

Understanding the Promotional Effect of Mn₂O₃ on Micro-/Mesoporous Hybrid Silica Nanocubic-Supported Pt Catalysts for the Low-Temperature Destruction of Methyl Ethyl Ketone: An Experimental and Theoretical Study

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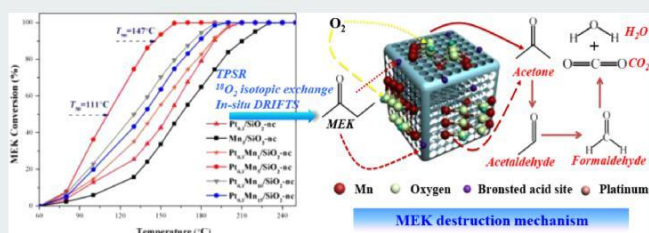
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* Supporting Information

ABSTRACT: Pt_{0.3}Mn_x/SiO₂ nanocubic (nc) micro-/meso-porous composite catalysts with varied Mn contents were synthesized and tested for the oxidation of methyl ethyl ketone (MEK). Results show that MEK can be efficiently decomposed over synthesized Pt_{0.3}Mn_x/SiO₂-nc materials with a reaction rate and turnover frequency respectively higher than 12.7 mmol g_{Pt}⁻¹ s⁻¹ and 4.7 s⁻¹ at 100 °C. Among these materials, the Pt_{0.3}Mn₅/SiO₂-nc catalyst can completely oxidize MEK at just 163 °C under a high space velocity of 42600 mL g⁻¹ h⁻¹.

The remarkable performance of these catalysts is attributed to a synergistic effect between the Pt nanoparticles and Mn₂O₃. NH₃-TPD and NH₃-FT-IR experiments revealed that exposed Mn₂O₃ (222) facets enhance the quantity of Brønsted acid sites in the catalyst, which are considered to be responsible for promoting the desorption of surface-adsorbed O₂ and CO₂. It is suggested that the desorption of these species liberates active sites for MEK molecules to adsorb and react. ¹⁸O₂ isotopic labeling experiments revealed that the presence of a Pt–O–Mn moiety weakens the Mn–O bonding interactions, which ultimately promotes the mobility of lattice oxygen in the Mn₂O₃ system. It was determined that the Mn⁴⁺/Mn³⁺ redox cycle in Mn₂O₃ allows for the donation of electrons to the Pt nanoparticles, enhancing the proportion of Pt⁰/Pt²⁺ and in turn increasing the activity and stability of catalyst. In situ DRIFTS, online FT-IR, and DFT studies revealed that acetone and acetaldehyde are the main intermediate species formed during the activation of MEK over the Pt_{0.3}Mn₅/SiO₂-nc catalyst. Both intermediates were found to partake in sequential reactions resulting in the formation of H₂O and CO₂ via formaldehyde.

KEYWORDS: micro-/mesoporous composite nanocubic silica, Pt–Mn bimetallic center, methyl ethyl ketone, catalytic oxidation, DFT calculation, activation mechanism



INTRODUCTION

Volatile organic compounds (VOCs) are major contributors to air pollution and are extremely damaging to human health due to the formation of photochemical smog and secondary aerosols, in addition to their general carcinogenicity.¹ One such VOC, methyl ethyl ketone (MEK), is used in a number of industrial applications and classified as an oxygenated volatile organic compound (OVOC). Given that these compounds are so hazardous, it is crucial that reliable and efficient methods be developed for their disposal. The complete catalytic oxidation

of VOCs into CO₂ and water is one such method and is especially useful for removing low concentration of VOCs (<0.5 vol %) from waste streams.² There are two different approaches to catalyst design presented in the current literature: the application of supported noble-metal catalysts and that of transition metal oxide catalysts.³ Both types of

catalysts possess their own specific advantages; however, supported noble-metal catalysts are perhaps considered to be most promising for the total oxidation of VOCs due to their high specific activity, resistance to deactivation, and ability to be regenerated.⁴ Among them, platinum-supported catalysts have been extensively studied for the total oxidation of OVOCs due to their superb catalytic efficiency.

Current drives to improve the performance of supported noble-metal-based catalysts for catalytic oxidation is predominantly focused toward increasing the dispersion of the metal particles, reducing the loading of the noble metals used, and varying the preparation method and/or metal precursor.^{5,6} Investigations into the application of single-site noble-metal catalysts are limited, which is likely due to the difficulties associated with their synthesis, susceptibility to poisoning by S/ Cl, and proneness to sintering at high reaction temperatures.⁷ Interestingly, noble-metal and transition-metal cosupported catalysts have been found to be more active and stable for VOC destruction than materials containing single noble-metal active sites.⁸ It has been reported previously that introducing transition-metal oxides into supported noble-metal catalysts can enhance their catalytic activity due to synergistic effects between the multicomponent metal phases.⁹ The transition-metal oxides are reported to increase the performance of these materials by enhancing the activation of oxygen and instigating a change in the physicochemical properties of the noble-metal active sites.⁹ For instance, Qu et al.⁸ recently showed that AgCo/APTES@MCM-41 (Ag/Co = 3/1) could completely decompose formaldehyde at temperatures as low as 90 °C, while only a 30% decomposition was achieved over a Ag/APTES@MCM-41 catalyst under the same reaction conditions. Additionally, Cui et al.¹⁰ revealed that the activity of a Pt/Al₂O₃ catalyst could be significantly enhanced through the incorporation of FeO_x for the oxidation of formaldehyde. This increased performance was attributed to the formation of surface Pt–O–Fe species.

The properties of the support material and transition-metal oxide have been found to have a significant effect on the performance of these noble-metal catalysts. Boaro and co-workers, for example, showed that increasing the surface area of the support material increased the dispersion of the noble-metal particles.¹¹ As such, many studies investigating the hierarchical effect of silica supports with different surface areas have been carried out to find supports for noble-metal-based catalysts.^{12,13} In our previous work, we found that the activity of Pd/SC (SC denotes short column SBA-15) catalysts was proportional to the volume of the support micropores for the oxidation of toluene.¹² For this reason, it is rational to expect that micro-/ mesoporous hybrid silica materials would be an ideal support material for noble- and transition-metal cosupported catalysts, given that one would expect these materials to possess sufficiently high porosities to achieve a good noble-metal dispersion and promote the diffusion rates for reactants and products in a given reaction. Furthermore, we also confirmed that the morphology of the support can have a significant effect on the catalytic activity of these materials, which could further influence the approach invoked for the design of these materials.¹³

The type of transition-metal oxides used in these composite catalysts has also been investigated for the total oxidation of VOCs. Scireand Liotta¹⁴ concluded that a Au/CoO_x/Al₂O₃ catalyst was significantly more active for the oxidation of C₃H₆ than Au/MnO_x/Al₂O₃ and Au/FeO_x/Al₂O₃ catalysts. Tran-

sition-metal oxides in these composite catalysts can act as cocatalysts in this system, which can enhance the redox properties and introduce surface defects at the gold/oxide interfaces. Other reports have shown that manganese oxides are catalytically active for the total oxidation of VOCs such as propane, n-hexane, benzene, and toluene.¹⁵ The influence of MnO_x on noble-metal supported catalysts in total oxidation reactions has attracted a great deal of attention due to its low volatility and ability to easily bind and release oxygen. Arias et al.¹⁶ investigated the performance of MnO_x/Al₂O₃, Pd/Al₂O₃, and Pd-MnO_x/Al₂O₃ catalysts for the oxidation of methanol. The Pd-MnO_x/Al₂O₃ catalyst was found to exhibit a much higher activity and thermal stability in comparison to the corresponding MnO_x/Al₂O₃ and Pd/Al₂O₃ catalysts. Colman-Lerner et al.¹⁷ showed that the activity of Pt/Mn/B is much higher than that of the corresponding Pt/B and Mn/B (B = bentonite monoliths) materials for the oxidation of toluene due to synergetic effects between Pt and Mn. The enhancement in activity was suggested to be related to the presence of Mn³⁺/Mn⁴⁺ species. Other works have correlated the catalytic performance of MnO_x to exposed facets on the materials surface. Xie et al.¹⁸ studied the total oxidation of propane over nanosized MnO₂ particles with α , β , γ , and δ crystal phases and revealed that the activity of these catalysts varied in the order α -MnO₂ > γ -MnO₂ > β -MnO₂ > δ -MnO₂, which have (310), (120), (110), and (001) exposed facets, respectively. It was suggested that the presence of translational motion in the α -MnO₂ phase and its stronger deformation and stretching modes were responsible for its better catalytic activity in the oxidation of propane.¹⁸

The catalytic oxidation of MEK over a PdO_x-MnO_x/Al₂O₃ catalyst was investigated by Arzamendi and co-workers.¹⁹ In this study, it was revealed that the temperature for the complete oxidation of MEK was as high as 320 °C over a 1.0 wt % PdO_x-MnO_x/Al₂O₃ catalyst. High noble-metal loadings, inferior MEK activation capabilities, low CO₂ selectivity, and the production of hazardous byproducts have so far limited the application of these types of catalysts industrially. Pt-Mn-based catalysts supported on micro-/mesoporous hybrid silica have yet to be trialed as catalysts for the oxidation of OVOCs. In this work, Pt- and Mn-coddecorated nanocubic silica (SiO₂-nc) catalysts with large specific surface areas and uniform 3D micro-/ mesoporous hybrid structures were synthesized. A promotional effect is observed for the oxidation of MEK when Mn₂O₃ is deposited onto a Pt/SiO₂-nc material. We found that the exposed (222) facets of Mn₂O₃ enhance the quantity and strength of the Brønsted acid sites in the catalyst, thereby promoting the mobility of lattice oxygen in the catalyst. It is also proposed that the presence of Mn⁴⁺/Mn³⁺ redox cycle in Mn₂O₃ oxide facilitates the movement of electrons to and from the Pt metal particles, which increases the ratio of Pt⁰/Pt²⁺ species present on the surface, ultimately increasing the stability of the catalyst. In addition to this, the MEK destruction routes and surface mechanism over Pt_{0.3}Mn_x/SiO₂-nc catalysts were proposed, which were based on results from in situ DRIFTS, TPSR, ¹⁸O₂ isotopic experimentation, and DFT experiments/ calculations.

EXPERIMENTAL SECTION

Catalyst Preparation. The synthesis of the nanocubic silica support was based on an approach used initially by Stöber but was later modified by Zhao et al.²⁰ For this, 1.0 g of cetyltrimethylammonium bromide (CTAB) was dissolved in

160 mL of deionized water with stirring. An 8.0 mL portion of a concentrated ammonia-water solution (25 wt %) was subsequently added, forming a clear solution. A mixture of tetraethoxysilane (TEOS) and n-hexane was then added to this solution dropwise over 40 min with continuous stirring, and the temperature of the solution was maintained at 30 °C, forming a homogeneous milky colloidal solution. The solution was stirred for another 12 h, after which the product was collected by centrifugation and washed with deionized water and ethanol. The final SiO₂-nc material was obtained by vacuum drying and calcining at 550 °C for 4 h in air with a ramp rate of 1 °C min⁻¹.

Polyvinylpyrrolidone (PVP)-capped Pt nanoparticles with a mean particle size of ca. 2 nm were synthesized by an ethylene glycol reduction method. For this, 20 mL of aqueous NaOH (0.25 M) was added to a 20 mL solution containing ethylene glycol-H₂PtCl₆·6H₂O (0.22 g) and was stirred at room temperature for 1 h, yielding a transparent yellow suspension. The mixture was subsequently heated at 90 °C for 2 h under a flow of N₂, resulting in the formation of a dark brown transparent homogeneous colloidal solution of Pt nanoparticles. The Pt nanoparticles were subsequently precipitated from the addition of about 2–3 mL of a 2 M HCl solution (dropwise until pH 3–4), which was subsequently collected by centrifugation and dispersed in ethanol containing 112 mg of PVP (K. 30). A proportion of the Pt NPs and manganous acetate were subsequently added to 70 mL of ethanol with stirring for 30 min, after which the solution turned gray. The SiO₂-nc support was then added to this solution with stirring and ultrasonication for an additional 5 h. After filtering, washing, and calcining at 500 °C for 4 h, the final catalysts were obtained and denoted as Pt_{0.3}Mn_x/SiO₂-nc (x represents the content of Mn).

Catalyst Characterizations. The synthesized samples were systematically characterized by X-ray diffraction (XRD), low-temperature N₂ adsorption-desorption, inductively coupled plasma optical emission spectrometry (ICP-OES), hydrogen and oxygen titration (HOT), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM), Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy adsorption spectra (UV-vis), ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR), X-ray photoelectron spectroscopy (XPS), oxygen temperature-programmed desorption (O₂-TPD), CO₂ temperature-programmed desorption (CO₂-TPD), NH₃ temperature-programmed desorption (NH₃-TPD), FT-IR spectroscopy for NH₃ adsorption (NH₃-IR), FT-IR spectroscopy for CO adsorption (CO-IR), temperature-programmed isotopic exchange (TPIE), and TGA-FT-IR analysis. The detailed methods for each technique are described in the [Supporting Information](#).

Catalytic Activity. The performance of each material for MEK oxidation was investigated in a continuous-flow fixed-bed reactor consisting of a steel tube (6 mm i.d.) at atmospheric pressure. In each test, 0.3 g of catalyst (40–60 mesh) was placed into the tube reactor. Prior to testing, the catalyst was pretreated at 200 °C with N₂ for 1 h. The MEK feed (800 ppm) was generated by using a N₂ bubbler in a thermostatic bath at 35 °C and mixing with air (79% N₂ + 21% O₂). The total flow rate was maintained at 212 mL min⁻¹ (space velocity 42600 mL g⁻¹ h⁻¹). The catalyst bed was subsequently set to

the desired temperature and left to equilibrate for 30 min before online sampling was initiated. The concentrations of MEK, CO, and CO₂ were measured by an online gas chromatograph (GC-9890B; Linghua, China) equipped with a flame ionization detector (FID) and HT-Wax column (30 m × 0.32 mm (i.d.) × 0.5 μm). The conversion of MEK

(X_{MEK}) was calculated as shown by eq 1

$$X_{\text{MEK}} (\%) = \frac{[\text{MEK}]_{\text{in}} - [\text{MEK}]_{\text{out}}}{[\text{MEK}]_{\text{in}}} \times 100\% \quad (1)$$

where [MEK]_{in} and [MEK]_{out} represent the MEK concentrations in the inlet and outlet gas, respectively.

The CO₂ selectivity (S_{CO₂}) was calculated as shown by eq 2

$$S_{\text{CO}_2} (\%) = \frac{[\text{CO}_2]_{\text{out}}}{4[\text{MEK}]_{\text{in}} X_{\text{MEK}}} \times 100\% \quad (2)$$

where [CO₂]_{out} is the CO₂ concentrations in the outlet gas.

