Supplementary Material for

Identification of active sites in CO oxidation and water-gas shift over supported Pt catalysts

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Materials and Methods

Synthesis of mesoporous HZSM-5 support

The mesoporous HZSM-5 (mesopore surface area 70 m²/g, Si/Al = 62) was synthesized via the following process. Briefly, 15 g of 1M tetrapropylammonium hydroxide (TPAOH) solution was diluted with 78 g of DI H₂O in a 250-ml KIMAX Media/Storage Bottle before 10.66 g of the Al(sec-BuO)₃/Si(EtO)₄ solution (molar ratio of 1/50) was added. The bottle was tightly sealed and stirred for two days at room temperature. After which the bottle was transferred to a preheated (120°C) oil bath and stirred for one day. The mixture was then cooled down and the product was separated by filtration through a 220 nm membrane filter with thorough H₂O and ethanol rinses. The product was dried at 80°C overnight and subsequently calcined in a programmable furnace with a ramping rate of 1.5°C/min and kept at 550°C for 8 hours.

After the calcination, the zeolite is partially in the potassium form because of the potassium cations in the commercial TPAOH solution. Ammonium ion exchange and subsequent calcination are necessary in order to convert it to the HZSM-5 form. 1 g of the calcined zeolite powder was added to 50 ml of 0.5 M NH₄NO₃ aqueous solution, stirred at room temperature overnight, the solid was separated by filtration through a 220 nm membrane filter and washed for a minimum of three times with DI H₂O. The above process was repeated to ensure all the potassium cations were replaced by NH₄⁺ cations before the product was dried at 80°C overnight. The dried sample was further calcined in a programmable furnace with a ramping rate of 1.5°C/min and kept at 550°C for 8 hours.

Synthesis of Pt/HZSM-5 and grafted Pt/SiO₂(Al)

The site-specific deposition of Pt was performed using a viscous flow atomic layer deposition (ALD) reactor described previously (38, 39), trimethyl(methylcyclopentadienyl) platinum (MeCpPtMe₃, Strem) for the Pt precursor and nitrogen (UHP) as the carrier gas. HZSM-5 powder was loaded into a powder holder (40), dried inside the ALD chamber at 250°C under vacuum overnight prior to Pt deposition. The MeCpPtMe₃ reservoir was heated to 50°C to achieve sufficient vapor pressure and the inlet lines were heated to 100°C to prevent MeCpPtMe₃ condensation on the inner walls. A half-cycle of Pt ALD was used to deposit Pt at either 100°C or 150°C. The half cycle was composed of several pulses in which the exhaust valve is closed in order to maximize the contact time between the precursor and the zeolite support. Each pulse was composed of a 30 s MeCpPtMe₃ dose, followed by a 600 s of soaking and a 240 s of evacuation in order to remove any remaining precursor. 0.9, 1.2 and 2.6 wt.% Pt/HZSM-5 were obtained from depositions at 100°C with 4 pulses, 100°C with 10 pulses and 150°C with 10 pulses, respectively.

The grafted 0.5 wt.% Pt/HZSM-5 and 0.6 wt.% Pt/SiO₂(Al-doped, Si/Al > 300, synthesized via sol-gel process adapted from the literature (41)) were synthesized via the following process. HZSM-5 and SiO₂ (Al-doped) supports were dried at 150°C overnight prior to the grafting process. 1 g of HZSM-5 or SiO₂(Al) was immersed in 20 ml of pentane and MeCpPtMe₃ (1 mg/ml) solution for 2 h at room temperature. The grafted solids were recovered by filtration and pentane rinsing.
Synthesis of impregnated Pt on various supports

SiO₂ (~1000 m²/g) was synthesized via sol-gel process adapted from the literature (41). ZrO₂ (monoclinic, 90 m²/g) was purchased from Alfa Aesar (#43815). Al₂O₃ (γ phase, 250 m²/g, #SA6276) and TiO₂ (anatase phase, 150 m²/g, #ST61120) were provided by Saint-Gobain NorPro. All supports were crushed, sieved, and dried at 150°C overnight prior to impregnation. Desired amount of Pt(NH₃)₄(NO₃)₂ was dissolved in DI H₂O and then added to the supports at room temperature. The impregnated supports were dried at 40°C for 24 h, and then at 100°C for 12 h. The dried particles were then calcined in a programmable furnace with a temperature ramping rate of 2°C/min up to 400°C and kept at 400°C for 4 h.

