probe (WSB-2-H2, Zhengzhou Boyang). The concentration of toluene and oxidative products in the tail gases were analyzed by a gas chromatography (Kexiao, GC1690) equipped with a flame ionization detector (FID) using a 19091N-113 INNOWAX capillary column (Agilent, 30 m×0.32 mm×0.25 μm) for toluene, and a gas chromatography (Kexiao, GC1690) equipped with a thermal conductivity detector (TCD) using a Carboxen packed column (JieDao, 2 m×2 mm) for CO_2 and CO. The conversion of toluene was obtained from toluene consumption, calculated by the inlet and outlet concentration of toluene. The selectivity to CO_2 was calculated by toluene consumption and outlet concentration of CO_2. Carbon balance reached 100±5% in this work. The catalytic activity was evaluated by the values of T_5, T_{50}, and T_{98}, which were defined as the temperatures at 5%, 50%, and 98% of toluene conversion, respectively.

2. Supplementary Tables

Table S1 Conditions for preparation of the size-controllable Pt nanoparticles.

Pt	$C_{H2PtCl6\cdot H2O}$ (g/L)[a]	Solvent	Volume ratio EG/H_2O	Mean diameter (nm)[b]
Pt-1.3	2.5	EG		1.3±0.2
Pt-1.5	5	EG		1.5±0.2
Pt-1.7	10	EG		1.7±0.2
Pt-1.9	10	EG+H_2O	5:1	1.9±0.2
Pt-2.1	10	EG+H_2O	3:1	2.1±0.2
Pt-2.3	10	EG+H_2O	1:1	2.3±0.2

[a] Concentration of $H_2PtCl_6\cdot 6H_2O$.

[b] Determined from TEM images (Fig. S1).

Table S2 Textural parameters of the various samples.

Sample	BET surface area (m^2/g)[a]	Pore volume (cm^3/g)[a]	Pt content[b]
ZSM-5	368	0.24	
Pt-1.3/ZSM-5	380	0.27	0.96%
Pt-1.5/ZSM-5	381	0.27	0.98%
Pt-1.7/ZSM-5	374	0.25	0.95%
Pt-1.9/ZSM-5	371	0.26	0.97%
Pt-2.1/ZSM-5	376	0.27	0.97%
Pt-2.3/ZSM-5	369	0.27	0.96%
0.5% Pt-1.9/ZSM-5	367	0.25	0.45%
2% Pt-1.9/ZSM-5	370	0.26	1.92%

[a] Determined from N_2 sorption isotherms (Fig. S3).

[b] Determined from ICP-OES measurements.

Table S3 XPS results of the various catalysts[a].

Catalyst	Pt species	Peak area		$P(\mathrm{Pt}^0)$[b]
		$\mathrm{Pt4f}_{7/2}$	$\mathrm{Pt4f}_{5/2}$	
Pt-1.3/ZSM-5	Pt^0	126	95	47%
	Pt^{2+}	143	107	
Pt-1.5/ZSM-5	Pt^0	353	265	56%
	Pt^{2+}	281	211	
Pt-1.7/ZSM-5	Pt^0	732	550	67%
	Pt^{2+}	362	272	
Pt-1.9/ZSM-5	Pt^0	918	690	75%
	Pt^{2+}	308	232	
Pt-2.1/ZSM-5	Pt^0	925	695	80%
	Pt^{2+}	226	170	
Pt-2.3/ZSM-5	Pt^0	485	364	82%
	Pt^{2+}	103	77	

[a] Determined from XPS measurements (Fig. S4).

[b] Proportion of $\mathrm{Pt}^0 = \mathrm{Area}(\mathrm{Pt}^0)/[\mathrm{Area}(\mathrm{Pt}^0)+\mathrm{Area}(\mathrm{Pt}^{2+})] \times 100\%$.

The XPS results are just semi-quantitative, which are used to show a tendency of the Pt^0 proportion in the catalysts with increasing Pt particle size, as shown in Fig. S5.

Table S4 Catalytic data in the complete oxidation of toluene over the Pt-*x*/ZSM-5 catalysts.

Pt particle size (nm)	Activity (°C)		
	T_5	T_{50}	T_{98}
1.3	165	172	175
1.5	153	162	165
1.7	142	152	159
1.9	138	147	155
2.1	141	152	159
2.3	158	167	170

Table S5 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 in the feed gases containing water or CO_2.

RH[a]	CO_2 concentration	Activity (°C)		
		T_5	T_{50}	T_{98}
0%	0%	138	147	155
50%	0%	139	147	155
0%	5%	137	147	155
50%	5%	137	147	155

[a] Relative humidity.

Table S6 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 with Pt loadings from 0.5 to 2.0 wt.%.

Pt loading (wt%)	Activity (°C)		
	T_5	T_{50}	T_{98}
0.5%	161	172	175
1.0%	138	147	155
2.0%	122	133	140

Table S7 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 under space velocity (SV) from 30,000 to 120,000 mL/(g·h).

