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# Titanium Silicalite-1 Nanosheet-Supported Platinum for Nonoxidative Ethane Dehydrogenation

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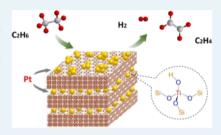
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ABSTRACT: Studies of stable catalysts for non-oxidative dehydrogenation of ethane (NDE) have been challenged by coke deposition from side reactions and thermal sintering of active species. Herein, we report a catalyst mechanism that overcomes both challenges to enable highly stable, active, and selective NDE. The catalyst is made of subnanometric platinum (Pt) species (i.e., single atoms and clusters) habituated on a two-dimensional (2D) multilamellar titanium silicalite-1 (M-TS-1) zeolite nanosheet support (i.e., Pt/M-TS-1). The ultrathin (~3 nm) M-TS-1 nanosheets provide high external surface areas, high terminal silanol/titanol (–OH) groups, and weak Lewis acid sites. The first two characteristics enhance molecular transport and Pt dispersion in the catalyst support. The



third characteristic prohibits side reactions to avoid coking and create strong Pt-support interaction, leading to well-dispersed Pt species against thermal sintering. The M-TS-1 nanosheet-supported Pt catalyst exhibited durable catalytic activity and high ethylene selectivity in the NDE.

KEYWORDS: non-oxidative ethane dehydrogenation, multilamellar titanium silicalite-1, stability, subnanometric Pt species, coke formation, thermal sintering

# 1. INTRODUCTION

Rising world's population coupled with the increase in personal income of the consumers has led to a growing demand for chemical commodity products. Ethylene (C2H4), an olefinic hydrocarbon, is the major building block for many petrochemical products. 1-3 The industrial-scale C<sub>2</sub>H<sub>4</sub> producttion is practiced by steam cracking of naphtha derived from crude oil refinery at high temperatures (>1273 K), enduring low energy efficiency and carbon dioxide (CO2) and nitrogen oxide (NO<sub>x</sub>) emissions.<sup>4</sup> The shale gas revolution in recent years in the United States has significantly lowered the cost of C2H6 and stimulated great interest in exploiting its potential as a direct feedstock for C2H4 production. 2,5 Compared to the high reaction temperature, low energy efficiency, and high greenhouse gas emissions in steam cracking, oxidative dehydrogenation of ethane (ODE)6-8 and non-oxidative dehydrogenation of ethane (NDE)<sup>8-10</sup> have great promise in reducing process energy consumption and environmental impact. In the presence of oxygen, the C2H6 conversion in ODE is relatively higher in single pass, but it suffers from low C2H4 yield and substantial waste as large amounts of C2H6 feed leave the system as fully or partially oxidized carbon species (CO<sub>2</sub> and CO).<sup>7,11,12</sup> In contrast, the NDE process can produce C2H4 and hydrogen (H2) in one step that has the highest carbon utilization among these three C2H6 conversion schemes. Unfortunately, high activity and selectivity to C<sub>2</sub>H<sub>4</sub> are challenged by coke deposition from side reactions and thermal sintering of active species in the NDE catalysts. 13-15

A potential solution to the aforementioned challenges is to develop selective and coke-resistant catalysts under NDE conditions. Supported platinum (Pt)<sup>16-21</sup> and chromium oxide (Cr<sub>2</sub>O<sub>3</sub>)<sup>22-26</sup> are the state-of-the-art NDE catalysts, among which the Pt-based catalysts have higher specific activity and longer stability than the Cr<sub>2</sub>O<sub>3</sub>-based ones. <sup>13</sup> It is known that Pt has high activity due to its capability of C-H bond rupture and poor ability for C-C bond cleavage. 13 A very small ensemble of Pt atoms and, in borderline cases, a single Pt atom are ideal for C2H6 dehydrogenation because the side reactions involved with hydrogenolysis (C-C cleavage) and/or coke formation (C-C coupling) only occur on geometrically complex and large ensembles of metal atoms. This motivates studies on the development of Pt atom ensembles/single atoms to improve the selectivity in NDE reactions. 20,27,28 The small Pt metal ensembles or Pt single atoms, however, often have low sintering resistance. A support is used to improve the dispersion and stability of active sites.