The reaction rate (r_{MEK}, mmol g_{Pt}⁻¹ s⁻¹) was calculated as shown by eq 3

$$r_{\text{MEK}} = \frac{X_{\text{MEK}} V_{\text{MEK}}}{W_{\text{cat}} (\text{wt } \% \text{ Pt})} \quad (3)$$

where W_{cat} represents the catalyst weight (g), wt % Pt is the content of Pt in the catalyst (%), and V_{MEK} is the MEK gas flow rate (mol s⁻¹).

When the conversion of MEK is <15%, a dependence of the reaction rate (r_{MEK}) on the products of CO₂ and H₂O may be ignored and the empirical kinetic expression of the reaction rate equation of MEK oxidation can be described as shown by eq 4:

$$r_{\text{MEK}} = A \exp - \frac{E}{RT} P_{\text{MEK}}^\alpha P_{\text{O}_2}^\beta \quad (4)$$

From the natural logarithm of eq 4, eq 5 can be obtained:

$$\ln r = \ln A + \alpha \ln P_{\text{MEK}} + \beta \ln P_{\text{O}_2} - E_a/RT \quad (5)$$

The components of the reactant gas feed undergo minor changes during the kinetics data testing, and the conversion of MEK is <15%. Therefore, ln A, α ln P_{MEK}, and β ln P_{O₂} can be supposed to be approximately constant, and eq 5 can be simplified to eq 6:

$$\ln r = - \frac{E_a}{RT} + C \quad (6)$$

The activation energy (E_a) can be obtained from the slope of the resulting linear plot of ln r versus 1/T.

The turnover frequency based on the Pt nanoparticles (TOF_{Pt}, s⁻¹) was calculated as shown by eq 7^{21,22}

$$\text{TOF}_{\text{Pt}} = \frac{X_{\text{MEK}} V_{\text{MEK}} N_A}{W_{\text{cat}} (\text{wt } \% \text{ Pt}) D_{\text{Pt}}} \quad (7)$$

where N_A is Avogadro's constant and D_{Pt} represents the dispersion of Pt nanoparticles on catalysts (%).

Reaction Route Determination. Temperature-programmed surface reaction (TPSR) experiments were conducted in air (20% O₂) and in N₂, respectively. For these, 0.3 g of catalyst (40–60 mesh) was loaded into a U-type quartz tube of Builder PCA-1200. Prior to analysis, the catalyst was pretreated in an air flow (40 mL min⁻¹) at 400 °C for 1 h and then cooled to room temperature (25 °C). A 800 ppm amount of MEK diluted by air (100 mL min⁻¹) was introduced into the reaction system, and an adsorption-desorption equilibrium was

Table 1. Textural Properties of All Synthesized Catalysts

sample	Pt content ^a (wt %)	Pt dispersion ^b (%)	SBEI ^c (m ² g ⁻¹)	V _{pore} ^d (cm ³ g ⁻¹)	V _{micro} ^e (cm ³ g ⁻¹)	V _{micro} /V _{pore} (%)	d _{pore} ^f (nm)
SiO ₂ -nc			970.5	1.12	0.42	38	3.6
Pt _{0.3} /SiO ₂ -nc	0.31	49.7	836.1	0.82	0.35	43	3.4
Mn ₅ /SiO ₂ -nc			751.4	0.80	0.32	40	3.5
Pt _{0.3} Mn ₁ /SiO ₂ -nc	0.28	53.1	809.9	0.79	0.35	44	3.3
Pt _{0.3} Mn ₅ /SiO ₂ -nc	0.27	59.6	803.4	0.92	0.35	38	3.8
Pt _{0.3} Mn ₁₀ /SiO ₂ -nc	0.25	52.9	811.7	0.78	0.34	44	3.4
Pt _{0.3} Mn ₁₅ /SiO ₂ -nc	0.29	57.2	772.0	0.81	0.33	41	3.5

^aActual Pt content detected by ICP-OES. ^bDispersion of Pt estimated by HOT. ^cSpecific surface area obtained at P/P₀ = 0.05–0.30. ^dTotal pore volume estimated at P/P₀ = 0.99. ^eMicropore volume estimated from the t-plot method. ^fBJH pore diameter calculated from the desorption branch.

achieved. The reactor was subsequently heated from 50 to 550 °C at a ramp rate of 5 °C min⁻¹ in air (40 mL min⁻¹). Signals corresponding to CO₂ (m/z 44) and formaldehyde (m/z 29) were monitored and recorded online using a Sunny Hengping SHP8400PMS-L mass spectrometer.

¹⁸O₂ isotopic studies were conducted using a PCA-1200 instrument. For this, 0.3 g of catalyst was pretreated in a pure N₂ flow (40 mL min⁻¹) at 400 °C for 1 h and then cooled to room temperature (25 °C). A MEK gas mixture with 2 vol % ¹⁸O₂/N₂ (Isotec, Lianhong, China, 97 atom % ¹⁸O) was subsequently injected and maintained for 20 min. Following this, the temperature of the catalyst bed was increased to 300 °C at a rate of 5 °C min⁻¹ and maintained for 10 min. All three oxygen isotopic species, namely C¹⁸O₂ (m/z 48), C¹⁶O¹⁸O (m/z 46), and C¹⁶O₂ (m/z 44) were continuously monitored online using a SHP8400PMS-L mass spectrometer.

In situ DRIFTS of MEK oxidation was performed using a Bruker Tensor 37 infrared spectrometer, equipped with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. A Harrick reaction cell was fitted with KBr windows and connected to a purging and adsorption gas control system. The total flow rate was controlled by a mass flow meter. Prior to the catalytic oxidation of MEK, the catalyst samples were pretreated under N₂ at 500 °C for 1 h to remove the surface impurities. In each case, a spectrum corresponding to the catalyst powder was recorded at selected reaction temperatures under an N₂ flow. This spectrum was then subtracted from the corresponding spectrum of the catalyst and reaction mixture in the cell. For the MEK oxidation experiment, the catalysts were exposed to a gas mixture consisting of 800 ppm MEK/20% O₂/N₂ at temperatures in the range of 80–240 °C. The system reached a steady state in about 20–25 min, as verified by the stabilized MS peak intensities. All spectra were collected at a resolution of 4 cm⁻¹ with 100 scans.

DFT Studies. Crystalline Mn₂O₃ and noncrystalline SiO₂ surfaces were constructed and immobilized with a Pt cluster. The vacuum space was set to be 15 Å, which is considered to be sufficient to avoid interaction between the two neighboring images. The reactants, intermediates, and products were added onto the surface of each model substrate. The first-principles calculations in the framework of the density functional theory were carried out using the Cambridge Sequential Total Energy Package (CASTEP). The exchange-correlation function under the generalized gradient approximation (GGA) with norm-conserving pseudopotentials and Perdew–Burke–Ernzerhof functional was adopted to describe the electron–electron interactions. An energy cutoff of 750 eV was used, and a k-point sampling set of 5 × 5 × 1 was tested to be converged. A force tolerance of 0.01 eV Å⁻¹, energy tolerance of 5.0 × 10⁻⁷ eV per atom, and maximum displacement of 5.0 × 10⁻⁴ Å were

considered. Each atom in the storage models was allowed to relax to the minimum enthalpy without any constraints.

The adsorption energy E_{ads} of A (A = reactants, intermediates, and products) group on the surface of substrates was defined as

$$E_{\text{ads}} = E_{*A} - (E_* + E_A) \quad (8)$$

where *A and * denote the adsorption of A onto the substrates and the bare substrates and E_A denotes the energy of the A group.

RESULTS

Structural and Textural Properties. The powder X-ray diffraction patterns associated with each of the synthesized materials are displayed in Figure S1. The diffraction peak at 2θ

= 23.1°, which is observed in the diffraction patterns of all the materials, can be assigned to the amorphous silica support.¹²

With the exception of the Mn₅/SiO₂-nc material, all of the materials have three diffraction peaks at 2θ = 40.1, 46.4, and 67.6°, which correspond to the (111), (200), and (220) planes of metallic Pt, respectively.²³ In comparison to the Pt_{0.3}/SiO₂-nc material, the characteristic Pt diffractions become weaker with the Pt_{0.3}Mn_x/SiO₂-nc materials, which suggests that the dispersion of Pt on the surface is improved by the introduction of manganese oxide, in agreement with other previous observations.²⁴ Interestingly, no diffraction peaks that are characteristic of manganese oxide are observed in any of the materials, suggesting that the Mn, when present in this materials, is likely to also be well dispersed.

The N₂ adsorption-desorption isotherms of the synthesized micro-/mesoporous nanocubic silica exhibit a type IV isotherm, with a large and clear H2 hysteresis loop (Figure S2A).²⁵ The sharp increase at P/P₀ < 0.1 in the adsorption isotherm of SiO₂-nc material indicates that there is a large quantity of micropores present. A clear condensation step at relative pressure (P/P₀) ranges of 0.4–0.8 indicates that there are uniform framework-confined mesopores also present in the material.²⁶ The average pore diameter, total pore volume, and BET specific surface area of the SiO₂-nc material were determined to be ca. 3.6 nm, 1.12 cm³ g⁻¹, and 970.5 m² g⁻¹, respectively (Figure S2B and Table 1). Interestingly, large amounts of micropores with an average pore volume of 0.42 cm³ g⁻¹ are also detected, which is indicative of a defined porosity of the SiO₂-nc support (Table 1). After this material is loaded with Pt and/or Mn, the specific surface area (751.4–836.1 m² g⁻¹), total pore volume (0.78–0.82 cm³ g⁻¹), and micropore volume (0.32–0.35 cm³ g⁻¹) all decrease slightly. Perhaps most noticeable is the correlating reduction in the specific surface area when increasing quantities of Mn are added to the material. This indicates that the Mn

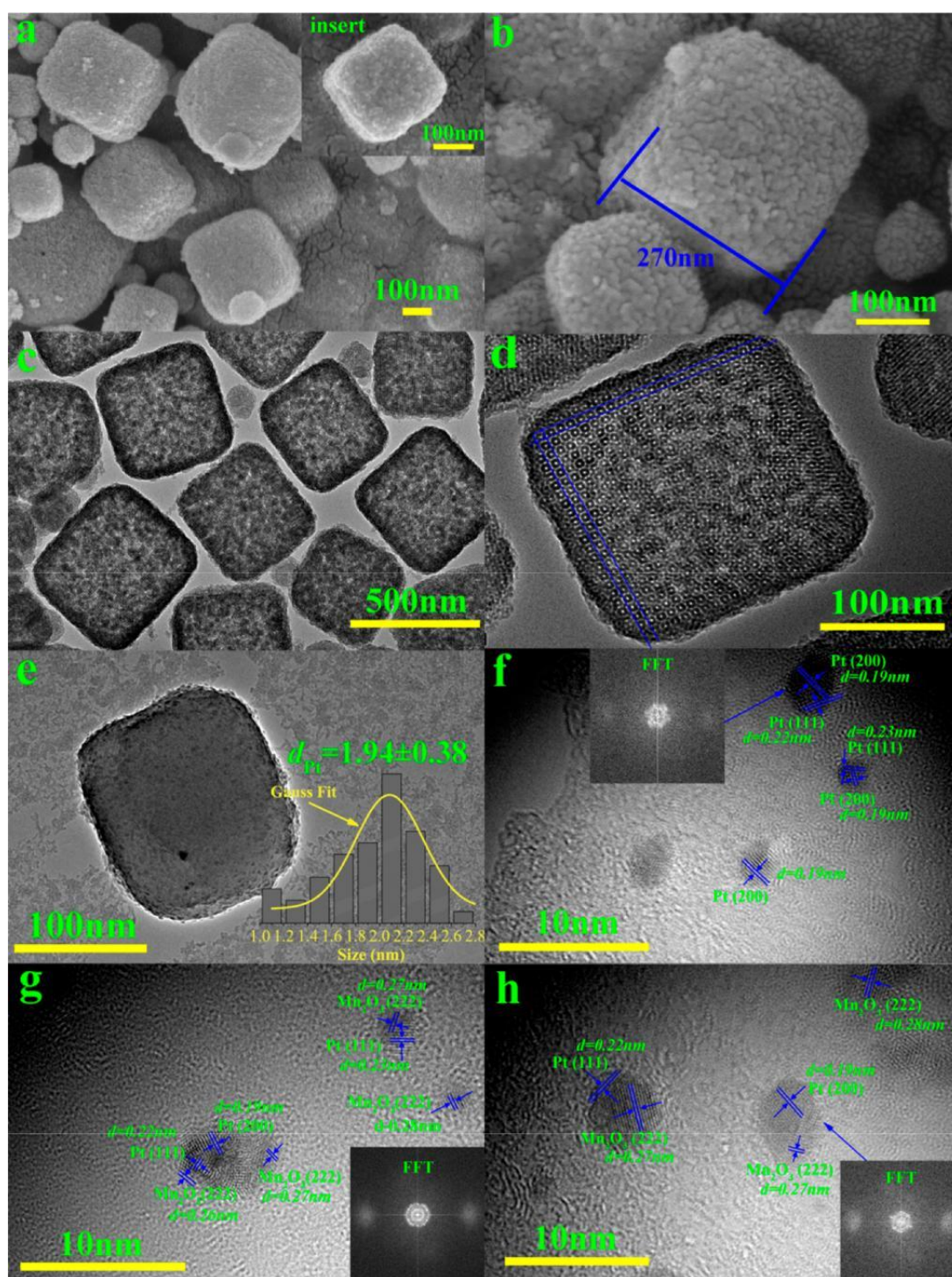


Figure 1. FE-SEM (a, b) and HR-TEM (c, d) images of SiO₂-nc and HR-TEM images of (e, g, h) Pt_{0.3}Mn₅/SiO₂-nc and (f) Pt_{0.3}/SiO₂-nc.

phases likely have a strong influence on the pore structure of these materials.