SV [mL/(g·h)]	Activity (°C)		
	T_5	T_{50}	T_{98}
30,000	131	142	150
60,000	138	147	155
120,000	142	152	160

Table S8 Chemisorption results of the various catalysts.

Catalyst	H_2-chemisorption		CO-chemisorption	
	Pt dispersion	Pt particle size (nm)	Pt dispersion	Pt particle size (nm)
Pt-1.3/ZSM-5	41%	2.8	42%	2.7
Pt-1.5/ZSM-5	43%	2.6	38%	3.0
Pt-1.7/ZSM-5	42%	2.7	40%	2.8
Pt-1.9/ZSM-5	39%	2.9	40%	2.8
Pt-2.1/ZSM-5	40%	2.8	35%	3.2
Pt-2.3/ZSM-5	42%	2.7	36%	3.1

The chemisorption results are markedly inconsistent with the results determined from the TEM images (Fig. S1 and S6). This unresolved issue will be researched in the future, and the TEM data are used in this work.

3. Supplementary Figures

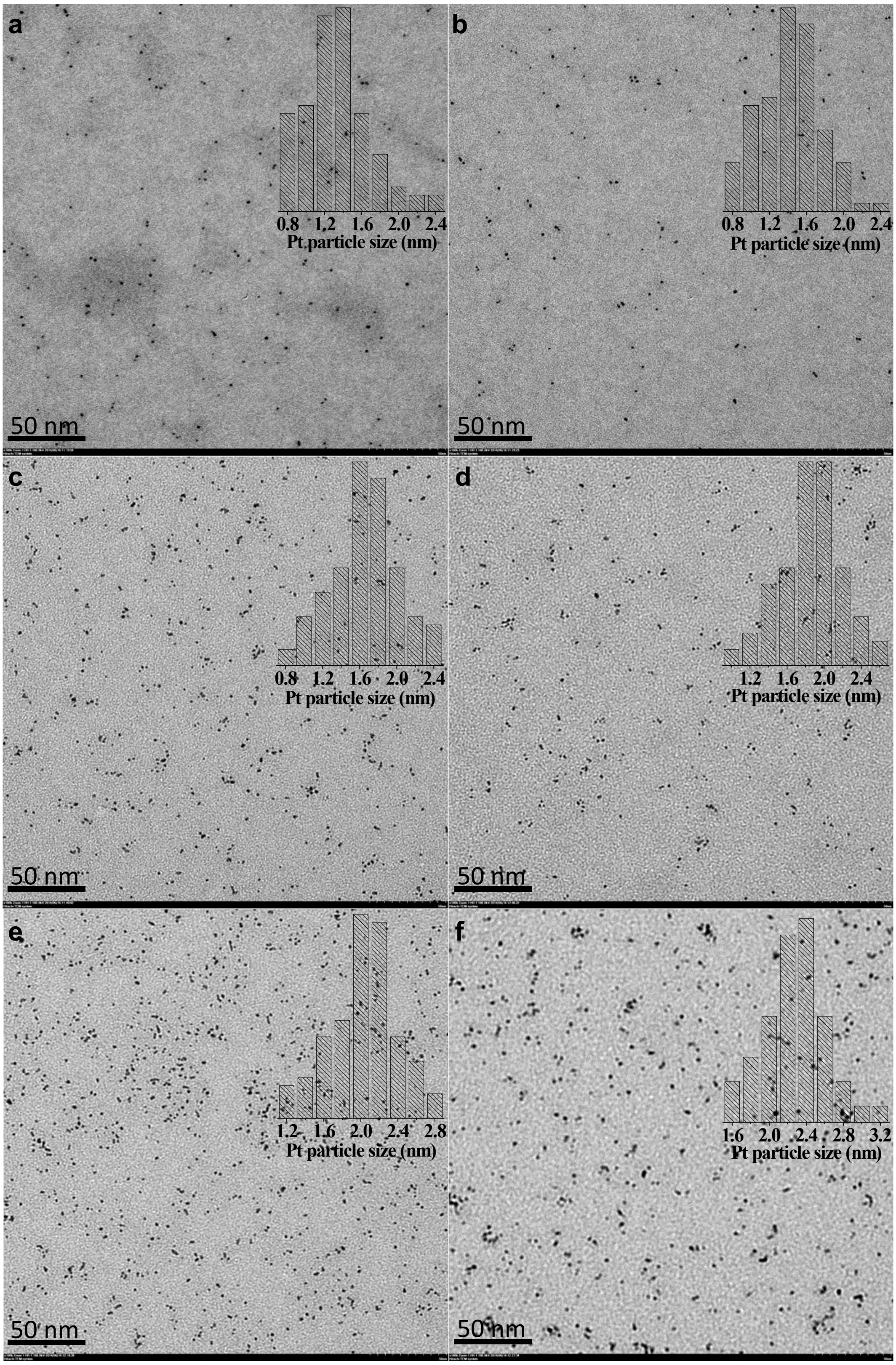

Fig. S1 TEM images and size distributions of the size-controllable Pt nanoparticles for (a) Pt-1.3, (b) Pt-1.5, (c) Pt-1.7, (d) Pt-1.9, (e) Pt-2.1, and (f) Pt-2.3.