In order to form stable Pt-based NDE catalysts, the support should be thermally stable, have a sufficiently high specific surface area, be free of Brønsted acidity for hosting undesirable

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side reactions, and have Lewis acidity and amphoteric silanol (-OH) groups to contribute to optimum metal dispersion. 29,30 In search of a suitable support material, metal oxides such as alumina (Al<sub>2</sub>O<sub>3</sub>) or aluminate (e.g., MgAl<sub>2</sub>O<sub>4</sub>) have been used for Pt-based catalysts. 16,17,31 Zeolite-based materials are ideal alternatives to metal oxide supports due to their high surface area, uniform micropores, and tunable acidity by adding alkaline cations and/or isomorphous substitution of Lewis acidity centers. For example, the aluminosilicate zeolite with an MFI (Mobil-type five) framework structure (i.e., ZSM-5, Zeolite Socony Mobil-5) has been used as the support for rhenium (Re),<sup>32-34</sup> molybdenum (Mo),<sup>35</sup> and iron (Fe)<sup>36</sup> species for NDE reactions, in which metal species were loaded by the wetness impregnation approach. In order to enhance metal dispersion and modulate zeolite acidity, the heteroatom (i.e., Fe<sup>37</sup> and gallium (Ga)<sup>38</sup>)-isomorphously substituted ZSM-5 zeolites were reported. Because the heteroatoms are built into the MFI framework, they form isolated sites and are stabilized by the siliceous support, thus showing high durability and selectivity in the NDE process. Similarly, the chabazite (CHA) zeolite framework containing surface-isolated indium (In) hydrides was also the effective NDE catalyst. 39,40 It should be noted that all these studies are focused on the threedimensional (3D) zeolites and the heteroatom substitutions are limited to Fe and Ga elements.

Herein, we report a catalyst support mechanism that has high external surface areas, high terminal silanol/titanol (-OH) groups, low acidity, and high Pt dispersion to enable highly stable, active, and selective NDE processes. The catalyst is made of subnanometric platinum (Pt) species (i.e., single atoms and clusters) habituated on the two-dimensional (2D) multilamellar titanium silicalite-1 (M-TS-1) zeolite nanosheet support (i.e., Pt/M-TS-1). Two-dimensional (2D) zeolite nanosheets with single-unit-cell or near single-unit-cell thickness (~2-3 nm) represent an emerging type of zeolite material.41-43 The extremely thin slices of crystals in 2D zeolites produce high external surface areas (up to 50% of total surface area compared to ~2% in micron-sized 3D zeolite) and expose most of their active sites on external surfaces, enabling beneficial effects for the adsorption and mass transport in catalytic reactions. 44,45 The ultrathin (~3 nm) TS-1 nanosheets provide high external surface areas, high terminal -OH groups, and weak Lewis acid sites. The first characteristic enhances molecular transport in the catalyst support. The combination of the first two properties promotes active site dispersion and metal-support interaction. The last characteristic can prohibit side reactions to avoid coking and create optimal Pt anchoring that led to well-dispersed Pt species against thermal sintering. The Pt/M-TS-1 nanosheet catalyst, together with other 3D and 2D zeolite-supported Pt catalysts for comparison purposes, was examined for NDE in this study.

#### 2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. 2.1.1. Synthesis of Zeolite Supports. To verify the effects of acidity (Brønsted versus Lewis) and dimensionality (3D versus 2D) of zeolite supports on the performance of Pt-based catalysts in NDE, zeolites with different heteroatom substitutions and dimensions were prepared, as summarized in Table S1 in the Supporting Information. The multilamellar titanium silicalite-1 (M-TS-1) that contains 2D TS-1 nanosheets was synthesized according to the previous publications, 46,47 in which hexanediamine and

di-quaternary ammonium surfactant templates  $(C_{22\text{-}6\text{-}6}Br_2)$  were used as templates.

The conventional 3D TS-1 (denoted as C-TS-1) was synthesized according to a reported procedure using a tetra-*n*-propylammonium hydroxide as the template. The multi-lamellar ZSM-5 (i.e., M-ZSM-5) composed of 2D ZSM-5 nanosheets was synthesized following the recipe reported by Choi *et al.* The 2D multilamellar silicalite-1 (defined as M-Silicalite-1) was synthesized following the same recipe as that of M-ZSM-5 except that the aluminum source was not added. Details on the preparation of these 2D zeolites and 3D C-TS-1 are included in Section S1 of the Supporting Information.