Pt-Na/SiO₂ catalyst was synthesized via a similar procedure except that NaNO₃ was co-impregnated with Pt(NH₃)₄(NO₃)₂.

Diffuse reflectance infrared Fourier transform spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a Thermo Nicolet 6700 instrument with a Hg-Cd-Te (MCT) detector, and a Praying Mantis™ high temperature reaction chamber with ZnSe windows. For Pt/HZSM-5 and grafted Pt/SiO₂(Al) samples, the catalysts were purged with 100 sccm of argon (UHP) for 1 h at 100°C. For impregnated Pt on the various supports, the catalysts were pretreated with 100 sccm of 10% O₂/Ar at 400°C for 1 h. The CO adsorption on Pt/HZSM-5 and grafted Pt/SiO₂(Al) samples was performed at room temperature. 100°C was used for the CO adsorption on the rest of catalysts. 1% CO/Ar (UHP) was introduced into the DRIFTS cell at a flow rate of 125 sccm. After the CO saturation, an argon purge at a flow rate of 100 sccm was performed to remove gas phase CO from the DRIFTS cell. A temperature programmed desorption process was carried out for Pt/HZSM-5. Then either 10% O₂/Ar or 2.3% H₂O/Ar was introduced into the DRIFTS cell at a flow rate of 50 sccm in order to react with the CO molecules adsorbed on Pt. All the spectra were recorded using 32 scans and a resolution of 4 cm⁻¹. In the isotope experiments, ¹³CO (Sigma-Aldrich, #388505) was used and 2% ¹³CO/Ar was introduced into the DRIFTS cell at a flow rate of 150 sccm. Most IR spectra were displayed in absorbance unit for qualitative analyses. The spectra were converted to Kubelka-Munk unit using Omnic™ software when used for quantification.

CO oxidation, water-gas shift, and site counting

The CO oxidation and water-gas shift reactions and site counting were conducted in an atmospheric pressure fixed bed flow reactor system with 3/8 inch stainless steel reactor. 5% CO/Ar, 10% O₂/Ar, and Ar were provided by Airgas in UHP grade. The gas flow rates were controlled by mass flow controllers (MKS Instruments). The products were analyzed by an on-line Quadrupole mass spectrometer (SRS RGA200).

100 mg of catalyst was used for the temperature programmed CO oxidation and WGS reactions. The catalyst was pretreated with 100 sccm of 10% O₂/Ar at 400°C for 1 h before it was cooled down to the target temperatures for catalytic tests. For CO oxidation reaction, the reaction temperature was ramped up from 25°C to 300°C with a
ramping rate of 5°C/min. A total flow rate of 100 sccm was used. The reactant mixture contains 2.5% of CO and 5% of O₂, with Ar as balance. For WGS reaction, the reaction temperature was ramped up from 100°C to 400°C with a ramping rate of 5°C/min. A total flow rate of 125 sccm was used. The reactant mixture contains 1% of CO and 2.3% of H₂O, with Ar as balance.

300 mg of impregnated 1 wt.% Pt/SiO₂ was used for site counting. The reaction conditions for site counting were kept identical with the DRIFTS conditions of this catalyst. The catalyst was pretreated with 100 sccm of 10% O₂/Ar at 400°C for 1 h, and then cooled down to 100°C and purged with 100 sccm of Ar for 30 min. 125 sccm of 1% CO/Ar was introduced for 15 min to saturate the catalyst, then the reactor was purged with 100 sccm of Ar for 7 min. Then 10% O₂/Ar was introduced into the reactor at a flow rate of 50 sccm in order to react with the CO molecules adsorbed on Pt nanoparticles (NPs). The temperature of reactor was kept at 100°C for 7 min and then ramped up from 100°C to 400°C with a ramping rate of 30°C/min. The amount of CO₂ released from the catalyst was quantified by MS signal with known overall flow rate and CO₂ response factor on MS.