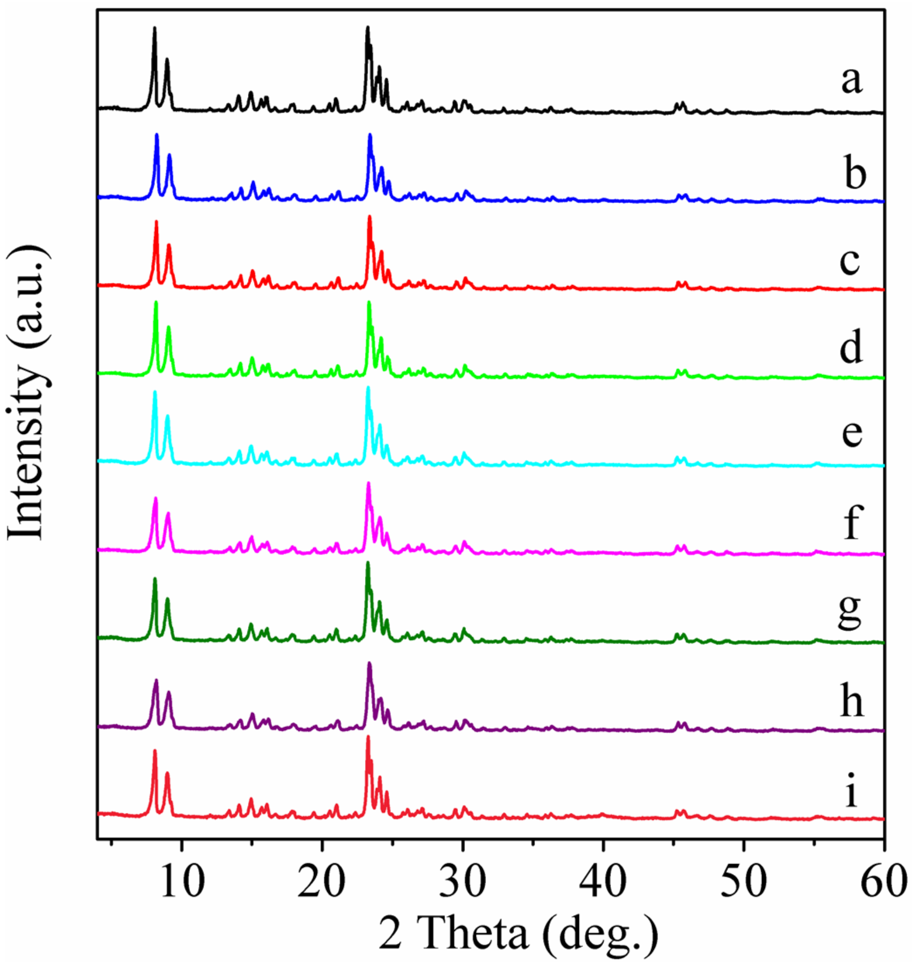

Fig. S2 XRD patterns of the (a) ZSM-5, (b) Pt-1.3/ZSM-5, (c) Pt-1.5/ZSM-5, (d) Pt-1.7/ZSM-5, (e) Pt-1.9/ZSM-5, (f) Pt-2.1/ZSM-5, (g) Pt-2.3/ZSM-5, (h) 0.5% Pt-1.9/ZSM-5, and (i) 2.0% Pt-1.9/ZSM-5 samples.