FE-SEM and HR-TEM images corresponding to the supported SiO₂-nc materials are displayed in Figure 1. From Figure 1a,b, it is evident that the SiO₂-nc support occupies a uniform nanocubic morphology (side length of ca. 270 nm) with defined edges and corners. The TEM images (Figure 1c,d) offer a more detailed insight into the pore distribution of the SiO₂-nc support. A highly ordered 3D porous structure is clearly observed in the SiO₂-nc material, with an average pore size of approximately 3 nm, which aligns with the results

derived from the N₂ adsorption study (Figure S2 and Table 1). From Figure 1e, the average size of the Pt nanoparticles in the Pt_{0.3}Mn₅/SiO₂-nc material was found to be 1.94 ± 0.38 nm, indicating a uniform, well-defined particle size distribution (59.6%, Table 1) of Pt particles. Figure 1f shows two different lattice planes with spacing of 0.19 and 0.22 nm over Pt_{0.3}/SiO₂-nc, which correspond to the (220) and (111) planes of metallic Pt, respectively. From Figure 1g,h, it is clear that the Pt atoms coordinate with the Mn₂O₃ (222) facets, which are approximately 10–20 nm in size. To confirm this, the Pt atoms on the Mn₂O₃ (222) facets were examined using higher

magnifications (Figure 1g,h). From these additional images, it can be concluded that the Pt nanoparticles preferentially occupy over the (222) facet of the Mn₂O₃. HAADF-STEM (Figure S3a) characterization was subsequently used to probe the surface of the Pt_{0.3}Mn₅/SiO₂-nc material. From this image, it is clear that there is a highly ordered mesoporous structure present in the material and that the Pt nanoparticles appear to be homogeneously dispersed on the surface. Additional EDS mapping images of O, Mn, and Pt in the Pt_{0.3}Mn₅/SiO₂-nc sample are shown in Figure S3b-d. These reveal that there is a uniform distribution of O, Mn, and Pt throughout the material.

Properties and Composition. ²⁹Si solid-state MAS NMR (Figure 2A) was subsequently used to probe the unit structure of the SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc materials. For both of these materials, the main peak observed is at a chemical shift of approximately -111 ppm and can be attributed to tetrahedral Si with four Si neighbors (i.e., Si(OSi)₄)²⁷ and is indicative of the asymmetric stretching of the Si-O-Si from silicon-oxygen tetrahedral species. Interestingly, this peak is noticeably less intense in the ²⁹Si solid-state NMR of the Pt_{0.3}Mn₅/SiO₂-nc material. As such, it can be concluded that the introduction of Mn₂O₃ balances the electronegativity of the SiO₂-nc support, thereby weakening the Si-O interaction, which is considered to be beneficial for enhancing the stability of the catalyst.

The FT-IR spectra of all of the synthesized materials are displayed in Figure 2B. The transmission peaks at approximately 3745 and 3635 cm⁻¹ can be attributed to the surface silanol groups, which appear to interact weakly with adsorbed water over the silica surface.²⁸ The small feature at around 3289 cm⁻¹ can be assigned to the stretching and bending vibrations of surface hydroxyls.²⁹ The surface hydroxyls also give rise to a band of δ(Si-OH) and ν(Si-OH) at 1633 cm⁻¹.³⁰ With regard to the framework of the materials, the intense and broad band observed at approximately 1083 cm⁻¹ can be ascribed to the asymmetric stretching of the Si-O-Si moiety in the silicon-oxygen tetrahedral species. A weak band corresponding to the symmetric stretching of this moiety is observed at 810 cm⁻¹, which aligns with the results of ²⁹Si MAS NMR (Figure 2A).³¹ The band observed at 458 cm⁻¹ is attributed to symmetric stretching vibrations and tetrahedral Si-O bending modes.²⁸ The band at 3289 cm⁻¹ corresponds to the stretching of the Mn-O moiety in the Mn₂O₃ phase, which becomes stronger with an increase in Mn content.

The coordination geometry of Pt and Mn₂O₃ in the various materials was investigated by UV-vis absorption spectroscopy, the corresponding spectra of which are displayed in Figure 2C. The band at approximately 241 nm can likely be attributed to O²⁻-Mn³⁺,³² which is indicative of charge transfer transitions of trivalent manganese ions in tetrahedral coordination geometries. This band could be assigned to the strong bonding of oxygen ligands to Mn³⁺ ions. The intensity of these bands is enhanced proportionally with an increase in Mn content in the material. Interestingly, there is a band at 304 nm in the Pt_{0.3}/SiO₂-nc sample which appears to shift toward lower energies after the incorporation of Mn into the material. This shift is attributed to the formation of a Mn-O-Pt moiety.³³ The intensity of the characteristic peak at approximately 461 nm is ascribed to Pt-O-Mn moieties, which is enhanced with an increase in Mn₂O₃.³⁴ This suggests that, when Mn is present, Pt may interact with Mn₂O₃ (222) facets via conjugated π bonding, yielding Mn-O-Pt moieties. This would facilitate electron transfers from Mn to Pt and ultimately increase the

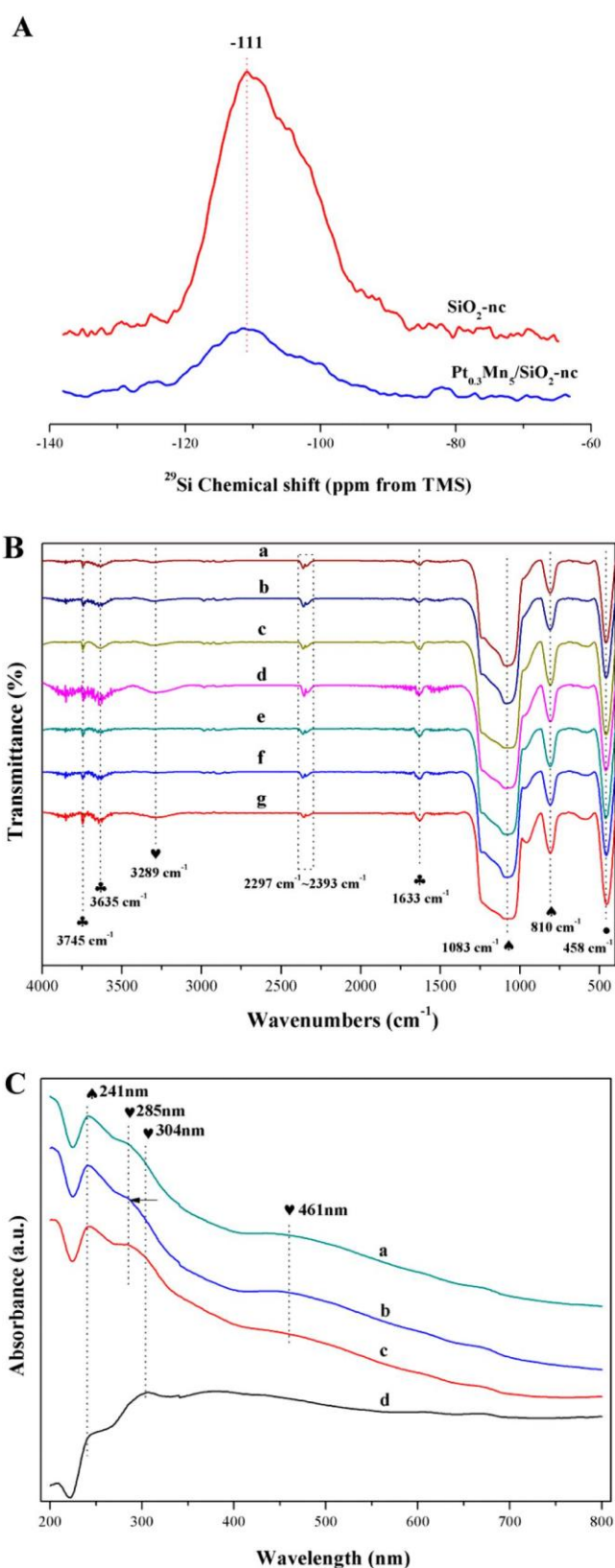


Figure 2. (A) ²⁹Si MAS NMR of SiO₂-nc support and Pt_{0.3}Mn₅/SiO₂-nc catalyst. (B) FT-IR spectra of (a) Pt_{0.3}Mn₁/SiO₂-nc, (b) Pt_{0.3}Mn₅/SiO₂-nc, (c) Pt_{0.3}Mn₁₀/SiO₂-nc, (d) Pt_{0.3}Mn₁₅/SiO₂-nc, (e) Pt_{0.3}/SiO₂-nc, (f) SiO₂-nc support, and (g) Mn₅/SiO₂-nc. (C) UV-vis absorption spectra of (a) Pt_{0.3}Mn₁₀/SiO₂-nc, (b) Pt_{0.3}Mn₅/SiO₂-nc, (c) Pt_{0.3}Mn₁/SiO₂-nc, and (d) Pt_{0.3}/SiO₂-nc.

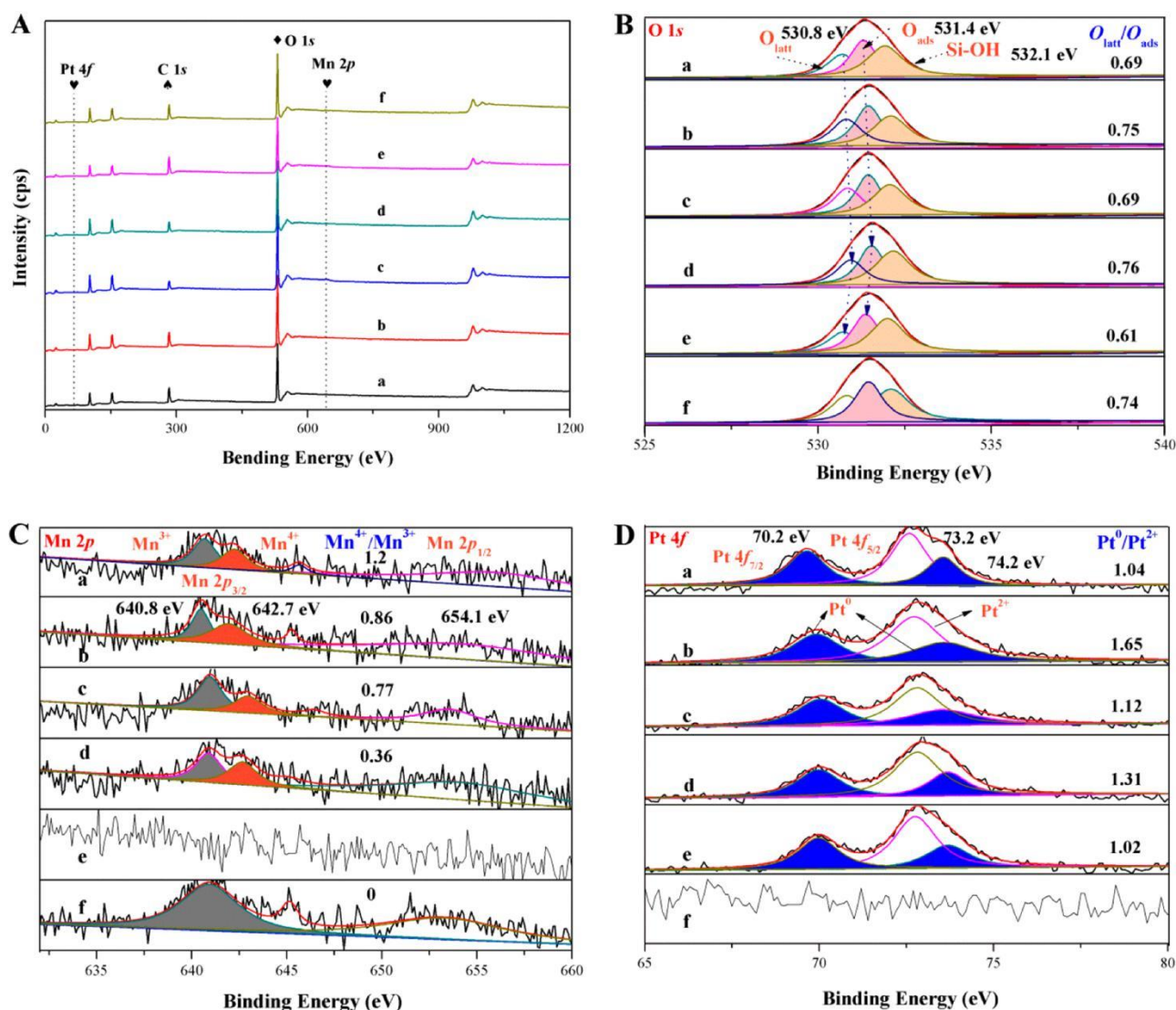


Figure 3. XPS spectra of (a) Pt_{0.3}Mn₁/SiO₂-nc, (b) Pt_{0.3}Mn₅/SiO₂-nc, (c) Pt_{0.3}Mn₁₀/SiO₂-nc, (d) Pt_{0.3}Mn₁₅/SiO₂-nc, (e) Pt_{0.3}/SiO₂-nc, and (f) Mn₅/SiO₂-nc: (A) survey scan of XPS spectra; (B) O 1s; (C) Mn 2p; (D) Pt 4f.

Pt⁰/Pt²⁺ ratio, which could promote the oxidation of MEK molecules.

X-ray photoelectron spectroscopy (XPS) experiments were carried out to identify the chemical states of the surface O, Pt, and Mn in each of the prepared materials. The corresponding spectra are displayed in Figure 3. The C 1s and O 1s peaks are clear, while signals corresponding to the Mn 2p and Pt 4f states are very weak by comparison. The O 1s XPS spectra (Figure 3B) for all of the materials can be deconvoluted into three peaks with binding energies (BE) centered at approximately 532.1, 531.4, and 530.8 eV. These peaks can be assigned to oxygen associated with Si-OH (silanol group), surface-adsorbed O₂, and lattice oxygen, respectively.^{35,36} Increasing the Mn content in the material leads to a high-energy shift in the peaks attributed to surface-adsorbed oxygen and lattice oxygen. This indicates that the introduction of Mn₂O₃ has a fairly substantial effect on the distribution of oxygen in the material. It is known that, with certain catalysts, lattice oxygen can have a significant influence on catalytic performance for the oxidation of VOCs.³⁵ Quantification of the peaks attributed to lattice oxygen (O_{latt}) and surface-adsorbed oxygen (O_{ads}) provided some interesting results. The O_{latt}/O_{ads} ratio for the

Pt_{0.3}/SiO₂-nc material was calculated to be 0.61, which is noticeably lower than the O_{latt}/O_{ads} ratio calculated for the Mn₅/SiO₂-nc material (0.74). For the Pt_{0.3}Mn₅/SiO₂-nc material, the O_{latt}/O_{ads} ratio increased to 0.75, which is higher than that of Pt_{0.3}Mn₁/SiO₂-nc (0.69) and Pt_{0.3}Mn₁₀/SiO₂-nc (0.69) samples. The high O_{latt}/O_{ads} ratio ensures the superior catalytic performance of Pt_{0.3}Mn₅/SiO₂-nc for total oxidation of VOCs. As shown in Figure 3C, the Mn 2p XPS spectra can be split into Mn 2p_{3/2} and Mn 2p_{1/2}.³⁷ The asymmetrical Mn 2p_{3/2} spectra can be deconvoluted into two components centered at BE values of 640.8 and 642.7 eV, which are characteristic of surface Mn³⁺ and Mn⁴⁺ species, respectively.³⁷ Interestingly, only one peak is observed in the Mn 2p_{3/2} region of the Mn₅/SiO₂-nc at 640.9 eV, which corresponds to the Mn³⁺ species. This suggests that, with this material, Mn is likely to only be present as Mn₂O₃. However, the peaks at binding energies which are characteristic of Mn⁴⁺ species appear in the XPS spectra of the Pt_{0.3}Mn_x/SiO₂ materials, suggesting that the Pt and Mn in the materials form Pt-O-Mn moieties. It has previously been reported that Mn⁴⁺ species are highly active in VOC oxidation³⁸ and, as such, the Mn⁴⁺/Mn³⁺ ratio could provide insights into the catalytic activities of these materials.