Characterizations

Scanning electron microscopy (SEM) observations were conducted on Hitachi SU8030. For transmission electron microscopy (TEM) analyses two different microscopes were utilized. For beam sensitive specimen, a JEOL JEM-2100 FasTEM operating at 200 kV was used at TEM mode. In these measurements, the samples were dispersed in pentane and drops deposited onto a Cu grid supported carbon film and then air dried. For the specimen with SiO₂ support, high spatial resolution HAADF imaging with an inner diameter of 68 mrad and outer 230 mrad was performed on a JEOL JEM-ARM200CF electron microscope, with a probe side Cs-corrector yielding a probe size of approximately 0.078 nm, operating at 200 kV. Under daily operating conditions, the third order aberrations can remain stable for days while the second order aberrations were monitored and corrected as needed during the experiments. Dry powder specimens on a Cu grid with a carbon film support were used for HAADF characterization to minimized contamination. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Scientific ESCALAB 250Xi. The binding energies were adjusted to the C1s peaks at 285 eV.
Fig. S1.
SEM and TEM images of HZSM-5.
Fig. S2.
Time-dependent IR spectra of HZSM-5 during CO adsorption and subsequent Ar purge process.
Fig. S3.
TEM images of the solution grafted 0.5 wt.% Pt/HZSM-5 at different electron beam exposure time.
Fig. S3 (continue). 
TEM images of the solution grafted 0.5 wt.% Pt/HZSM-5 at different electron beam exposure time.
Fig. S4A.
TEM image of 0.9 wt.% Pt/HZSM-5.
Fig. S4B.
TEM image of 1.2 wt.% Pt/HZSM-5.
Fig. S4C.
TEM image of 2.6 wt.% Pt/HZSM-5.
Fig. S4D.
TEM image of 2.6 wt.% Pt/HZSM-5.
Fig. S5.
Time-dependent IR spectra of Pt/HZSM-5 during CO adsorption and subsequent Ar purge and oxidation processes.
Fig. S5 (continue).
Time-dependent IR spectra of Pt/HZSM-5 during CO adsorption and subsequent Ar purge and oxidation processes.
Fig. S6.
Time-dependent IR spectra of 0.5 wt.% Pt/HZSM-5 during repeated CO adsorption and Ar purge processes at room temperature.
Fig. S7.
Pt(4f) and Al(2p) XPS of HZSM-5, Pt/HZSM-5 with different loadings, and 0.5 wt. % Pt/HZSM-5 after CO adsorption at room temperature and subsequent desorption up to 100°C. The Pt single atoms in the 0.5 wt.% Pt/HZSM-5 sample prepared from room temperature solution grafting have an average oxidation state between +2 and +4, which identically matches the XANES results of grafted MeCpPtMe3 reported in the literature (42). The Pt XPS peaks shift towards the lower oxidation state, Pt$^{2+}$, with additional Pt NPs in the Pt/HZSM-5 samples. The Pt NPs are likely oxidized due to their ultra small sizes (less than 2nm). This trend agrees well with the adsorbed CO IR spectra. The Pt species in the 0.5 wt.% Pt/HZSM-5 after CO adsorption are still cationic, which is likely due to the charge transfer from Pt to the zeolite support via Pt–O bond, as well as to the adsorbed CO molecule via d-electron back-donation.
Fig. S8.
Time-dependent IR spectra of the solution grafted 0.6 wt.% Pt/SiO₂(Al doped) during CO adsorption, Ar purge, and oxidation processes. Note that the CO peak related to Pt single atoms contains more than one IR band, which may originate from Pt single atoms grafted on different sites. Stronger acidity of the grafting site will cause the Pt single atom to be more electron-deficient. Therefore, less d-electron will be back-donated into the antibonding orbital of CO molecule, resulting in less red-shift from the gas phase CO vibration (2143 cm⁻¹). CO adsorption at 100°C (bottom figure) leads to mild sintering of Pt single atoms, as evidenced by the appearance of Pt NP-related CO peak.
Fig. S9.
HAADF images of the solution grafted 0.6 wt.% Pt/SiO$_2$(Al doped).
Fig. S10.
HAADF images of the solution grafted 0.6 wt.% Pt/SiO$_2$(Al doped) after CO adsorption and subsequent Ar purge at 100°C. Pt single atoms sinter mildly during CO adsorption, in concert with the appearance of Pt NP-related CO peak on the IR spectra shown in Fig. S8.
Fig. S11.
Time-dependent IR spectra of various wet-impregnated Pt catalysts during CO adsorption and subsequent Ar purge and O₂ exposure.
Fig. S11 (continue).
Time-dependent IR spectra of various wet-impregnated Pt catalysts during CO adsorption and subsequent Ar purge and O₂ exposure.
Fig. S12.
HAADF images of the wet-impregnated 1 wt.% Pt/SiO₂.
Fig. S13.