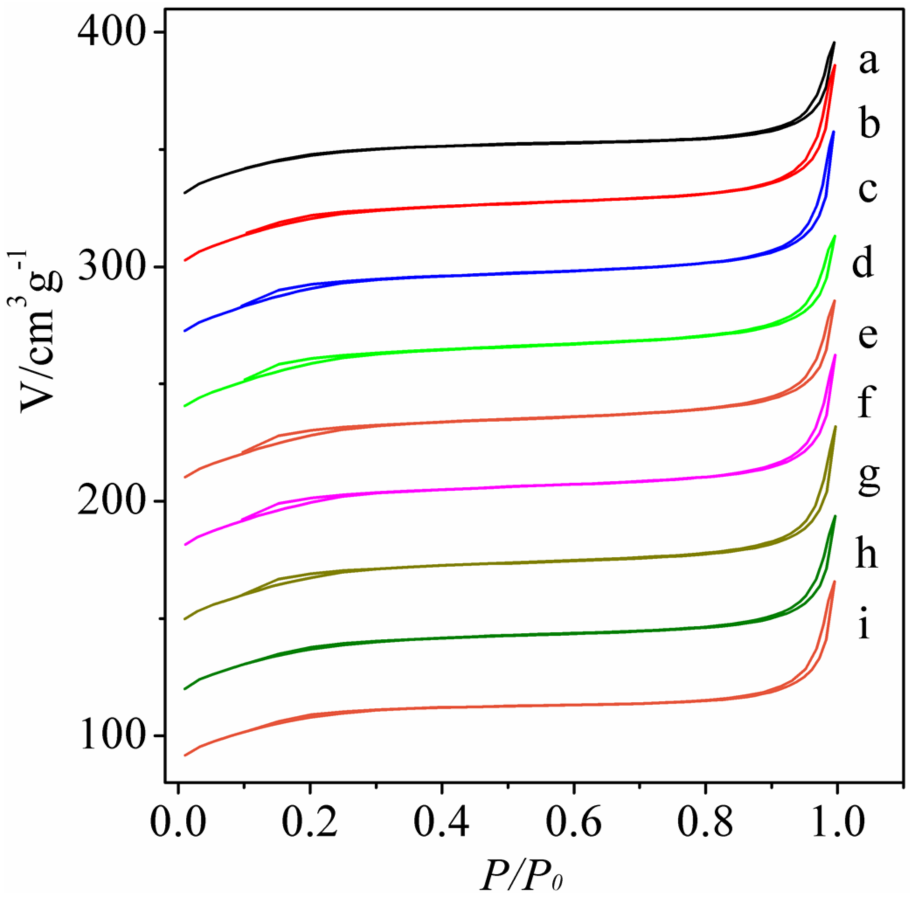

Fig. S3 N_2 sorption isotherms of the (a) ZSM-5, (b) Pt-1.3/ZSM-5, (c) Pt-1.5/ZSM-5, (d) Pt-1.7/ZSM-5, (e) Pt-1.9/ZSM-5, (f) Pt-2.1/ZSM-5, (g) Pt-2.3/ZSM-5, (h) 0.5% Pt-1.9/ZSM-5, and (i) 2.0% Pt-1.9/ZSM-5 samples. The isotherms (a), (b), (c), (d), (e), (f), (g), and (h) have been off-set by 240, 210, 180, 150, 120, 90, 60, and 30 cm^3/g at the beginning for clarity, respectively.

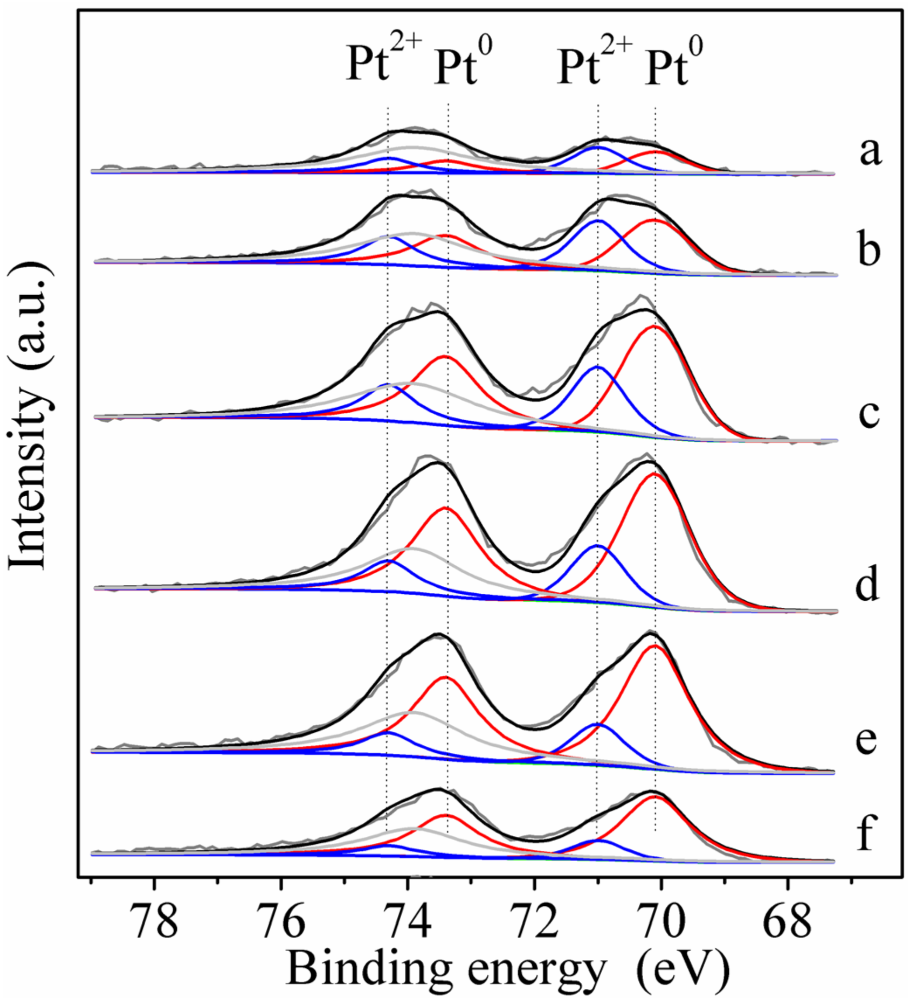

Fig. S4 Pt4f XPS spectra of the (a) Pt-1.3/ZSM-5, (b) Pt-1.5/ZSM-5, (c) Pt-1.7/ZSM-5, (d) Pt-1.9/ZSM-5, (e) Pt-2.1/ZSM-5, and (f) Pt-2.3/ZSM-5 catalysts.