Table 2. Catalytic Performance of All Catalysts

sample	T ₅ ^a (°C)	T ₅₀ ^a (°C)	T ₉₀ ^a (°C)	r _v ^b (mmol g _{Pt} ⁻¹ s ⁻¹)	TOF _{Pt} ^c (s ⁻¹)	E _a ^d (kJ mol ⁻¹)	C _{wp} ^e
Pt _{0.3} /SiO ₂ -nc	80	156	190	10.2	4.0	55.04	2.17 × 10 ⁻³
Mn ₅ /SiO ₂ -nc	93	165	210				
Pt _{0.3} Mn ₁ /SiO ₂ -nc	79	145	188	12.7	4.7	48.88	2.70 × 10 ⁻³
Pt _{0.3} Mn ₅ /SiO ₂ -nc	72	111	147	32.9	10.7	41.36	6.99 × 10 ⁻³
Pt _{0.3} Mn ₁₀ /SiO ₂ -nc	75	130	175	21.8	8.1	48.56	4.63 × 10 ⁻³
Pt _{0.3} Mn ₁₅ /SiO ₂ -nc	80	138	179	16.8	5.7	61.12	3.57 × 10 ⁻³

^aTemperatures at 5%, 50%, and 90% conversion of MEK. ^bReaction rate of MEK molecules transformed per surface area per unit time of various catalysts at 100 °C. ^cTurnover frequency based on the dispersion of Pt obtained at 100 °C. ^dApparent activation energy obtained from Arrhenius plots. ^eParameter calculated according to the Weisz-Prater criterion.

For this reason, the proportion of Mn⁴⁺/Mn³⁺ present in each material was quantified and the ratios determined were as follows: Mn₅/SiO₂-nc (0) < Pt_{0.3}Mn₁₅/SiO₂-nc (0.36) < Pt_{0.3}Mn₁₀/SiO₂-nc (0.77) < Pt_{0.3}Mn₅/SiO₂-nc (0.86) < Pt_{0.3}Mn₅/SiO₂-nc (1.2). Figure 3D highlights how the asymmetrical Pt 4f peak can be deconvoluted into peaks representative of the Pt 4f_{7/2} and Pt 4f_{5/2} species. The peaks

with BE energies of 70.2 and 74.2 eV are attributed to Pt⁰ and Pt²⁺, and the peak at a BE value of 73.24 eV can be assigned to Pt²⁺.

As discussed previously, the Pt⁰ species is highly active and plays an important role in VOC combustion.³ From Figure 3D it is clear that the incorporation of Mn into these materials significantly enhances the proportion of Pt⁰/Pt²⁺. We believe that this is due to the transfer of electrons from Mn³⁺ to Pt²⁺. In

addition to this, the Pt⁰/Pt²⁺ ratio in the Pt_{0.3}Mn₅/SiO₂-nc material (1.65) is much higher than that observed in Pt_{0.3}/SiO₂-nc (1.02).

Catalytic Performance. Values for the Weisz-Prater (C_{wp}) criterion for all the catalysts are shown in Table 2, and the maximum value is on the order of 10⁻³.²² As such, both the external and internal diffusional effects on the catalytic performance can be ignored. The catalytic behaviors of each of the materials for the oxidation of MEK were studied, and parameters such as MEK conversion temperature, destruction rate, activation energy, and turnover frequency were calculated and are displayed in Figure 4 and Table 2. Over the Mn₅/SiO₂-nc and Pt_{0.3}/SiO₂-nc catalysts, MEK is fully converted at 230 and 200 °C, respectively (Figure 4A), indicating that the Pt sites are more active than the Mn sites for the oxidation of MEK. Interestingly, the activity for MEK oxidation is greatly enhanced over the Pt_{0.3}Mn_x/SiO₂-nc catalysts, suggesting that introducing Mn into the materials has a dramatic effect on the catalytic performance. The Pt_{0.3}Mn₅/SiO₂-nc catalyst exhibited the highest catalytic activity, with approximately 90% of the MEK converted at 147 °C. To the best of our knowledge, this is the most promising active catalyst to date for the conversion of MEK at low temperature (Table S1). Sanz et al. had previously reported that a highly active 1.0 wt % Pt/OMS-2 catalyst could achieve 50% and 90% of MEK destruction at 170 and 190 °C, respectively, under a flow rate of 500 mL min⁻¹. In view of the specified reaction conditions, e.g., space velocities and noble-metal content, the Pt_{0.3}Mn₅/SiO₂-nc catalyst also has its advantages over some of other types of catalysts. For instance, the GHSV in this work is 42600 mL g⁻¹ h⁻¹ or 25440 h⁻¹; the 0.5 wt % Pd-Ce/ZSM-5 catalyst exhibits inferior activity (T₅₀ of 210 °C, T₉₀ of 225 °C) for MEK oxidation with a similar space velocity (28000 h⁻¹). Taking the CO₂ yield as a value, T₅₀ (139 °C), T₉₀ (161 °C), and E_a (41.3 kJ mol⁻¹) of

our Pt_{0.3}Mn₅/SiO₂-nc catalyst are lower than those (T₅₀ = 190 °C and T₉₀ = 205 °C based on CO₂ yield) over Pt/NaX with

GHSV of 15300 h⁻¹ and those over 1.0 wt % Pd-Mn/Al₂O₃ with GHSV of 425 h⁻¹ (T₅₀ = 290 °C, T₉₀ = 305 °C, and E_a = 117 kJ mol⁻¹ based on CO₂ yield).

The CO₂ selectivity observed over three of the synthesized catalysts (Pt_{0.3}Mn₅/SiO₂-nc, Pt_{0.3}/SiO₂-nc, and Mn₅/SiO₂-nc) were also assessed, the results from which are displayed in Figure 4B. The CO₂ selectivity was highest for Pt_{0.3}Mn₅/SiO₂-nc, with 100% selectivity to CO₂ observed at only 210 °C. The Pt_{0.3}/SiO₂-nc and Mn₅/SiO₂-nc required much higher reaction temperatures in order to achieve the same CO₂ selectivity (250 and 260 °C, respectively). Interestingly, a sudden drop is observed in the CO₂ selectivity associated with the Pt_{0.3}/SiO₂-nc between 210 and 230 °C. This abnormality was not observed in the selectivity data associated with the Pt_{0.3}Mn₅/SiO₂-nc and Mn₅/SiO₂-nc, which may be attributed to sufficient lattice oxygen being present in these materials. Nevertheless, these selectivity data provide further evidence that the exposed Mn₂O₃ (222) facets accelerate the MEK oxidation process.

The stability of these catalysts is also an important parameter to consider for supported noble-metal catalysts, as the susceptibility of these to undergo thermal deactivation is often responsible for their limited industrial applications.^{39,40} In order to determine whether these catalysts undergo thermal deactivation, an additional study was conducted where the performances of the Pt_{0.3}Mn₅/SiO₂-nc and Pt_{0.3}/SiO₂-nc catalysts were monitored for an extended amount of time. The results of this study are displayed in Figure 4C. Very little deactivation is observed with both materials, indicating that they possess excellent stability in the total oxidation of MEK.

As water is one of the reaction products and is also commonly found in industrial exhaust streams, it was important to determine whether it had a detrimental effect on the long-term oxidation behavior of the catalysts. Figure 4D illustrates how different concentrations of water vapor (3 and 5 vol %) affect the catalytic performance of these materials at 180 °C. Water vapor was found to have a negative effect on the oxidation of MEK, which is likely to be due to the competitive adsorption of H₂O, MEK, and O₂ molecules on the catalyst surface. A loss in MEK conversion of ca. 27.7% and 32.0% is

observed over the Pt_{0.3}Mn₅/SiO₂-nc and Pt_{0.3}/SiO₂-nc catalysts, respectively, when 5 vol % water vapor is introduced into the stream. Interestingly, when the water vapor was switched off, the conversion of MEK returned to the original values for Pt_{0.3}Mn₅/SiO₂-nc and Pt_{0.3}/SiO₂-nc catalysts within 45 and 65 min, respectively. A similar effect was observed when 3 vol % water vapor was introduced into the reaction stream; conversion dropped from 19.6% and 23% for the Pt_{0.3}Mn₅/SiO₂-nc and Pt_{0.3}/SiO₂-nc catalysts, respectively, but once again their activity returned within 30 and 45 min when the water

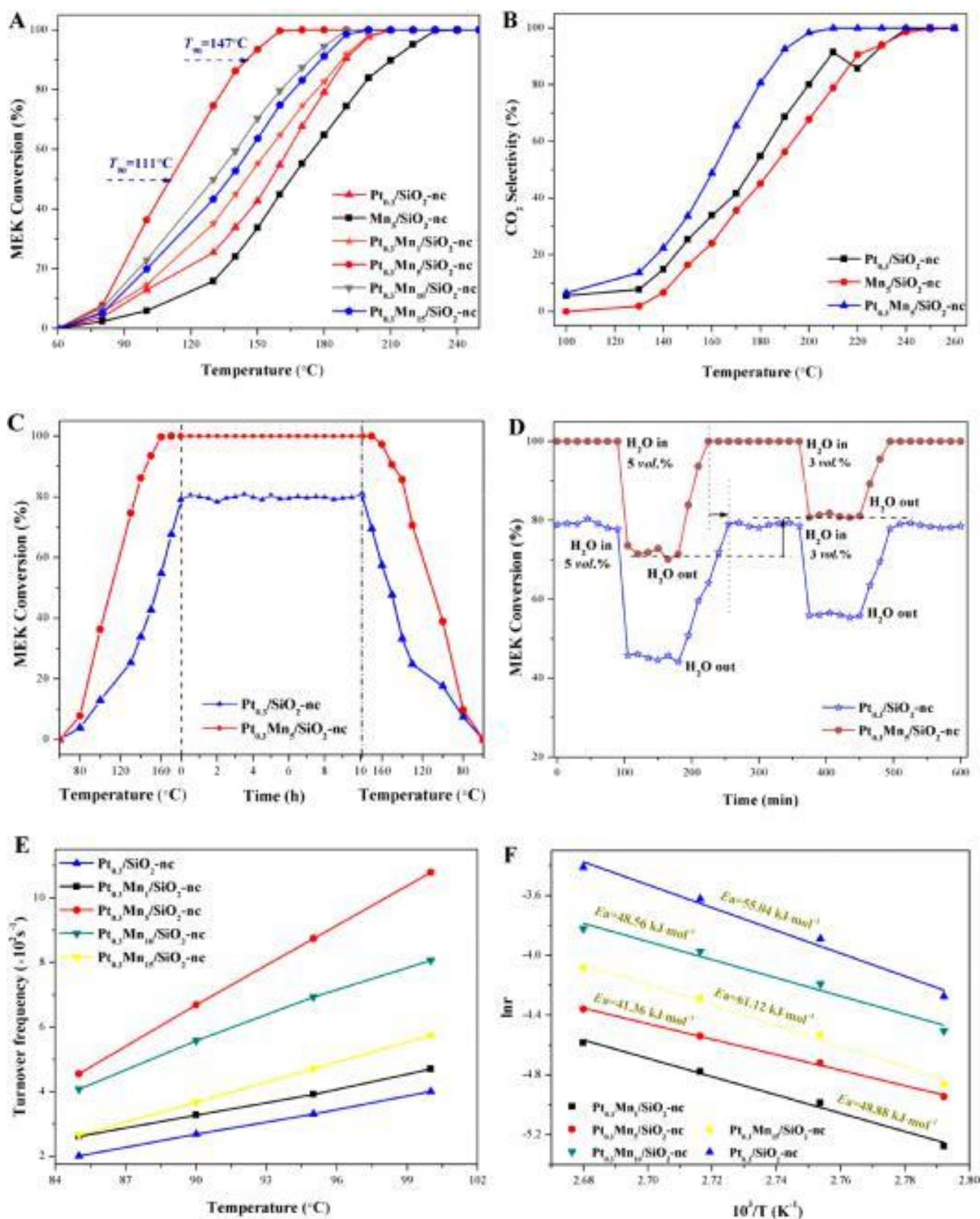


Figure 4. (A) Catalytic activity and (B) CO₂ selectivity of different catalysts for MEK combustion. (C) Stability test of active samples for MEK oxidation. (D) Effect of water vapor on MEK combustion at 180 °C. (E) Turnover frequency of active samples based on the dispersion of Pt. (F) Arrhenius plots of active samples for MEK catalytic oxidation.

vapor was switched off. Despite this detrimental effect on the catalytic performance, it is interesting that the Pt_{0.3}Mn₅/SiO₂-nc exhibited a smaller drop in conversion upon the addition of water in comparison to the Pt_{0.3}/SiO₂-nc catalyst. As discussed

previously, Mn₂O₃ can balance the negative charge of the silica support and enhance the Brønsted acid sites on the catalyst, which are beneficial for producing more well dispersed Pt nanoparticles.¹⁷ In addition to this, the Mn₂O₃ has the ability to