The conventional 3D ZSM-5 in both proton (C-ZSM-5(H)) and sodium (C-ZSM-5(Na)) forms was prepared from the commercial ZSM-5 (Alfa Aesar, Product No. 45880). The aspurchased ZSM-5 zeolite in its ammonium (NH<sub>4</sub><sup>+</sup>) form was treated in dry air (100 mL min-1, Airgas, Breathing Quality Grade) by increasing the temperature from ambient to 823 K at 5 K min-1 and holding for 4 h to decompose NH4+ into NH<sub>3</sub> and proton (H<sup>+</sup>) to form C-ZSM-5(H). One portion of C-ZSM-5(H) was kept for Pt-based catalyst synthesis, while the other portion was converted into C-ZSM-5(Na) by ion exchange three times using 1 M aqueous NaNO<sub>3</sub> (Alfa Aesar, 98%) with a 1:10 weight ratio of zeolite to NaNO<sub>3</sub> solution at 353 K for 8 h and subsequently collected by centrifugation, washed with deionized (DI) water three times, and dried at 343 K overnight. Finally, the sample was calcined under the same condition as that of the NH<sub>4</sub>+-form ZSM-5 noted above.

2.1.2. Platinum Loading onto Zeolite Supports. Three different methods, electrostatic adsorption, solvent evaporation, and wetness impregnation, were used to load Pt onto the M-TS-1 support to prepare Pt/M-TS-1 catalysts. In all these approaches, the tetraammineplatinum(II) nitrate [(NH<sub>3</sub>)<sub>4</sub>Pt-(NO<sub>3</sub>)<sub>2</sub>, Alfa Aesar, 99.99%] was used as the Pt precursor. In the electrostatic adsorption process, the M-TS-1 zeolite was dispersed in 1.55 mM aqueous (NH<sub>3</sub>)<sub>4</sub>Pt(NO<sub>3</sub>)<sub>2</sub> solution (weight ratio of zeolite to  $(NH_3)_4Pt(NO_3)_2$  solution = 1:10) at ambient temperature under magnetic stirring for 24 h. Subsequently, the solid was collected by centrifugation, washed with DI water three times, and dried at 343 K overnight. The solvent evaporation process was conducted by dispersing M-TS-1 zeolite in 0.45 mM aqueous (NH<sub>3</sub>)<sub>4</sub>Pt(NO<sub>3</sub>)<sub>2</sub> solution (weight ratio of zeolite to  $(NH_3)_4Pt(NO_3)_2$  solution = 1:10) under magnetic stirring at room temperature for 24 h. Afterward, the mixture was placed in a convective oven that was preheated to 343 K to evaporate the solvent, which took ~24 h to become dry powder. In the impregnation process, the M-TS-1 zeolite was impregnated with 11.37 mM (NH<sub>3</sub>)<sub>4</sub>Pt-(NO<sub>3</sub>)<sub>2</sub> aqueous solution (weight ratio of zeolite to (NH<sub>3</sub>)<sub>4</sub>Pt- $(NO_3)_2$  solution = 1:0.4). Following solvent evaporation at ambient temperature overnight, the sample was kept at 393 K in a convective oven for 5 h.

All the dry powders of Pt/M-TS-1 catalysts were calcined in flowing air (100 mL min<sup>-1</sup>, Breathing Quality Grade, Airgas) by increasing the temperature from ambient to 823 K at 2 K min<sup>-1</sup> and holding for 5 h. Finally, the catalyst samples were pelleted, crushed, and sieved to retain particle sizes between 180 and 425  $\mu$ m (80–40 mesh) for property characterizations and catalysis tests. For all other zeolite supports, i.e., C-TS-1, M-ZSM-5, C-ZSM-5(H), C-ZSM-5(Na), and M-Silicalite-1, the Pt loading was done by the solvent evaporation method. For comparison purposes, silica-supported (SiO<sub>2</sub>, high-purity, Davisil Grade 636) and titania-supported (TiO<sub>2</sub>, >99.5%

purity, Aldrich) Pt catalysts (Pt/SiO<sub>2</sub> and Pt/TiO<sub>2</sub>) were also prepared by this method. All the samples were subjected to the same treatment steps as those of Pt/M-TS-1 used in the solvent evaporation method. Table S2 in the Supporting Information summaries all the Pt/zeolite samples prepared in the study.