The binding energies are calibrated against C1s (285.0 eV) and Al2p (73.9 eV) peaks. Since Al2p peak strongly overlaps with Pt4f peaks in the range of 79-67 eV, it is necessary to separate the Al2p peak from these spectra. In our case, the Al2p is used at 73.9 eV, the Pt4f$_{7/2}$ spectra could be deconvoluted into two peaks at 70.1 together with 71.0 eV, and the Pt4f$_{5/2}$ spectra could be also deconvoluted into two peaks at 73.4 together with 74.3 eV. The peaks at 70.1 and 73.4 eV and the peaks at 71.0 and 74.3 eV are associated with Pt^{0} and Pt^{2+} species, which are well consistent with those in the literature.[4,7,8] The oxidation state of Pt should be interpreted by the interaction between the framework oxygen with Pt nanoparticles (Pt-zeolite interaction), which has been reported previously.[9-13] For example, Treesukol *et al.* pointed out that the interaction by the electron transfer from the framework oxygen to the Pt atom occured in the Pt/ZSM-5 sample;[9] Koningsberger *et al.* showed that the metals at the interface might be polarized sufficiently, which bonded with the oxygen of the supports such as zeolites.[10-12]

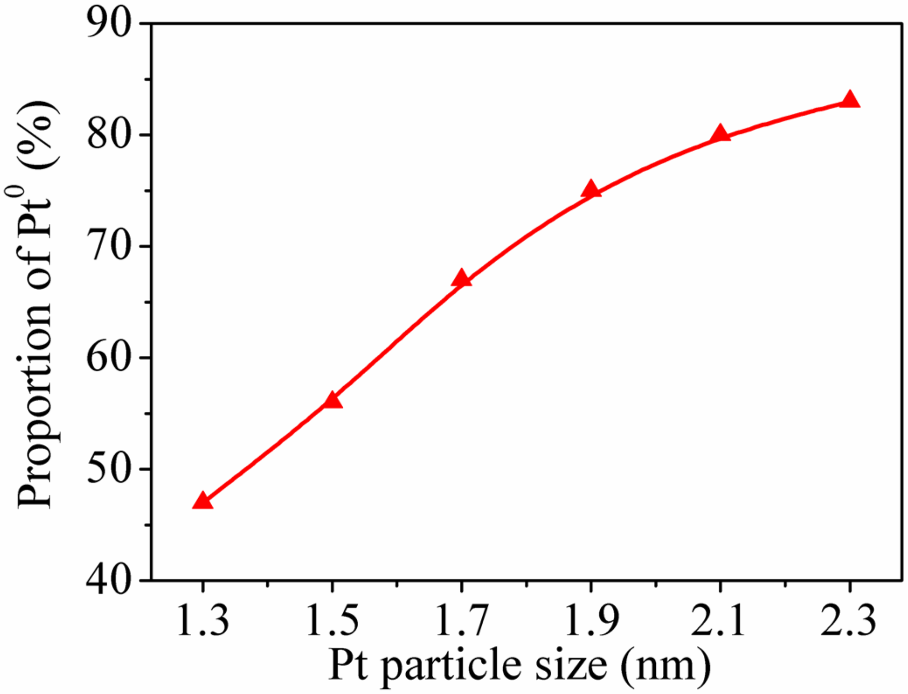

Fig. S5 Dependence of Pt^0 proportion on Pt particle size in the Pt-*x*/ZSM-5 catalysts.