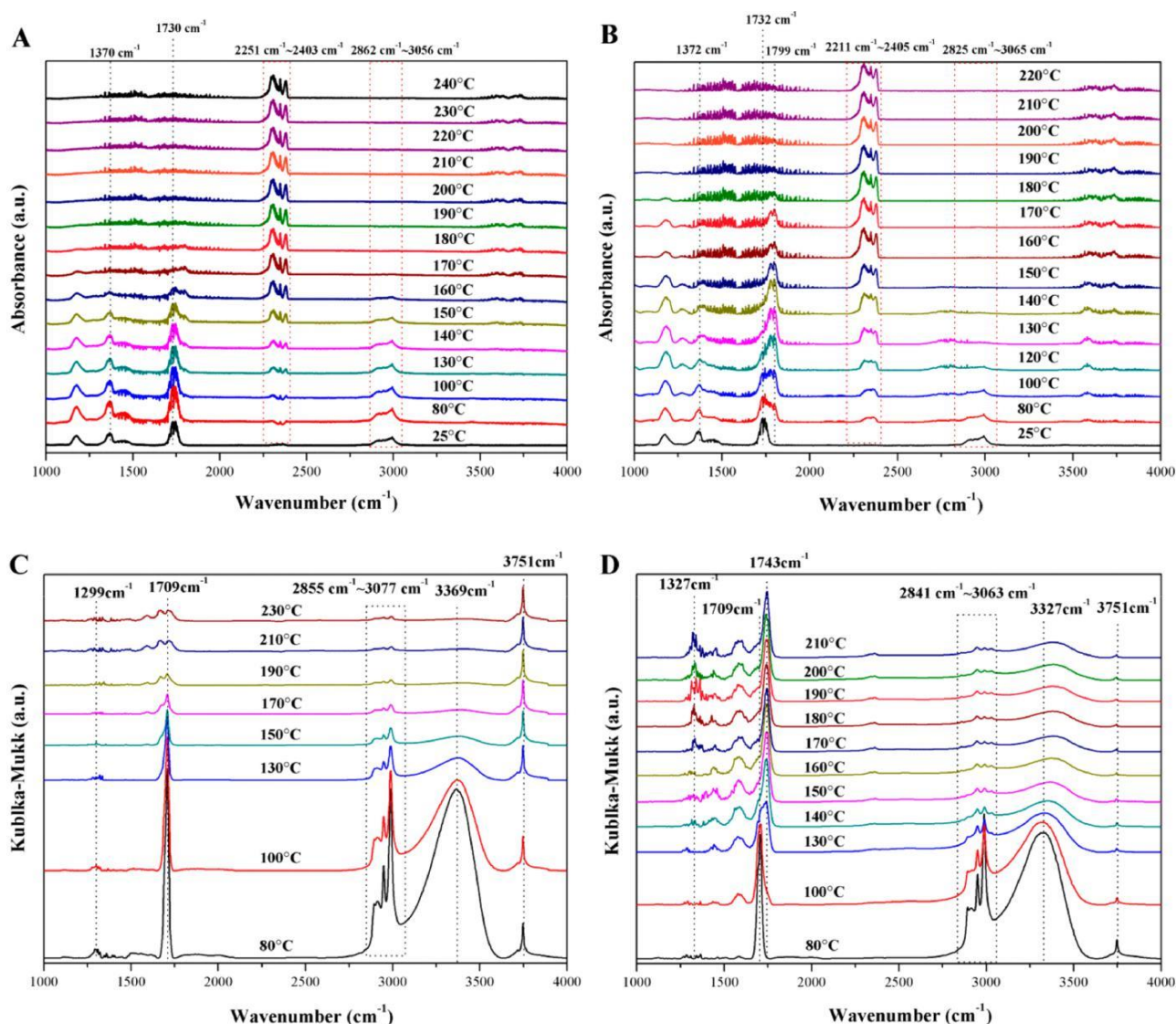


Figure 5. Online FT-IR spectra of outlet stream after MEK combustion over (A) Pt_{0.3}/SiO₂-nc and (B) Pt_{0.3}Mn₅/SiO₂-nc. In situ DRIFTS spectra of (C) Pt_{0.3}/SiO₂-nc and (D) Pt_{0.3}Mn₅/SiO₂-nc for MEK oxidation as a function of reaction temperature in flowing MEK + N₂ + O₂ from 80 to 230 °C.

transfer electrons to Pt active sites via the Mn–O–Pt moiety formation, which increases the Pt⁰/Pt²⁺ ratio and enhances the interaction between active sites and support.¹⁶ As such, catalysts with a higher proportion of Pt⁰ and higher metal dispersion are likely to resist aggregation at high temperatures and maintain a better performance. It is possible that the Mn species reduce the adsorption of H₂O onto the catalyst surface, which ultimately liberates more adsorption sites for MEK molecules to adsorb. The reactivity data which highlight the superior stability of the Pt_{0.3}Mn₅/SiO₂-nc is supplemented by additional TGA-FT-IR, XRD, and FT-IR spectroscopy data of both the fresh and used Pt_{0.3}Mn₅/SiO₂-nc samples, which are displayed in Figure S4.

The turnover frequencies (TOFs) and activation energies can also be used to compare the activities of each catalyst. The TOF_{Pt} values were calculated from the quantity of Pt active sites on each catalyst and are displayed in Figure 4E. These data reveal that the TOF_{Pt} value of Pt_{0.3}Mn₅/SiO₂-nc for MEK oxidation is 2–3 times higher than that observed over Pt_{0.3}/SiO₂-nc material. The highest TOF_{Pt} value was observed over the Pt_{0.3}Mn₅/SiO₂-nc material (10.79 s⁻¹ at 100 °C),

demonstrating its excellent low-temperature activity for MEK destruction. The calculated TOF_{Pt} value for catalytic decomposition of MEK at 100 °C decreases in the sequence Pt_{0.3}Mn₅/SiO₂-nc (10.79 s⁻¹) > Pt_{0.3}Mn₁₀/SiO₂-nc (8.07 s⁻¹) > Pt_{0.3}Mn₁₅/SiO₂-nc (5.74 s⁻¹) > Pt_{0.3}Mn₁/SiO₂-nc (4.70 s⁻¹) > Pt_{0.3}/SiO₂-nc (4.00 s⁻¹) (Table 2). The results confirm that Pt_{0.3}Mn_x/SiO₂-nc species are clearly excellent catalysts for the oxidation of MEK.

The activation energy (*E*_a) of MEK oxidation was subsequently used as an additional measure for comparing catalytic performance. For this, low MEK conversions (between 5 and 10%) was used to compare the low-temperature activity of each of the catalysts. Replotting the reaction data in an Arrhenius plot allows for the calculation of *E*_a values for each of the catalysts. The corresponding Arrhenius plots are displayed in Figure 4F, and corresponding data are shown in Table 2. The activation energies were found to increase according to the sequence Pt_{0.3}Mn₅/SiO₂-nc (41.36 kJ mol⁻¹) < Pt_{0.3}Mn₁₀/SiO₂-nc (48.56 kJ mol⁻¹) < Pt_{0.3}Mn₁/SiO₂-nc (48.88 kJ mol⁻¹) < Pt_{0.3}/SiO₂-nc (55.04 kJ mol⁻¹) < Pt_{0.3}Mn₁₅/SiO₂-nc (61.12 kJ mol⁻¹). The Pt_{0.3}Mn₅/SiO₂-nc catalyst was found to possess the

lowest E_a (41.36 kJ mol⁻¹), suggesting that MEK oxidation proceeds more readily over this material in comparison to the others which were tested.

MEK Destruction Mechanism. In addition to MEK, some of the byproducts which can form from the partial oxidation of the substrate can also be toxic and damaging to the environment. As such, it is crucially important that the mechanistic pathways for the decomposition of MEK are fully understood, so that these systems operate as close to a 100% CO₂ yield as possible.¹⁸ In this study, we have already shown that Mn₂O₃ has a promotional effect on the Pt nanoparticles for the combustion of MEK. In situ DRIFTS experiments were subsequently conducted in order to provide information on the products distribution formed during the reaction. To supplement this, additional experiments were conducted at different temperatures using an online FT-IR for analysis.

Figure 5A,B shows the online FT-IR results of MEK oxidation over the Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts, respectively. With the Pt_{0.3}/SiO₂-nc catalyst, a broad peak appears between 2862 and 3056 cm⁻¹ at 25 °C which can be attributed to the -CH₃ group in MEK.⁴¹ Another intense peak at 1730 cm⁻¹ and a weakly intense peak at 1370 cm⁻¹ are also observed, which can be attributed to the C O in MEK.^{42,43} These peaks reduce in intensity as the temperature increases and completely disappear at 180 °C. Interestingly, bands characteristic of CO₂ vibrations (between 2251 and 2403 cm⁻¹) appear to gradually increase as the reaction temperature approaches 190 °C. This correlates with observations made in previous studies.⁴⁴ Interestingly, with the Pt_{0.3}Mn₅/SiO₂-nc catalyst, a new band at 1799 cm⁻¹ appears at 80 °C and gradually increases when the temperature is increased, before reaching a maxima at 130 °C and then descending gradually. This peak corresponds to the vibration of a symmetric C O moiety from an intermediate species, which is not observed when the reaction is conducted over the Pt_{0.3}/SiO₂-nc catalyst.⁴⁵ It can therefore be concluded that the Pt_{0.3}Mn₅/SiO₂-nc catalyst offers an alternative mechanistic route to MEK combustion from that which occurs over the Pt_{0.3}/SiO₂-nc catalyst, where acetone is believed to be the main intermediate product. The characteristic peaks which are indicative of MEK (2825–3065, 1732, and 1372 cm⁻¹) decrease when the temperature increases and vanish at 150 °C, which coincides with the results from the activity tests (illustrated in Figure 4A). The vibration of CO₂ appears between 2211 and 2405 cm⁻¹ and maximizes at 170 °C, which suggests that MEK is decomposed to CO₂ at 170 °C over the Pt_{0.3}Mn₅/SiO₂-nc catalyst (Figure 4B).

Similar conclusions can be drawn from the in situ DRIFTS experiments which were conducted over the Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts. Once again, the DRIFTS spectra for each catalyst were assessed at different reaction temperatures with MEK flowing over the materials. The results of these experiments are displayed in Figure 5C,D. The sharp peak at 3751 cm⁻¹ is attributed to the Brønsted acid sites of the catalyst.⁴³ Interestingly, with increasing temperature this peak remains unchanged for the Pt_{0.3}/SiO₂-nc material but a decrease in the intensity of this peak is observed with the Pt_{0.3}Mn₅/SiO₂-nc material with increasing temperature. As discussed previously, acid sites are essential for MEK combustion over Pt_{0.3}Mn₅/SiO₂-nc catalyst, as they provide a proton to break the conjugation and fracture the -CH₃ moiety. As such, the intensity of this peak is reduced as the reaction proceeds. With the Pt_{0.3}/SiO₂-nc catalyst (Figure 5C), the

broad peak at 3369 cm⁻¹ is attributed to hydroxyl groups which corresponds to 2-butanol, 2,3-butanediol, and adsorbed water.⁴³ The band at 1709 cm⁻¹ is indicative of vibrational asymmetric C O species, which could be indicative of MEK, acetaldehyde, or formaldehyde.⁴² The peak at 1299 cm⁻¹ is attributed to vibrations from the -CH₃ species in MEK or acetaldehyde.⁴³ The bands also observed between 2855 and 3077 cm⁻¹ may be attributed to the bending and stretching vibrations of C-H⁴¹ and thus must correspond to residual adsorbed hydrocarbon species from the decomposition of MEK. A new bend at 1743 cm⁻¹ which corresponds to the symmetric C O moiety in acetone can be detected in MEK oxidation over Pt_{0.3}Mn₅/SiO₂-nc⁴⁵ and proves that the Mn₂O₃ phase has a significant effect on the MEK reaction route and oxidation mechanism.

DISCUSSION

In this work, the promotional effect of Mn₂O₃ with highly exposed (222) planes on the performance of Pt_{0.3}Mn_x/SiO₂-nc micro-/mesoporous composite catalysts for the oxidation of MEK was investigated. It was determined that the Mn₂O₃ (222) facets increase the quantity of Brønsted acid sites in these materials, which promote the mobility of lattice oxygen. It is suggested that these increased Brønsted acid sites balance the negative charge of the support and accelerate the desorption of surface adsorbed O₂ and CO₂ (Figure S5).

The acidity of all the materials which were synthesized was evaluated by NH₃-TPD (Figure 6A) and NH₃-IR (Figure 6B). In Figure 6A, a small peak is observed at 195 °C for the SiO₂-nc support, which can be attributed to physisorbed NH₃.⁴⁶ The profiles of the Pt_{0.3}Mn₁/SiO₂-nc, fresh Pt_{0.3}Mn₅/SiO₂-nc, and used Pt_{0.3}Mn₅/SiO₂-nc materials were subsequently deconvoluted by the Gauss curve fitting method into two peaks, which correspond to physisorbed NH₃ (desorption peak at 173–194 °C) and ammonia adsorbed on Brønsted acid sites (desorption peak at 311–334 °C).⁴⁶ Interestingly, as the quantity of Mn₂O₃ in the material is increased, the desorption peak associated with ammonia adsorbed onto Brønsted acid sites increases to a higher temperature. Previous work has showed that such a shift is indicative of an increase in the strength of the acid sites.⁴⁷ The quantity of acid sites in each material was compared by examining the integrated areas of the corresponding NH₃ desorption peaks, an approach which has been used previously.⁴⁸ The areas of the NH₃ desorption peak for the Pt_{0.3}Mn₁/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts were determined to be 182 and 457, respectively, indicating that increasing the quantity of Mn₂O₃ in the material increases the quantity of Brønsted acid sites in the system. With the used Pt_{0.3}Mn₅/SiO₂-nc catalyst, the integrated area of the NH₃ desorption peak was reduced from 457 to 347, suggesting that some of the Brønsted acid sites are consumed during the combustion of MEK.

From the FT-IR spectra displayed in Figure 6B, it is clear that there are no characteristic peaks which can be attributed to the adsorption of NH₃ over the SiO₂-nc material. Interestingly, in the corresponding spectrum associated with the Pt_{0.3}Mn₅/SiO₂-nc material, bands appear at 1467 and 1673–1781 cm⁻¹ which are indicative of the symmetric and asymmetric bending vibrations of NH₄⁺ species on Brønsted acid sites.⁴⁸ An important observation to note is that the intensities of these bands are significantly lower in the corresponding spectrum of the used Pt_{0.3}Mn₅/SiO₂-nc catalyst. In conclusion, the NH₃-TPD and FT-IR experiments indicate that the presence of Mn₂O₃ in these catalysts increases the quantity and strength of

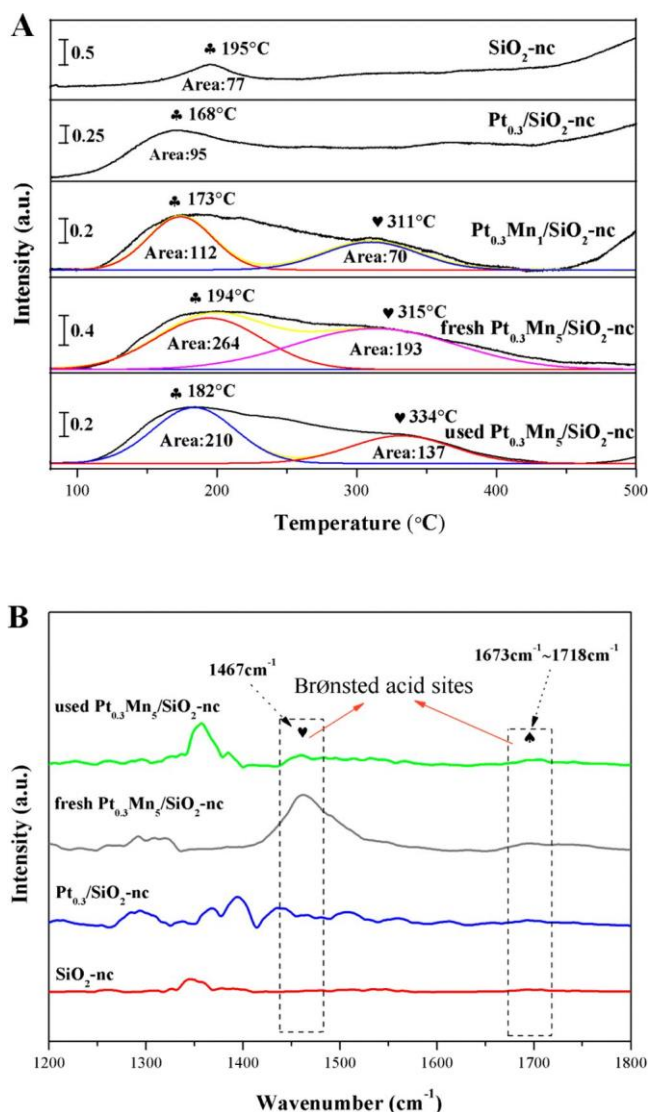


Figure 6. (A) NH₃-TPD profiles of active samples. (B) FT-IR spectra of various catalysts for NH₃ adsorption.