2.2. Catalyst Characterization. 2.2.1. Composition and Morphology Analyses. The as-prepared catalysts were subjected to a range of property characterizations. The elemental compositions were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 4300DV Instrument, Perkin-Elmer). The powder X-Ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance Lynx Powder Diffractometer (LynxEye PSD detector, sealed tube, Cu K $\alpha$  radiation with Ni  $\beta$ -filter). Scanning electron microscopy (SEM) images were taken on a Hitachi SU-70 electron microscope to visualize the zeolite morphologies. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 LaB6 electron microscope. Highangle annular-dark-field (HAADF) scanning transmission electron micrographs (STEM) were acquired using a JEM ARM200F transmission electron microscope operated at 200 keV. The attainable spatial resolution of the microscope is 80 pm with a probe spherical-aberration corrector. The dwell time for image acquisition was set at 40 µs per pixel to ensure that an appropriate signal to noise ratio was achieved. The collection angles for the HAADF images were fixed at 54-220 mrad. N<sub>2</sub> adsorption/desorption isotherms were measured using an Autosorb-iQ analyzer (Quantachrome Instruments) at 77 K. The samples were outgassed at 573 K for 8 h at 1 mmHg pressure prior to measurements. The Brunauer, Emmett, and Teller (BET) method was used to determine the specific surface areas of the samples. The types of silanol and titanol groups were identified by diffuse reflectance infrared spectroscopy (DRIFTS) recorded on a Nicolet Is-50R spectrometer with an associated Harrick Scientific Praying Mantis optical accessory and high-temperature reaction chamber (HVC-DRP-5). In a typical run, the DRIFTS sample cell was filled with a zeolite sample that was pretreated at 823 K for 4 h under flowing nitrogen (N<sub>2</sub>, 100 mL min<sup>-1</sup>) in a furnace. The zeolite sample was then activated at 823 K under the N<sub>2</sub> flow (100 mL min<sup>-1</sup>) for 1 h in the DRIFTS cell. After cooling the sample to 393 K, a spectrum was recorded against the background spectrum of the KBr powder measured under the same conditions with a resolution of 2 cm<sup>-1</sup>. The spent catalysts were studied using a thermogravimetric analyzer (TGA) (Shimadzu, TGA-50). In the analysis, the temperature was increased to 1073 K under an air atmosphere (50 mL min<sup>-1</sup>) at a ramp rate of 5 K min<sup>-1</sup>.

2.2.2. Assessment of Zeolite Acidity. The Brønsted and Lewis acid site concentrations of each zeolite support were measured by organic base titrations using isopropylamine (IPA, Alfa Aesar, 99+%) and pyridine (Alfa Aesar, 99.5+%) titrants, respectively. The selective decomposition of the IPA adsorbate on the Brønsted acid site in zeolites via Hoffmann elimination forms propylene and ammonia. The quantification of propylene using a gas chromatograph (GC) instrument determined the quantity of Brønsted sites in each zeolite sample. As a relatively small base molecule, pyridine can transport through the zeolite MFI channels to access both Brønsted and Lewis acid sites. As a relatively was calculated by deduction of acid sites determined from IPA measurement from those

determined by pyridine titration. Details on the IPA and pyridine titration experiments can be referred to Section S3 of the Supporting Information.

2.2.3. Metal Dispersion Analysis. To determine Pt dispersion in the Pt/zeolite catalysts, H2 temperatureprogrammed reduction (H2-TPR) and H2 pulse chemisorption were conducted. H2-TPR measurement was carried out using an Autosorb-iQ analyzer (Quantachrome Instruments, equipped with thermal conductivity detectors (TCDs)). The sample was pretreated in helium (He) (ultrapure, 50 mL min<sup>-1</sup>) at 823 K for 1 h. Then, it was cooled down to 323 K before switching to a 5% H<sub>2</sub>/N<sub>2</sub> atmosphere (ultrapure, 50 mL min<sup>-1</sup>) with the temperature ramping up from 323 to 1073 K at 10 K min<sup>-1</sup>. H<sub>2</sub> pulse chemisorption measurement was conducted using an AutoChemII2920 analyzer (Micromeritics) equipped with TCDs. The sample was pretreated in He (50 mL min<sup>-1</sup>) at 573 K for 2 h before switching to a 10%  $H_2$ / Ar (ultrapure, 50 mL min<sup>-1</sup>) atmosphere. The temperature was then ramped to 773 K at 10 K min<sup>-1</sup> and held for 2 h to fully reduce the sample. Then, the sample was switched to a He (50 mL min<sup>-1</sup>) atmosphere and cooled down to 323 K. Finally, the gas flow was switched back to a 10% H<sub>2</sub>/Ar (50 mL min<sup>-1</sup>) atmosphere and the pulse measurement was