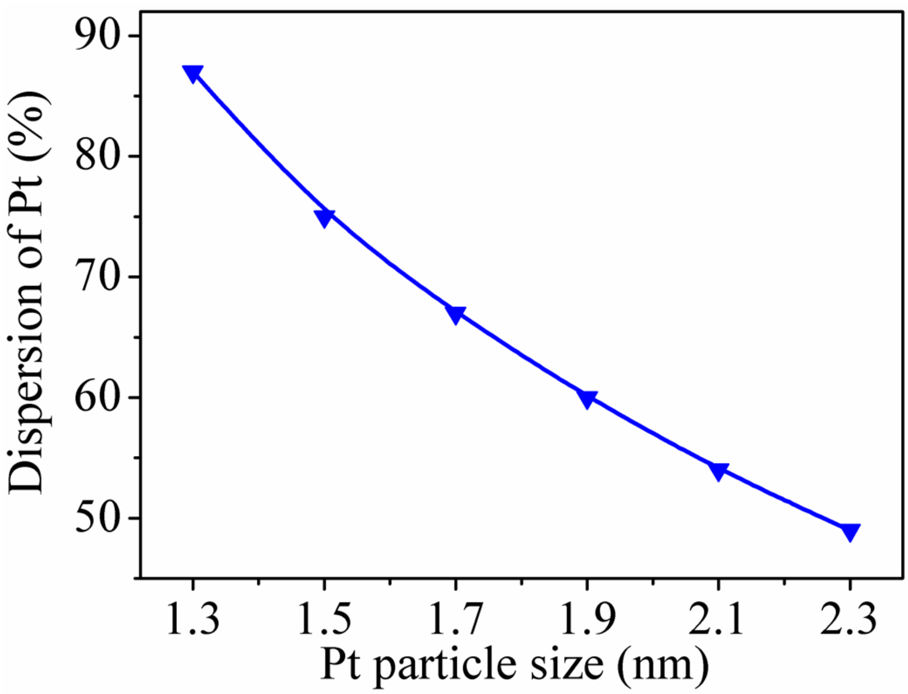

Fig. S6 Dependence of Pt dispersion on Pt particle size in the Pt-*x*/ZSM-5 catalysts.

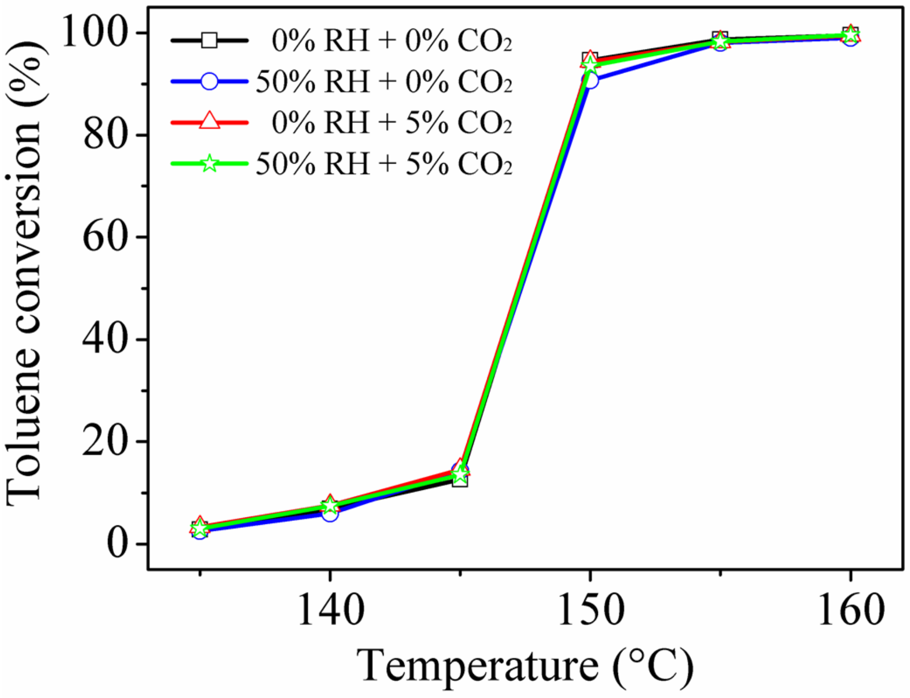

Fig. S7 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 in the feed gases containing water or CO_2.