Brønsted acid sites over the materials. The Brønsted acid sites have been shown previously to significantly promote noble-metal dispersion and stability due to their electrophilic character.⁴⁹ As such, the adsorption of MEK on the catalysts' surface is enhanced (Figure S6).

Metallic Pt nanoparticles are considered to be critically important for the combustion of VOCs.¹² As such, additional studies were conducted in order to investigate whether reduced Pt sites were important for the oxidation of MEK. To do this, CO was used as a probe molecule to investigate the nature of the Pt active sites in each of the catalysts. Chemisorption studies using CO in this way can reveal detailed information on the chemical environment in close proximity to the Pt nanoparticle active sites.⁵⁰ It is known that, when CO adsorbs to Pt active sites, electrons are partially transferred from a d orbital of the metal to the antibonding CO molecular orbital. This electron transfer strengthens the Pt-C bond and weakens the C-O bond. Any strengthening of the Pt-CO bond typically correlates with an increase in the vibrational frequencies of the Pt-C bond.⁵¹ As shown in Figure 7, bands corresponding to carbonates and CO₂ are observed at 1628 and 2344 cm⁻¹, respectively, which can be attributed to the oxidation of small quantities of the CO probe molecule by the Pt active sites; this is a phenomenon that has previously been attributed to the involvement of lattice oxygen.⁵² The

intensity of the CO₂ peak increases in the order Pt_{0.3}/SiO₂-nc < Pt_{0.3}Mn₁/SiO₂-nc < Pt_{0.3}Mn₅/SiO₂-nc, while the opposite trend is observed for the characteristic carbonate peak. Larger quantities of the CO probe molecule appear to be converted to CO₂ over the Pt_{0.3}Mn₅/SiO₂-nc material in comparison to that over the Pt_{0.3}/SiO₂-nc material. These results confirm that the Pt_{0.3}Mn_x/SiO₂-nc catalysts possess more lattice oxygen than the Pt_{0.3}/SiO₂-nc materials. For the Pt_{0.3}Mn₁/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc samples, a band at 2090 cm⁻¹ is observed which can be assigned to bridge-bond CO which is adsorbed on different terrace and step sites on the Pt nanoparticle.⁵³ This is characteristic of adsorbed CO on Pt (111) planes,⁵⁴ which suggests that a large proportion of the exposed Pt in these materials exists in the (111) plane. This observation is supported by the XRD diffraction patterns displayed in Figure S1. Interestingly, in the spectrum associated with the Pt_{0.3}/SiO₂-nc material, the band corresponding to the adsorbed

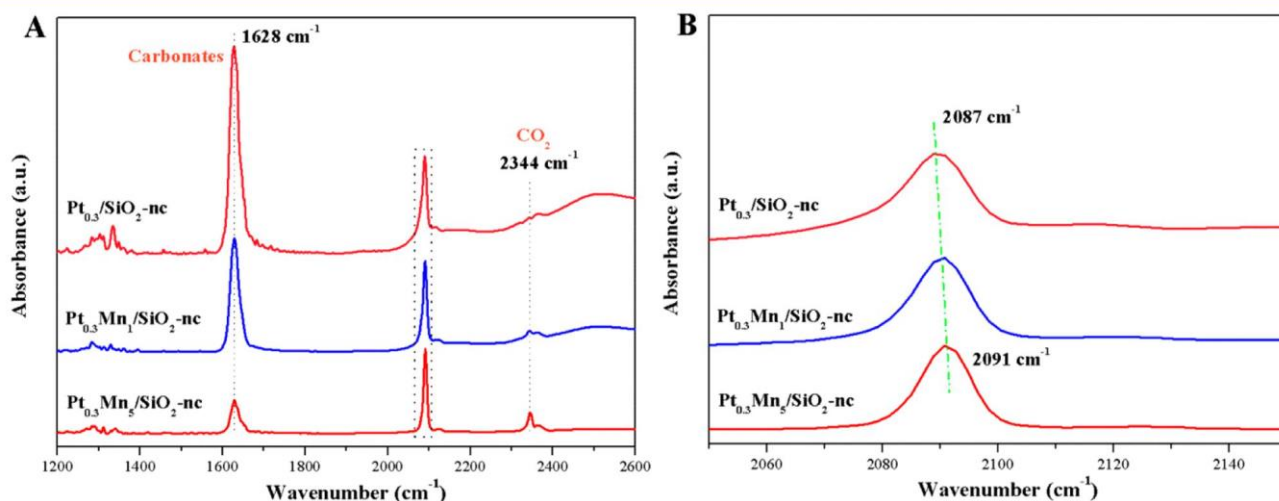


Figure 7. FT-IR spectra of typical catalysts for CO adsorption: (A) full spectrum analysis from 1200 to 2600 nm⁻¹; (B) magnification of region between 2050 and 2150 nm⁻¹.

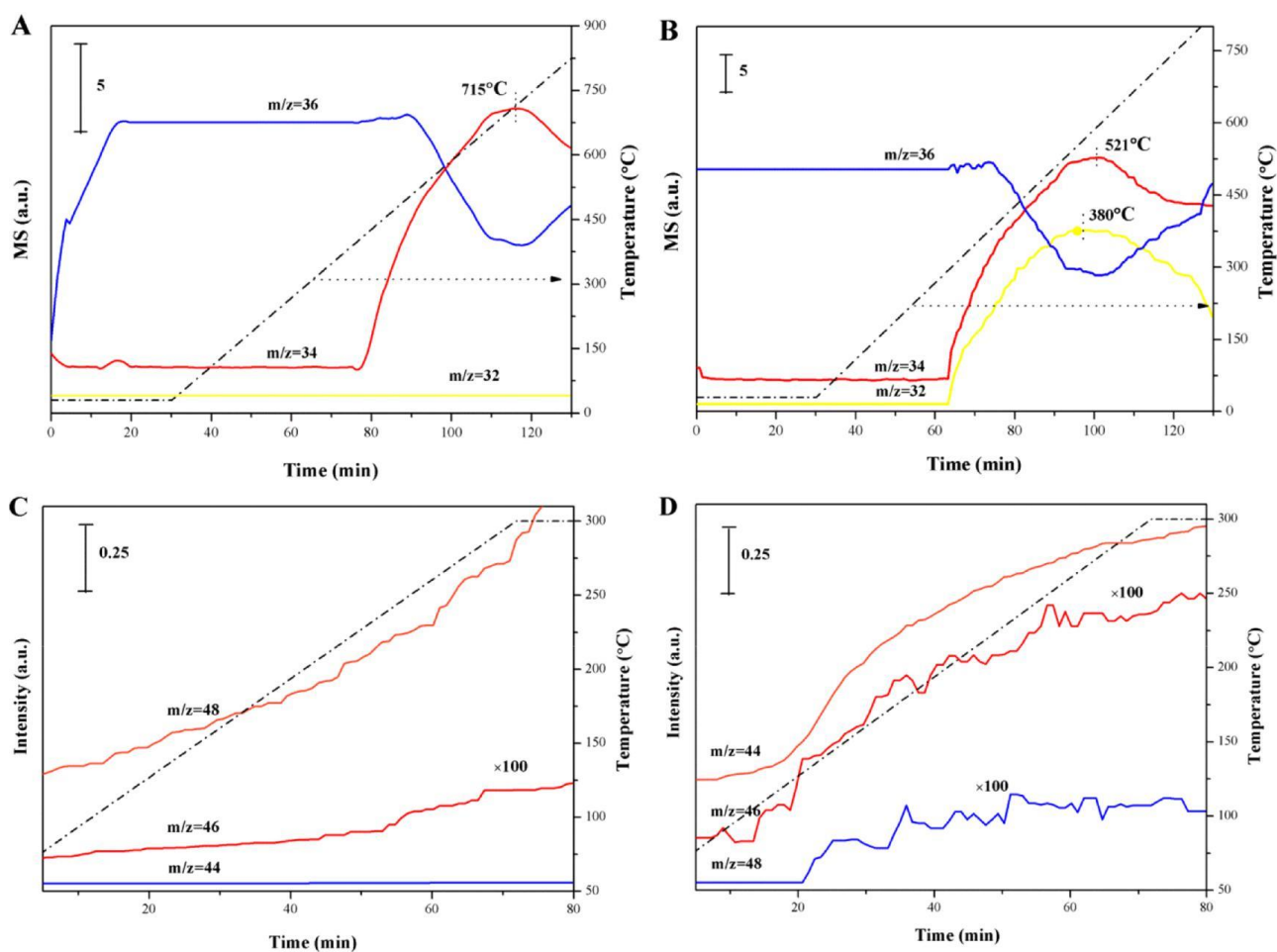


Figure 8. Temperature-programmed isotopic exchange (TPIE) experiment of (A) Pt_{0.3}/SiO₂-nc and (B) Pt_{0.3}Mn₅/SiO₂-nc. ¹⁸O₂ isotopic exchange studies of (C) Pt_{0.3}/SiO₂-nc and (D) Pt_{0.3}Mn₅/SiO₂-nc for MEK combustion.

bridging of CO shifts to lower energy (2078 cm⁻¹). Previous work has suggested that a downward shift of this nature can be attributed to the adsorption of CO on large platinum crystallites.^{55,56} Given that fully reduced, well dispersed Pt particles are considered to promote catalytic performance in the total oxidation of VOCs, it is somewhat unsurprising that the Pt_{0.3}Mn_x/SiO₂-nc materials display such a high performance for the total oxidation of MEK. More metallic Pt nanoparticles were confirmed over Pt_{0.3}Mn₅/SiO₂-nc catalyst in comparison with Pt_{0.3}/SiO₂-nc, which is ascribed to the transfer of electrons from Mn³⁺ to Pt²⁺ via conjugated π bonding from Mn-O-Pt moieties. This, in turn, increases the Pt⁰/Pt²⁺ ratio on the surface of the material, which we believe to be ultimately responsible for the enhanced MEK oxidation activity (Figure 4A) and increased stability of these Mn₂O₃-doped Pt-supported materials (Figure 4C and Figure S4).

Additional investigations were subsequently conducted in order to determine the influence in which O₂ has on the combustion of MEK over the materials synthesized in this study. For this, TPSR experiments were performed in air and N₂ and the corresponding results are displayed in Figure S7. These studies indicate that the lattice oxygen plays an important role in MEK combustion. The mobility of lattice oxygen was subsequently evaluated by TPIE (Figure 8A,B) and ¹⁸O isotopic studies (Figure 8C,D). Figure 8A,B illustrates that changes in the normalized signals for all three oxygen isotopic species, namely ¹⁸O₂ (m/z 36), ¹⁶O¹⁸O (m/z 34) and ¹⁶O₂ (m/

z 32), are observed by a heteroexchange process, which appears to be temperature dependent. A previous study suggested that gas-phase ¹⁶O₂ signals typically arise from multiple hetero-exchange mechanisms between an 18-dioxygen molecule (¹⁸O₂) and two surface oxygen atoms of the solid (¹⁶O¹⁶O-s).⁵⁷ However, it was also suggested that gas-phase ¹⁶O¹⁸O can be produced via a simple heteroexchange mechanism between one ¹⁸O atom of the ¹⁸O₂ isotope molecule and one ¹⁶O atom of the metal oxide surface.⁵⁷ When similar experiments were conducted over the Pt_{0.3}/SiO₂-nc material prepared in this study, no signal corresponding to ¹⁶O₂ was observed. However, a broad peak corresponding to ¹⁶O¹⁸O was observed at 430 °C (centered at 715 °C) and a negative peak corresponding to ¹⁸O₂ was observed between 500 and 800 °C. When a similar experiment was conducted over the Pt_{0.3}Mn₅/SiO₂-nc catalyst, there were noticeable changes to the profile. Over this material, the negative peak corresponding to the ¹⁸O₂ species appeared at a significantly lower temperature (centered at 512 °C), indicating that oxygen exchange appears to be enhanced when Mn₂O₃ is present on the surface of the catalyst. In addition to this, the formation of ¹⁶O₂ species was also observed (between °C) over the Pt_{0.3}Mn₅/SiO₂-nc catalyst, which 290 and 380 further demonstrates the efficient oxygen mobility which occurs in this material.