2.2.4. In Situ DRIFTS Measurement. To study the catalyst properties during the NDE reaction, the DRIFTS equipment described in Section 2.2.1 was used to measure the Pt/M-TS-1 (EA) catalyst at different pretreatment and reaction stages in NDE. First, the as-prepared catalyst was calcined at 823 K for 4 h under flowing nitrogen (N2, 100 mL min-1) in a furnace to remove adsorbed moisture or other impurities. The catalyst sample was loaded into the DRIFTS sample cell followed by the further pretreatment at 823 K under the N2 flow (100 mL min<sup>-1</sup>) for 1 h. After cooling the sample to 393 K, a spectrum was recorded. In the second stage, the N2 gas atmosphere was switched to a 5% H<sub>2</sub>/N<sub>2</sub> gas mixture (100 mL min<sup>-1</sup>) and the sample cell was heated to 673 K at a ramp rate of 5 K min<sup>-1</sup>. The sample was kept under this condition for 1 h, and the second spectrum was recorded. In the next stage, the gas atmosphere was switched back to N2 and the sample temperature was decreased to 393 K. The spectrum was recorded in this third stage to detect the effect of temperature on H<sub>2</sub> adsorption onto the sample. The fourth stage involved switching a N<sub>2</sub> atmosphere to a 5% C<sub>2</sub>H<sub>6</sub>/N<sub>2</sub> gas mixture. The sample was heated up to 673 K and kept at this temperature for 1 h. The spectrum was then recorded. The same procedure as that of stage three was used in the last stage. The asrecorded spectrum was used to reveal the effect of the temperature and gas atmosphere on the removal of adsorbed ethane on the catalyst.

**2.3. Catalyst Testing.** The non-oxidative dehydrogenation of ethane (NDE) reaction was performed in a U-shape quartz tubular fixed-bed reactor with 10 mm inner diameter at atmospheric pressure. The reactor was placed inside a temperature-controlled furnace (National Electric Furnace FA120 type) where the temperature was controlled using a Watlow Controller (96 series). Catalyst temperatures were measured using a K-type thermocouple touching the bottom of a well on the external surface of the quartz reactor. The catalyst sample (0.100 g) was supported on a coarse quartz disk inside the reactor and was treated in a mixture gas of  $H_2/N_2$  (30 mL min<sup>-1</sup>,  $H_2/N_2$  = 1:5, ultrapure, Airgas) when the temperature was ramped to 773 K (2 K min<sup>-1</sup>) and held for 3 h prior to

heating in N<sub>2</sub> flow (25 mL min<sup>-1</sup>, ultrapure, Airgas) to the reaction temperature (at a 2 K min<sup>-1</sup> rate). Afterward, the gas flow was switched to  $C_2H_6$  (15 mL min<sup>-1</sup>, research purity, Matheson) mixed with an Ar internal standard (5 mL min<sup>-1</sup>, ultrahigh purity, Airgas) to start the reaction. All transfer lines in the NDE were maintained at temperatures greater than 373 K by resistive heating to prevent any condensation. A gas chromatograph (Agilent 6890) equipped with a packed column (ShinCarbon ST80/100 packed column, 2 m in length, 2 mm ID × 1/8" OD, Silco HP) connected to a TCD and a methylsiloxane capillary column (HP-1, 50.0 m × 320  $\mu$ m × 0.52  $\mu$ m) connected to a flame ionization detector (FID) was used to separate and quantify the reactants and products.

The ethane conversion  $(X_{C2H6})$  and product selectivity (i.e.,  $S_{C2H4}$ ,  $S_{CH4}$ , and  $S_{C6H6}$ ) were calculated by the following equations:

$$X_{\text{C2H6}}$$
 (%) =  $(\dot{n}_{\text{C2H6,in}} - \dot{n}_{\text{C2H6,out}})/\dot{n}_{\text{C2H6,in}} \cdot 100\%$  (1)

$$S_{\text{C2H4}}$$
 (%) =  $\dot{n}_{\text{C2H4}}/(\dot{n}_{\text{C2H6,in}} \times X_{\text{C2H6}}) \cdot 100\%$  (2)