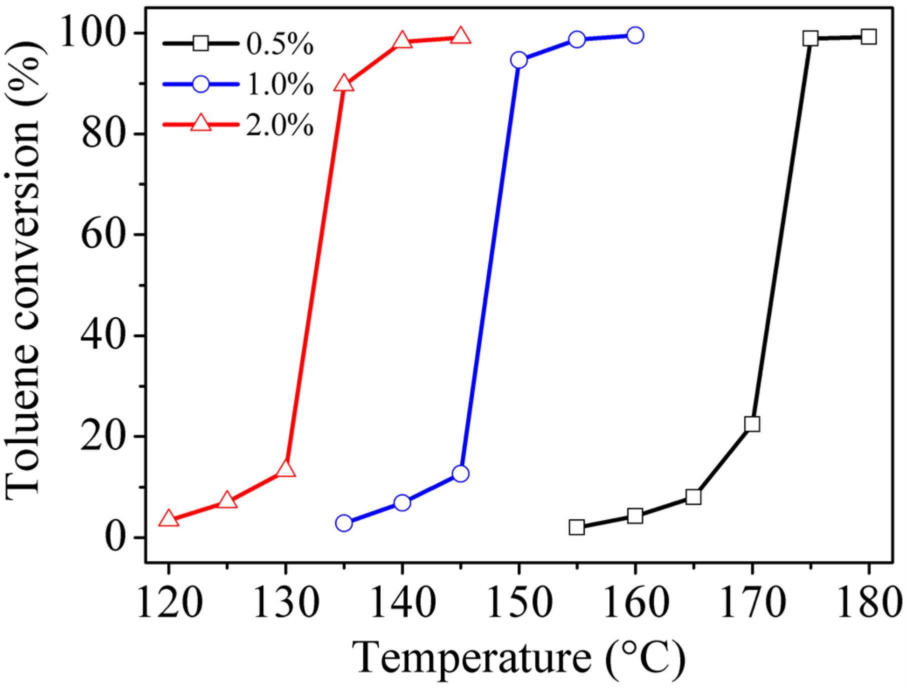

Fig. S8 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 with various Pt loading weights.

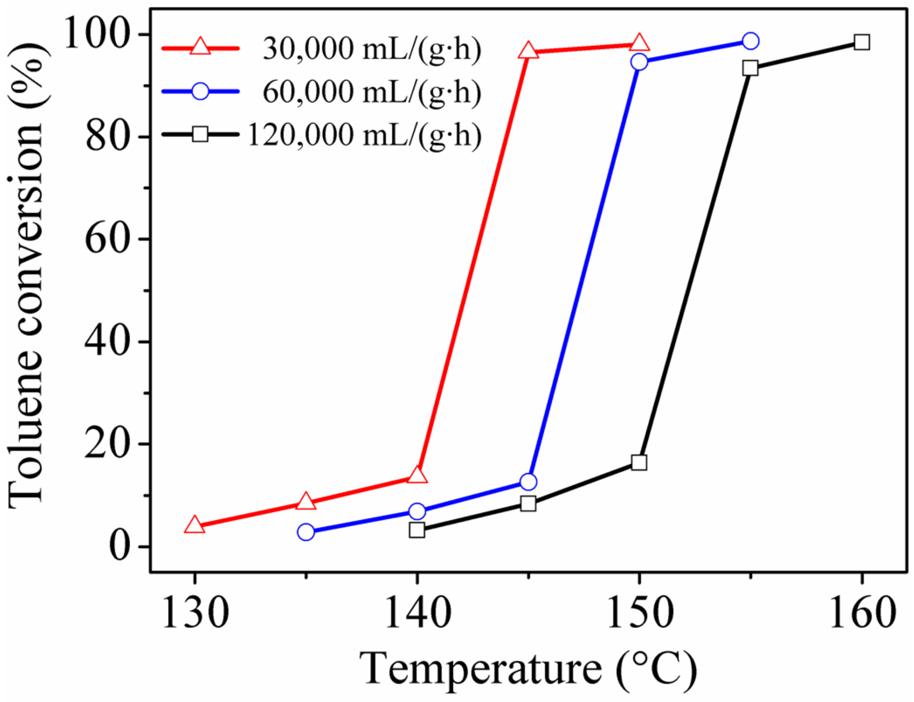

Fig. S9 Catalytic data in the complete oxidation of toluene over the Pt-1.9/ZSM-5 under space velocity (SV) from 30,000 to 120,000 mL/(g·h).