Figure 8C,D shows how some carbon-containing isotopic species (C¹⁸O₂, C¹⁶O¹⁸O, and C¹⁶O₂) are produced over the

Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts in the oxidation of MEK. Again, the temperature was varied over the course of the experiment to determine whether the formation of these species was temperature dependent. With the Pt_{0.3}/SiO₂-nc catalyst, the relative concentrations of the C¹⁸O₂ and C¹⁶O¹⁸O species were found to increase with increasing temperature. No signal corresponding to C¹⁶O₂ was detected, and the signal corresponding to C¹⁸O₂ was significantly more intense than the signal attributed to C¹⁶O¹⁸O. This implies that surface-adsorbed oxygen is essential for the combustion of MEK over the Pt_{0.3}/SiO₂-nc catalyst. However, the distribution of these isotopes (C¹⁸O₂, C¹⁶O¹⁸O, and C¹⁶O₂ species) produced over the Pt_{0.3}Mn₅/SiO₂-nc are vastly different. Over the Mn-doped catalyst, C¹⁶O¹⁸O and C¹⁶O₂ species were observed at all the investigated temperatures. The intensity of the signal corresponding to these isotopic species appeared to increase with time and, interestingly, no C¹⁸O₂ appears to be observed until temperatures above 130 °C are used. Given that such large proportions of ¹⁸O were incorporated into the reaction products over the Pt_{0.3}Mn₅/SiO₂-nc catalyst, this provides further evidence that of the mobility of the lattice oxygen promotes the combustion of MEK over this material. From this investigation, it can be concluded that the contributions of lattice oxygen in the combustion of MEK over Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc are vastly different. This observed enhancement in oxygen mobility may be a result of the exposed (222) Mn₂O₃ facets in the Mn-doped material. The presence of Pt likely weakens the Mn–O bonds, which ultimately promotes the mobility of lattice oxygen in the Pt_{0.3}Mn₅/SiO₂-nc catalyst.¹⁶

The nature by which a substrate adsorbs to the surface of a catalyst is considered to be a crucial step in most heterogeneous catalysis processes.⁵⁸ The adsorption mode and strength by which a substrate adsorbs to a surface can often dictate the activity and selectivity of a given reaction. As such, DFT calculations were conducted in order to investigate the role of the intermediate products anchoring on the catalyst, to provide further insights into how MEK adsorbs on these materials and what combustion pathways occur. The results of these calculations are illustrated in Figure 9 and show that MEK

molecules initially adsorb to the Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts on bridged sites with corresponding adsorption energies of -1.3 and -1.5 eV, respectively. This indicates that the MEK molecules have a higher affinity to adsorb onto the surface of the Pt_{0.3}Mn₅/SiO₂-nc material. Additional calculations revealed that acetone possesses a lower adsorption energy (-0.9 eV) in comparison to 2-butanol (-0.6 eV), indicating that the quantity and strength of the Brønsted acid sites which are enhanced by Mn₂O₃ are beneficial for acetone adsorption and provide a proton to break the C–C bonds. Subsequent calculations revealed that acetaldehyde is likely produced by demethylation from acetone. The adsorption energy of acetaldehyde over the Pt_{0.3}/SiO₂-nc material is higher than that calculated over the Pt_{0.3}Mn₅/SiO₂-nc catalyst (-0.6 and -0.8 eV, respectively). With the Pt_{0.3}Mn₅/SiO₂-nc catalyst, the adsorption energies of the intermediate species appear to decrease the farther you proceed through the oxidation pathway. This trend is not observed with the results from the adsorption calculations conducted over the Pt_{0.3}/SiO₂-nc material. As such, it can be concluded that the reaction route of MEK combustion over Pt_{0.3}Mn₅/SiO₂-nc is promoted by Mn₂O₃.

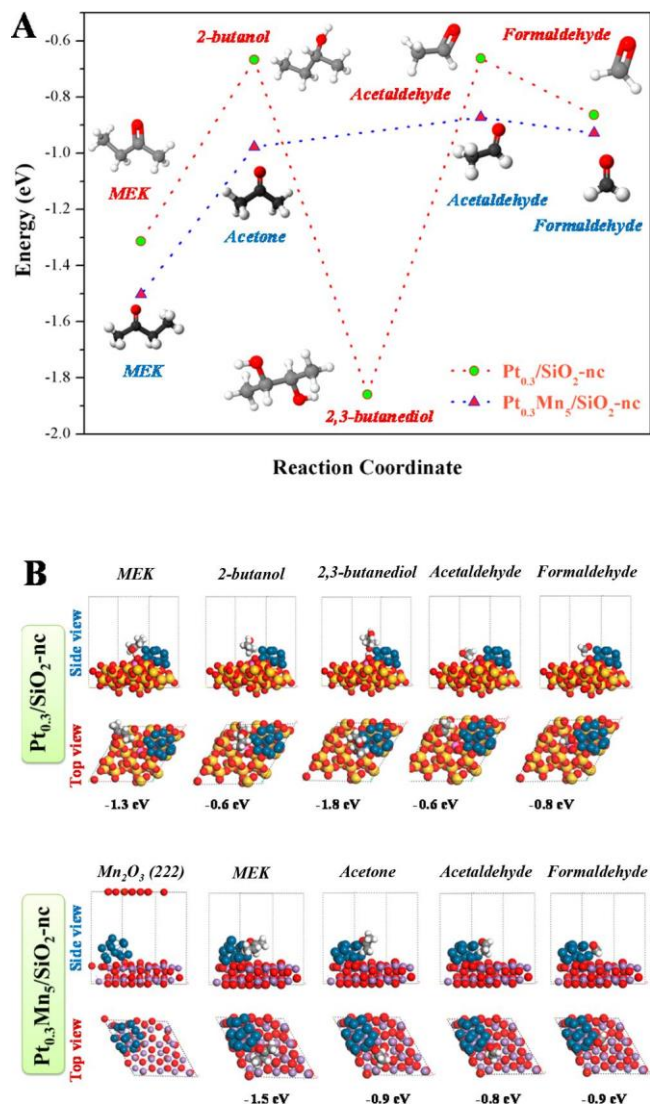
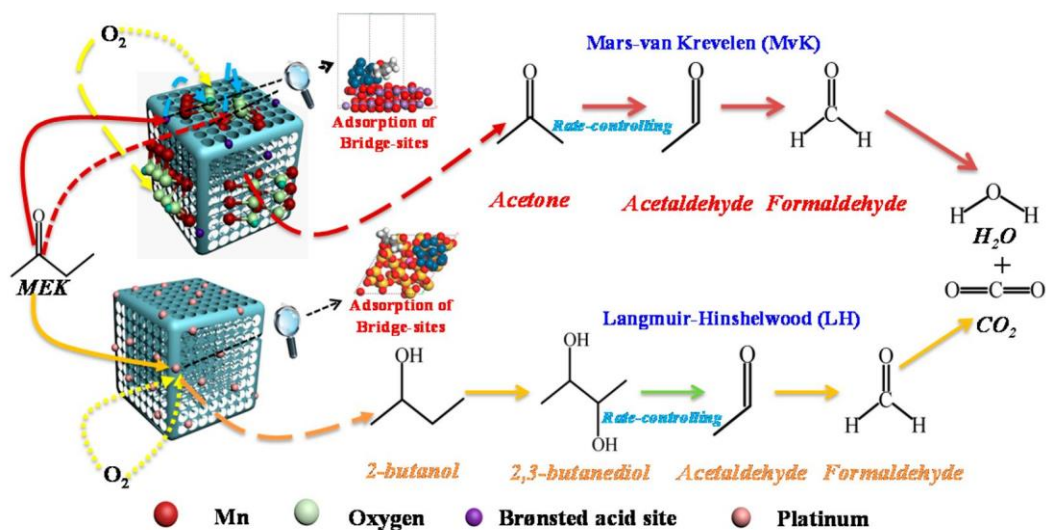


Figure 9. DFT studies of adsorption energy (A) and structure molding for adsorption of key intermediates (B) over Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts during MEK oxidation.

A reaction mechanism for the oxidation of MEK over the Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc catalysts is proposed in Scheme 1, which is based on the conclusions derived from the qualitative and quantitative experiments conducted in this study. Over the Pt_{0.3}/SiO₂-nc catalyst, MEK is adsorbed on the surface of the silica support (Figure S6), which is transformed to 2,3-butanediol via 2-butanol which is promoted by the presence of surface-adsorbed oxygen (Figure 8). The 2,3-butanediol then undergoes an oxidative cleavage to form acetaldehyde, which ultimately undergoes a sequential oxidation to produce CO₂ and H₂O (Figure 5). Importantly, considering a classical approach for the process of this reaction, the kinetics of the combustion of MEK in air at low concentrations over the Pt_{0.3}/SiO₂-nc catalyst is well described by the Langmuir–Hinshelwood (LH) mechanism.⁵⁹ The procedure of 2,3-butanediol cleaved to form acetaldehyde is the possible rate-determining step. The difference in proposed surface mechanism for MEK combustion can be confirmed over the Pt_{0.3}Mn₅/SiO₂-nc catalyst. The extensive characterizations in this study have shown that the Mn₂O₃ in Pt_{0.3}Mn₅/SiO₂-nc material significantly enhances the quantity and strength of the

Scheme 1. Reaction Mechanism for MEK Catalytic Oxidation over Pt_{0.3}/SiO₂-nc and Pt_{0.3}Mn₅/SiO₂-nc Catalysts



Brønsted acid sites (Figure 6) in this material, and lattice oxygen is incorporated in the reaction products (Figure 8 and Figure S7). The initial step involves the adsorption of MEK over the Brønsted acid sites of the catalyst (Figure S6). MEK is first decomposed to acetone, which is promoted by the protonic donation from the Brønsted acid sites. The acetone subsequently undergoes a similar transformation to acetaldehyde, which further converts to formaldehyde, a process that is again assisted by the Pt active sites. The resulting formaldehyde then undergoes a sequential oxidation to produce CO₂ and H₂O with the help of lattice oxygen (Figure 5). Especially, a classical approach to analyze the kinetics of reactions catalyzed by solids lies in proposing a reaction scheme consisting of a series of steps describing the adsorption of reactants, surface reaction over active sites with lattice oxygen, and product desorption, which is well described by the Mars–van Krevelen mechanism.⁶⁰ The lattice oxygen of Mn₂O₃ takes part in the combustion reaction and the oxygen vacancies remain, the latter being replenished by the chemisorbed oxygen. The possible rate-determining step is the process of acetone conversion into acetaldehyde.

CONCLUSIONS

In this work, Pt_{0.3}Mn_x/SiO₂ nanocubic (nc) micro-/mesoporous composite materials containing different quantities of Mn were synthesized and utilized as catalysts for the oxidation of methyl ethyl ketone (MEK) for the first time. All of the Pt_{0.3}Mn_x/SiO₂-nc materials exhibited an exceptional low-temperature oxidation activity, CO₂ selectivity, and stability for MEK oxidation. Of the catalysts synthesized, the Pt_{0.3}Mn₅/SiO₂-nc material was found to be the most active catalyst and could completely oxidize MEK at just 163 °C under a high space velocity of 42600 mL g⁻¹ h⁻¹. We believe this to be a new benchmark for low-temperature catalytic oxidation performance for the total oxidation of VOCs. Remarkable synergistic effects between the Pt nanoparticles and the Mn₂O₃ were observed. FTIR spectra corresponding to the adsorption of NH₃ on these materials in combination with a series of TPD experiments confirmed that highly exposed Mn₂O₃ (222) facets enhanced the quantity and strength of the Brønsted acid sites on the surface of these materials. These sites were found to promote the desorption of surface-adsorbed O₂ and CO₂, liberating

active sites for MEK molecules to adsorb to. Results from ¹⁸O isotopic exchange and temperature-programmed isotopic exchange experiments revealed that the presence of a Pt–O–Mn moiety weakens the strength of the Mn–O bonds, which promotes the mobility of lattice oxygen in Mn₂O₃. Perhaps most importantly, it was determined that the Mn⁴⁺/Mn³⁺ redox cycle in the Mn₂O₃ supplies electrons to Pt sites, which ultimately enhances the proportion of Pt⁰/Pt²⁺ on the surface and increases the activity and stability of the catalyst. In situ DRIFTS, online FTIR, and DFT results revealed that acetone and acetaldehyde are the main intermediates produced in the oxidation of MEK over Pt_{0.3}Mn₅/SiO₂-nc, which can subsequently undergo further oxidation to H₂O and CO₂ via a formaldehyde intermediate.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b04461.

Catalyst characterizations, XRD patterns, N₂ adsorption–desorption isotherms and pore size distribution, HAADF-STEM and EDS mapping images, TGA-FTIR analysis, O₂-TPD and CO₂-TPD profiles, TPSR profiles, in situ DRIFTS spectra of MEK adsorption, and summary of some active catalysts for MEK oxidation reported in the literature (PDF)