$$S_{\text{CH4}}$$
 (%) =  $(0.5 \times \dot{n}_{\text{CH4}})/(\dot{n}_{\text{C2H6,in}} \times X_{\text{C2H6}}) \cdot 100\%$  (3)

$$S_{C6H6}$$
 (%) =  $(3 \times \dot{n}_{C6H6})/(\dot{n}_{C2H6,in} \times X_{C2H6}) \cdot 100\%$  (4)

where  $\dot{n}_{\rm C2H6,in}$  and  $\dot{n}_{\rm C2H6,out}$  are the  $\rm C_2H_6$  flow rates at the inlet and outlet of the reactor and  $\dot{n}_{\rm C2H4}$ ,  $\dot{n}_{\rm CH4}$ , and  $\dot{n}_{\rm C6H6}$  are the  $\rm C_2H_4$ , methane (CH<sub>4</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>) outlet flow rates, respectively. The carbon and hydrogen balance analyses were done for each set of reaction data. The results show that both carbon and hydrogen balances are within  $\pm 2\%$  on the M-TS-1-supported catalysts (Table S6). For the Pt supported on C-ZSM-5(H) and Pt/M-TS-1 tested at very high temperatures or very low space velocities, due to the side reactions (i.e., reactions of products and gas phase reactions) and coke formation, the carbon and hydrogen balances were slightly off.

# 3. RESULTS AND DISCUSSION

3.1. Morphology and Textural Properties of Zeolite Supports. The morphology of the 2D M-TS-1 zeolite support, together with the morphologies of five control zeolite support samples, namely, 2D M-ZSM-5 and M-Silicalite-1 as well as 3D C-TS-1, C-ZSM-5(H), and C-ZSM-5(Na), is shown by the SEM images in Figure 1. The plate-like particles with irregular shapes and sizes are clearly visualized in 2D M-TS-1 (Figure 1A), M-ZSM-5 (Figure 1B), and M-Silicalite-1 (Figure 1C). In contrast, the 3D C-TS-1 zeolite (Figure 1D)

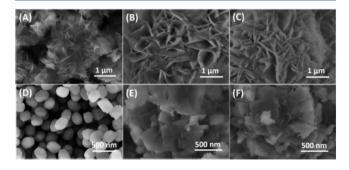


Figure 1. SEM images showing morphologies of zeolite supports: (A) M-TS-1, (B) M-ZSM-5, (C) M-Silicalite-1, (D) C-TS-1, (E) C-ZSM-5(H), and (F) C-ZSM-5(Na).

has round-shaped particles with widths of  $\sim$ 250 nm. The commercial 3D C-ZSM-5 in either H<sup>+</sup>-form (Figure 1E) or Na<sup>+</sup>-form (Figure 1F) has irregular particle aggregates that have an average size of  $\sim$ 250 nm. Figure 2 shows the XRD

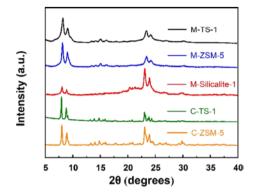


Figure 2. XRD patterns of 2D (M-TS-1, M-ZSM-5, and M-Silicalite-1) and 3D (C-TS-1 and C-ZSM-5) zeolite supports.

patterns of these six zeolite supports. All of them have the characteristic signature reflections of crystalline MFI framework structures. It should be noted that the precursors (i.e., before any calcination treatment) of 2D M-TS-1, M-ZSM-5, and M-Silicalite-1 zeolites have XRD patterns exhibiting low-angle reflections indexed as (010) and (030), which corresponds to interlamellar structural correlation in the multilamellar structure, <sup>46</sup> as shown in Figure S1 in the Supporting Information. The disappearance of these peaks after the calcination treatment indicates that the long-range ordering of these 2D nanosheet layers was destroyed. Nevertheless, these nanosheet layers still keep the plate-like morphology in 2D M-TS-1, M-ZSM-5, and M-Silicalite-1 zeolites.