4. Characterizations of the Pt-1.9/ZSM-5 after reaction of 50 h at 155°C

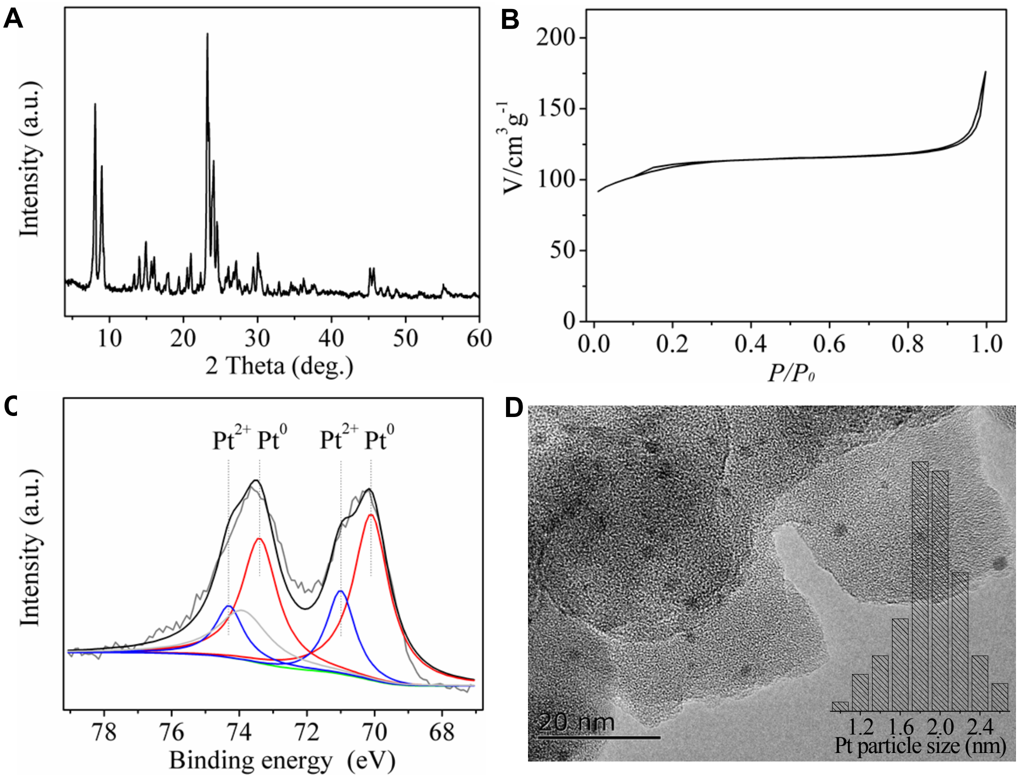

Fig. S10 (A) XRD pattern, (B) N_2 sorption isotherm, (C) Pt4f XPS spectrum, and (D) TEM image (insert: Pt particle size distribution) of the Pt-1.9/ZSM-5 after reaction of 50 h at 155°C.

Table S9 Textural parameters of the Pt-1.9/ZSM-5 after reaction of 50 h at 155°C^a.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)
Pt-1.9/ZSM-5-after reaction	374	0.27

^{a} Determined from N_2 sorption isotherm (Fig. S10B).

Table S10 XPS results of the Pt-1.9/ZSM-5 after reaction 50 h at 155°C.

Catalyst	Pt	Peak area		$P(Pt^0)^a$
		$Pt4f_{7/2}$	$Pt4f_{5/2}$	
Pt-1.9/ZSM-5-after reaction	Pt^0	1231	926	74%
	Pt^{2+}	440	331	

^{a} Proportion of Pt^0=Area(Pt^0)/[Area(Pt^0)+Area(Pt^{2+})] × 100%

5. Turnover frequency

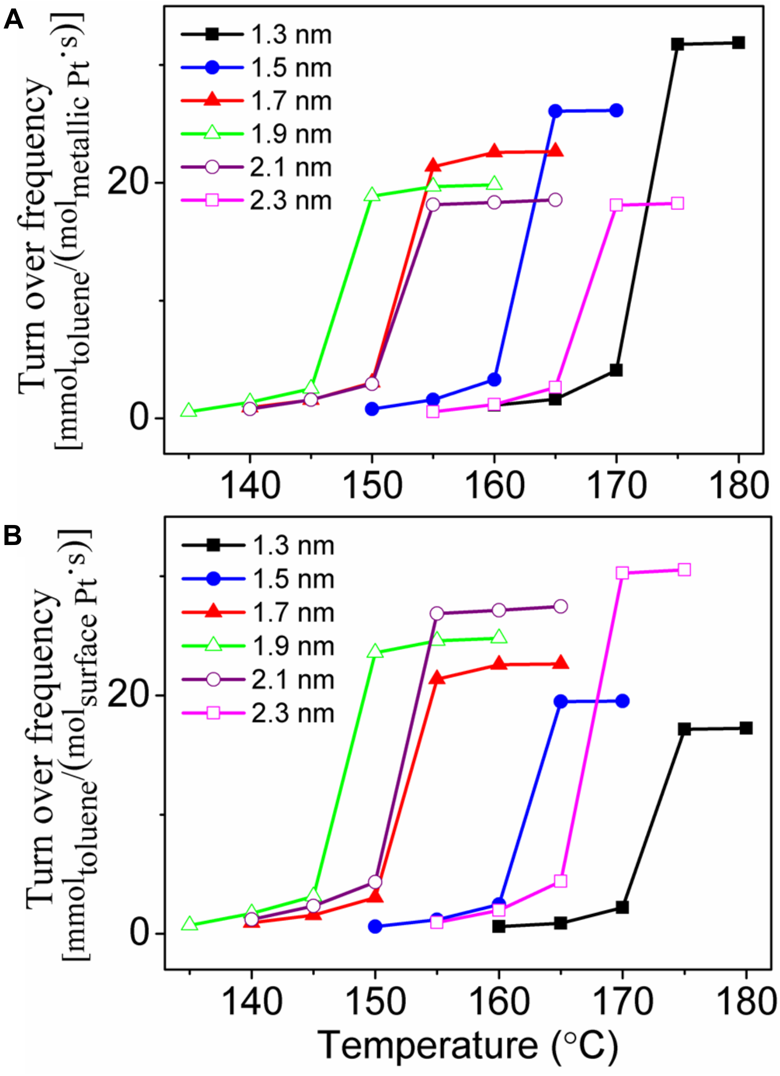

Fig. S11 Dependence of turnover frequency on reaction temperature: based on (A) the metallic Pt and (B) the total surface Pt atoms, respectively.

Supplementary references

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