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Notes

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REFERENCES

- (1) Pan, H.; Jian, Y.; Chen, C.; He, C.; Hao, Z.; Liu, H.; Shen, Z. Sphere-shaped Mn_3O_4 catalyst with remarkable low-temperature activity for methyl-ethyl-ketone combustion. *Environ. Sci. Technol.* 2017, 51, 6288–6297.
- (2) Zhang, C.; Wang, C.; Gil, S.; Boreave, A.; Retailleau, L.; Guo, Y.; Valverde, J. L.; Giroir-Fendle, A. Catalytic oxidation of 1, 2-dichloropropane over supported $LaMnO_x$ oxides catalysts. *Appl. Catal., B* 2017, 201, 552–560.
- (3) Royer, S.; Duprez, D.; Can, F.; Courtois, X.; Batiot-Dupeyrat, C.; Laassiri, S.; Alamdari, H. Perovskites as substitutes of noble metals for heterogeneous catalysis: dream or reality. *Chem. Rev.* 2014, 114, 10292–10368.
- (4) Liotta, L. F. Catalytic oxidation of volatile organic compounds on supported noble metals. *Appl. Catal., B* 2010, 100, 403–412.
- (5) Mistry, H.; Behafarid, F.; Zhou, E.; Ono, L. K.; Zhang, L.; Roldan Cuenya, B. Shape-Dependent Catalytic Oxidation of 2-Butanol over Pt Nanoparticles Supported on $\gamma-Al_2O_3$. *ACS Catal.* 2014, 4, 109–115.
- (6) An, K.; Alayoglu, S.; Musselwhite, N.; Plamthottam, S.; Melaet, G.; Lindeman, A. E.; Somorjai, G. A. Enhanced CO oxidation rates at the interface of mesoporous oxides and Pt nanoparticles. *J. Am. Chem. Soc.* 2013, 135, 16689–16696.
- (7) Wang, H.; Lu, Y.; Han, Y.; Lu, C.; Wan, H.; Xu, Z.; Zheng, S. Enhanced catalytic toluene oxidation by interaction between copper oxide and manganese oxide in Cu-O-Mn/ $\gamma-Al_2O_3$ catalysts. *Appl. Surf. Sci.* 2017, 420, 260–266.
- (8) Qu, Z.; Chen, D.; Sun, Y.; Wang, Y. High catalytic activity for formaldehyde oxidation of $AgCo/APTES@MCM-41$ prepared by two steps method. *Appl. Catal., A* 2014, 487, 100–109.
- (9) Li, D.; Yang, G.; Li, P.; Wang, J.; Zhang, P. Promotion of formaldehyde oxidation over Ag catalyst by Fe doped MnO_x support at room temperature. *Catal. Today* 2016, 277, 257–265.
- (10) Cui, W.; Yuan, X.; Wu, P.; Zheng, B.; Zhang, W.; Jia, M. Catalytic properties of $\gamma-Al_2O_3$ supported Pt-Fe O_x catalysts for complete oxidation of formaldehyde at ambient temperature. *RSC Adv.* 2015, 5, 104330–104336.
- (11) Vít, Z.; Gulkova, D.; Kaluza, L.; Boaro, M. Effect of catalyst precursor and its pretreatment on the amount of β -Pd hydride phase and HDS activity of Pd-Pt/silica-alumina. *Appl. Catal., B* 2014, 146, 213–220.
- (12) He, C.; Zhang, F.; Yue, L.; Shang, X.; Chen, J.; Hao, Z. Nanometric palladium confined in mesoporous silica as efficient catalysts for toluene oxidation at low temperature. *Appl. Catal., B* 2012, 111–112, 46–57.
- (13) He, C.; Zhang, X.; Gao, S.; Chen, J.; Hao, Z. Nanometric Pd-confined mesoporous silica as high-efficient catalyst for toluene low temperature removal: Effects of support morphology and textural property. *J. Ind. Eng. Chem.* 2012, 18, 1598–1605.
- (14) Scire, S.; Liotta, L. F. Supported gold catalysts for the total oxidation of volatile organic compounds. *Appl. Catal., B* 2012, 125, 222–246.
- (15) Jiang, Y.; Xie, S.; Yang, H.; Deng, J.; Liu, Y.; Dai, H. Mn_3O_4 -Au/3DOM $La_{0.6}Sr_{0.4}CoO_3$: High-performance catalysts for toluene oxidation. *Catal. Today* 2017, 281, 437–446.
- (16) O Shea, V. A. d. I. P.; Alvarez-Galvan, M. C.; Fierro, J. L. G.; Arias, P. L. Influence of feed composition on the activity of Mn and PdMn/ Al_2O_3 catalysts for combustion of formaldehyde/methanol. *Appl. Catal., B* 2005, 57, 191–199.
- (17) Colman-Lerner, J. E.; Peluso, M. A.; Sambeth, J. E.; Thomas, H. J. Volatile organic compound removal over bentonite-supported Pt, Mn and Pt/Mn monolithic catalysts. *React. Kinet., Mech. Catal.* 2013, 108, 443–458.
- (18) Xie, Y.; Yu, Y.; Gong, X.; Guo, Y.; Guo, Y.; Wang, Y.; Lu, G. Effect of the crystal plane figure on the catalytic performance of MnO_2 for the total oxidation of propane. *CrystEngComm* 2015, 17, 3005–3014.
- (19) Arzamendi, G.; Pena OShea, V. A. d. I. P.; Alvarez-Galvan, M. C.; Fierro, J. L. G.; Arias, P. L.; Gandía, L. M. Kinetics and selectivity of methyl-ethyl-ketone combustion in air over alumina-supported PdO_x - MnO_x catalysts. *J. Catal.* 2009, 261, 50–59.
- (20) Wang, X.; Zhang, Y.; Luo, W.; Elzatahry, A. A.; Cheng, X.; Alghamdi, A.; Abdullah, A. M.; Deng, Y.; Zhao, D. Synthesis of ordered mesoporous silica with tunable morphologies and pore sizes via a nonpolar solvent-assisted stober method. *Chem. Mater.* 2016, 28, 2356–2362.
- (21) Bai, B.; Qiao, Q.; Arandiyán, H.; Li, J.; Hao, J. Three-dimensional ordered mesoporous MnO_2 -supported Ag nanoparticles for catalytic removal of formaldehyde. *Environ. Sci. Technol.* 2016, 50, 2635–2640.
- (22) Kozuch, S.; Martin, J. M. L. “Turning over” definitions in catalytic cycles. *ACS Catal.* 2012, 2, 2787–2794.
- (23) Çelik, B.; Erken, E.; Eris, S.; Yıldız, Y.; Şahin, B.; Pamuk, H.; Sen, F. Highly monodisperse Pt(0)@AC NPs as highly efficient and reusable catalysts: the effect of the surfactant on their catalytic activities in room temperature dehydrocoupling of DMAB. *Catal. Sci. Technol.* 2016, 6, 1685–1692.
- (24) Arandiyán, H.; Dai, H.; Ji, K.; Sun, H.; Zhao, Y.; Li, J. Enhanced Catalytic Efficiency of Pt Nanoparticles Supported on 3D Ordered Macro-/Mesoporous $Ce_{0.6}Zr_{0.3}Y_{0.1}O_2$ for Methane Combustion. *Small* 2015, 11, 2366–2371.
- (25) Andrei, R. D.; Popa, M. L.; Fajula, F.; Hulea, V. Heterogeneous oligomerization of ethylene over highly active and stable Ni- $AlSBA-15$ mesoporous catalysts. *J. Catal.* 2015, 323, 76–84.
- (26) Jiang, Z.; He, C.; Dummer, N. F.; Shi, J.; Tian, M.; Ma, C.; Hao, Z.; Taylor, S. H.; Ma, M.; Shen, Z. Insight into the efficient oxidation of methyl-ethyl-ketone over hierarchically micro-mesostructured Pt/K-(Al)SiO₂ nanorod catalysts: Structure-activity relationships and mechanism. *Appl. Catal., B* 2018, 226, 220–233.
- (27) Kovarik, L.; Washton, N. M.; Kukkadapu, R.; Devaraj, A.; Wang, A.; Wang, Y.; Szanyi, J.; Peden, C. H. F.; Gao, F. Transformation of active sites in Fe/SSZ-13 SCR catalysts during hydrothermal aging: a spectroscopic, microscopic, and kinetics study. *ACS Catal.* 2017, 7, 2458–2470.
- (28) Huang, X.; Men, Y.; Wang, J.; An, W.; Wang, Y. Highly active and selective binary MgO-SiO₂ catalysts for the production of 1, 3-butadiene from ethanol. *Catal. Sci. Technol.* 2017, 7, 168–180.
- (29) Cai, J.; Huang, Y.; Huang, B.; Zheng, S.; Guo, Y. Enhanced activity of Pt nanoparticle catalysts supported on manganese oxide-carbon nanotubes for ethanol oxidation. *Int. J. Hydrogen Energy* 2014, 39, 798–807.
- (30) Yang, T.; Huo, Y.; Liu, Y.; Rui, Z.; Ji, H. Efficient formaldehyde oxidation over nickel hydroxide promoted Pt/ $\gamma-Al_2O_3$ with a low Pt content. *Appl. Catal., B* 2017, 200, 543–551.
- (31) Chen, C.; Li, B.; Zhou, L.; Xia, Z.; Feng, N.; Ding, J.; Wang, L.; Wan, H.; Guan, G. Synthesis of Hierarchically Structured Hybrid Materials by Controlled Self-Assembly of Metal-Organic Framework with Mesoporous Silica for CO₂ Adsorption. *ACS Appl. Mater. Interfaces* 2017, 9, 23060–23071.
- (32) Lopez-Benítez, A.; Berhault, G.; Guevara-Lara, A. NiMo catalysts supported on Mn- Al_2O_3 for dibenzothiophene hydrodesulfurization application. *Appl. Catal., B* 2017, 213, 28–41.
- (33) Wisniewska, J.; Ziolk, M. Formation of Pt-Ag alloy on different silicas-surface properties and catalytic activity in oxidation of methanol. *RSC Adv.* 2017, 7, 9534–9544.
- (34) Czaplinska, J.; Decyk, P.; Ziolk, M. S. Surface properties and catalytic performance of Pt-Ag supported on silica-The effect of preparation methods. *Appl. Catal., A* 2015, 504, 361–372.

- (35) Tangale, N. P.; Sonar, S. K.; Niphadkar, P. S.; Joshi, P. N. Hierarchical K/LTL zeolites: Synthesis by alkali treatment, characterization and catalytic performance in Knoevenagel condensation reaction. *J. Ind. Eng. Chem.* 2016, 40, 128–136.
- (36) Wang, C.; Zhang, C.; Hua, W.; Guo, Y.; Lu, G.; Gil, S.; Giroir-Fendler, A. Catalytic oxidation of vinyl chloride emissions over Ce composite oxide catalysts. *Chem. Eng. J.* 2017, 315, 392–402.
- (37) Si, W.; Wang, Y.; Zhao, S.; Hu, F.; Li, J. A facile method for in situ preparation of the MnO₂/LaMnO₃ catalyst for the removal of toluene. *Environ. Sci. Technol.* 2016, 50, 4572–4578.
- (38) He, C.; Yu, Y.; Shen, Q.; Chen, J.; Qiao, N. Catalytic behavior and synergistic effect of nanostructured mesoporous CuO-MnO_x-CeO₂ catalysts for chlorobenzene destruction. *Appl. Surf. Sci.* 2014, 297, 59–69.
- (39) You, H.; Zhang, F.; Liu, Z.; Fang, J. Free-standing Pt-Au hollow nanourchins with enhanced activity and stability for catalytic methanol oxidation. *ACS Catal.* 2014, 4, 2829–2835.
- (40) Zhao, H.; Wang, D.; Gao, C.; Liu, H.; Han, L.; Yin, Y. Ultrafine platinum/iron oxide nanoconjugates confined in silica nanoshells for highly durable catalytic oxidation. *J. Mater. Chem. A* 2016, 4, 1366–1372.
- (41) Yan, Z.; Xu, Z.; Yu, J.; Jaroniec, M. Highly active mesoporous ferrihydrite supported Pt catalyst for formaldehyde removal at room temperature. *Environ. Sci. Technol.* 2015, 49, 6637–6644.
- (42) Zou, X.; Rui, Z.; Song, S.; Ji, H. Enhanced methane combustion performance over NiAl₂O₄-interface-promoted Pd/γ-Al₂O₃. *J. Catal.* 2016, 338, 192–201.
- (43) Zhang, R.; Shi, D.; Liu, N.; Cao, Y.; Chen, B. Mesoporous SBA-15 promoted by 3d-transition and noble metals for catalytic combustion of acetonitrile. *Appl. Catal., B* 2014, 146, 79–93.
- (44) Lai, Y. T.; Chen, T. C.; Lan, Y. K.; Chen, B. S.; You, J. H.; Yang, C. M.; Lai, N. C.; Wu, J. H.; Chen, C. S. Pt/SBA-15 as a highly efficient catalyst for catalytic toluene oxidation. *ACS Catal.* 2014, 4, 3824–3836.
- (45) Chen, C. S.; Lai, Y. T.; Chen, T. C.; Chen, C. H.; Lee, J. F.; Hsu, C. W.; Kao, H. M. Synthesis and characterization of Pt nanoparticles with different morphologies in mesoporous silica SBA-15 for methanol oxidation reaction. *Nanoscale* 2014, 6, 12644–54.
- (46) Yao, X.; Kong, T.; Yu, S.; Li, L.; Yang, F.; Dong, L. Influence of different supports on the physicochemical properties and denitration performance of the supported Mn-based catalysts for NH₃-SCR at low temperature. *Appl. Surf. Sci.* 2017, 402, 208–217.
- (47) Tang, C.; Zhai, Z.; Li, X.; Sun, L.; Bai, W. Highly efficient and robust Mg_{0.388}Al_{2.408}O₄ catalyst for gas-phase decarbonylation of lactic acid to acetaldehyde. *J. Catal.* 2015, 329, 206–217.
- (48) Zhang, Q.; Tan, Y.; Liu, G.; Zhang, J.; Han, Y. Rhenium oxide-modified H₃PW₁₂O₄₀/TiO₂ catalysts for selective oxidation of dimethyl ether to dimethoxy dimethyl ether. *Green Chem.* 2014, 16, 4708–4715.
- (49) She, X. Y.; Kwak, J. H.; Sun, J. M.; Hu, J. Z.; Hu, M. Y.; Wang, C. M.; Peden, C. H. F.; Wang, Y. Highly Dispersed and Active ReO_x on Alumina-Modified SBA-15 Silica for 2-Butanol Dehydration. *ACS Catal.* 2012, 2, 1020–1026.
- (50) Wu, H.-C.; Chen, T.-C.; Lai, N.-C.; Yang, C.-M.; Wu, J.-H.; Chen, Y.-C.; Lee, J.-F.; Chen, C.-S. Synthesis of sub-nanosized Pt particles on mesoporous SBA-15 material and its application to the CO oxidation reaction. *Nanoscale* 2015, 7, 16848–16859.
- (51) Shen, S.; Wang, X.; Ding, Q.; Jin, S.; Feng, Z.; Li, C. Effect of Pt cocatalyst in Pt/TiO₂ studied by in situ FTIR of CO adsorption. *Chin. J. Catal.* 2014, 35, 1900–1906.
- (52) Rizo, R.; Sebastian, D.; Rodríguez, J. L.; Lazaro, M. J.; Pastor, E. Influence of the nature of the carbon support on the activity of Pt/C catalysts for ethanol and carbon monoxide oxidation. *J. Catal.* 2017, 348, 22–28.
- (53) Wan, J.; Ran, R.; Lin, M.; Wu, X.; Weng, D. Effect of acid and base modification on the catalytic activity of Pt/Al₂O₃ for propene oxidation. *J. Mol. Catal. A: Chem.* 2014, 383–384, 194–202.
- (54) Farias, M. J. S.; Buso-Rogero, C.; Gisbert, R.; Herrero, E.; Feliu, J. M. Influence of the CO adsorption environment on its reactivity with (111) terrace sites in stepped Pt electrodes under alkaline media. *J. Phys. Chem. C* 2014, 118, 1925–1934.
- (55) Wisniewska, J.; Ziolek, M.; Artioli, N.; Daturi, M. The effect of niobium and tantalum on physicochemical and catalytic properties of silver and platinum catalysts based on MCF mesoporous cellular foams. *J. Catal.* 2016, 336, 58–74.
- (56) Kale, M. J.; Christopher, P. Utilizing quantitative in situ FTIR spectroscopy to identify well-coordinated Pt atoms as the active site for CO oxidation on Al₂O₃-supported Pt catalysts. *ACS Catal.* 2016, 6, 5599–5609.
- (57) Choi, S. O.; Penninger, M.; Kim, C. H.; Schneider, W. F.; Thompson, L. T. Experimental and Computational Investigation of Effect of Sr on NO Oxidation and Oxygen Exchange for La_{1-x}Sr_xCoO₃ Perovskite Catalysts. *ACS Catal.* 2013, 3, 2719–2728.
- (58) Yan, L.; Liu, Y.; Zha, K.; Li, H.; Shi, L.; Zhang, D. Scale-Activity Relationship of MnO_x-FeO_y Nanocage Catalysts Derived from Prussian Blue Analogues for Low-Temperature NO Reduction: Experimental and DFT Studies. *ACS Appl. Mater. Interfaces* 2017, 9, 2581–2593.
- (59) Zasada, F.; Janas, J.; Piskorz, W.; Gorczynska, M.; Sojka, Z. Total Oxidation of Lean Methane over Cobalt Spinel Nanocubes Controlled by the Self-Adjusted Redox State of the Catalyst: Experimental and Theoretical Account for Interplay between the Langmuir-Hinshelwood and Mars-Van Krevelen Mechanisms. *ACS Catal.* 2017, 7, 2853–2867.
- (60) Kim, H. Y.; Henkelman, G. CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO₂(111) Surface by the Mars-van Krevelen Mechanism. *J. Phys. Chem. Lett.* 2013, 4, 216–221.