CO$_2$ signal monitored by MS during CO adsorption and subsequent TPO process on Pt/SiO$_2$. Based on our calculations, the CO molecules adsorbed on Pt single atoms and NPs correspond to ca. 11% and 10%, respectively, of the total Pt atoms in the 1 wt.% Pt/SiO$_2$ catalyst. The ratio between the nanoparticle-based CO adsorption sites and the overall nanoparticle-based Pt atoms (0.13) is rather low considering that the average Pt NP size is smaller than 3 nm (corresponding to a ratio of ca. 0.4 according to reference (30)), which is very likely due to the submonolayer CO adsorption on Pt NPs. The in situ reduction of Pt/SiO$_2$ during the CO adsorption process was also revealed by the MS data, as evidenced by the release of CO$_2$. The amount of oxygen atoms scavenged by CO corresponds to 28% of the overall Pt atoms. In a control experiment, the 1 wt.% Pt/SiO$_2$ was reduced in H$_2$ at 200°C prior to the CO adsorption. The major CO band on the pre-reduced Pt/SiO$_2$ is identical to that of the oxidized sample (Fig. S14), which confirms the occurrence of in-situ reduction of Pt species on oxidized Pt/SiO$_2$ during the CO adsorption process.
Fig. S14. Time-dependent IR spectra of CO adsorbed on Pt/SiO$_2$, which is pre-reduced at 200°C in 100 sccm of 5% H$_2$/Ar for 40 min.
Fig. S15.
Temperature-dependent IR spectra of Pt/SiO$_2$ during TPO process after CO adsorption and Ar purge at 100°C. The experimental conditions are identical to that described in Fig. S13.
Fig. S16.
Temperature programmed CO oxidation spectra and Arrhenius plots of Pt/SiO₂ and Pt/Al₂O₃. CO and O₂ concentrations are 2.5% and 5% respectively. Ramping rate is 5°C/min.
Fig. S17.
In situ IR spectra of Pt/SiO₂ in CO oxidation: (top) isothermal reaction at 100°C; (bottom) temperature programmed reaction. CO and O₂ concentrations are 0.5% and 5% respectively. Ramping rate is 5°C/min. Compared to that shown in Fig. S16, the light-off temperature shown here is slightly lower, which is likely due to the comparatively lower CO concentration and CO/O₂ ratio used here.
Fig. S18.
Time-dependent IR spectra of Pt/SiO₂ in the $^{12}$CO/$^{13}$CO exchange experiments.
Fig. S19.
HAADF images of the wet-impregnated Pt-Na/SiO$_2$. (1 wt.% Pt, Pt/Na atomic ratio of 1/3)
Fig. S20.
Time-dependent IR spectra of CO adsorbed on Pt-Na/SiO₂ during Ar purge and O₂/H₂O exposure.
Fig. S20 (continue).
Time-dependent IR spectra of CO adsorbed on Pt-Na/SiO₂ during Ar purge and O₂/H₂O exposure.