The N<sub>2</sub> adsorption/desorption isotherms and the corresponding pore size distributions extracted from the adsorption branch using the nonlocal density functional theory (NLDFT) method in Figure 3 are used to reveal the textural properties of these zeolite supports. In Figure 3A, at a relative pressure of P/  $P_0$  < 0.40, all the zeolite supports have similar adsorption, which indicate that they have similar microporous structures. However, at a higher relative pressure  $(P/P_0 = 0.40-0.95)$ , the increase in adsorption volume and appearance of hysteresis loops in 2D M-TS-1, M-ZSM-5, and M-Silicalite-1 are observed. This is caused by the capillary condensation in the mesopores of these three zeolites. The pore size distributions shown in Figure 3B further confirm the presence of mesopores in the 2D zeolites. In particular, 2D M-TS-1 and M-ZSM-5 have a broad mesopore peak centered at ~6 nm, while 2D M-Silicalite-1 has slightly larger mesopores centered at ~8 nm. All the zeolite supports, especially for 3D structures, have a small peak around 3 nm, which might be due to a phase transition in the N<sub>2</sub> adsorbate. 54 In addition, the 2D zeolite supports bear the features of relatively high external surface areas and high mesopore volumes compared with their 3D analogues, as summarized in Table 1.

3.2. Composition and Acidity Properties of Zeolite Supports. Elemental compositions of the zeolite supports are represented by the ratios of silicon (Si) to heteroatom metal (i.e., Si/Ti or Si/Al). As summarized in Table 2, M-TS-1 and C-TS-1 have very similar Si/Ti ratios, while M-ZSM-5 has a slightly lower Si/Al ratio than the Si/Ti ratios of TS-1 zeolites.

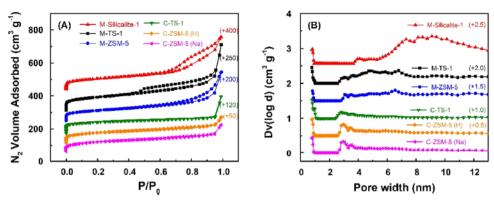


Figure 3. (A) N<sub>2</sub> isotherms and (B) NLDFT pore size distributions of M-TS-1, M-ZSM-5, M-Silicalite-1, C-TS-1, C-ZSM-5(H), and C-ZSM-5(N<sub>2</sub>)

Table 1. Textural Properties of the 2D and 3D Support Materials

zeolite	$S_{\rm BET}^a (\rm m^2 g^{-1})$	$S_{\text{micro}}^{b} (m^2 g^{-1})$	$S_{\text{ext}}^{c} \text{ (m}^{2} \text{ g}^{-1}\text{)}$	$V_{\rm t}^d \left({\rm cm}^3  {\rm g}^{-1}\right)$	$V_{\rm micro}^{b} ({\rm cm}^3 {\rm g}^{-1})$	$V_{\rm meso}^{e} ({\rm cm}^3 {\rm g}^{-1})$	$S_{\rm ext}/S_{\rm BET}$
M-TS-1	478	265	213	0.40	0.11	0.29	0.45
M-ZSM-5	410	245	165	0.34	0.10	0.24	0.40
M-Silicalite-1	378	208	170	0.43	0.09	0.34	0.45
C-TS-1	463	377	86	0.24	0.15	0.09	0.19
C-ZSM-5(Na)	441	322	119	0.26	0.14	0.12	0.27
C-ZSM-5(H)	428	314	114	0.26	0.13	0.13	0.27

<sup>&</sup>lt;sup>a</sup>Determined by the Brunauer, Emmett, and Teller (BET) method. <sup>b</sup>Determined from the t-plot method. <sup>c</sup>Calculated by  $S_{\text{ext}} = S_{\text{BET}} - S_{\text{micro}}$ . <sup>d</sup>Calculated by  $N_2$  adsorption at  $P/P_0 = 0.95$ . <sup>e</sup>Determined from  $V_{\text{meso}} = V_{\text{t}} - V_{\text{micro}}$ .

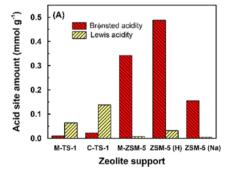
Table 2. Composition and Acidity (Measured by Organic Base Titrations at 423 K) of Zeolite Supports

	acid d	ensity (mm			
zeolite	total acidity <sup>a</sup>	Brønsted acidity $^b$	Lewis acidity <sup>c</sup>	Si/Ti Si/Al <sup>d</sup>	Heteroatom (mmol g <sup>-1</sup> ) <sup>e</sup>
M-TS-1	0.073	0.009	0.064	54	0.274
M-ZSM-5	0.349	0.342	0.007	50	0.326
M-Silicalite-1	0.000	0.000	0.000	00	
C-TS-1	0.161	0.023	0.138	57	0.295
$C-ZSM-5(Na)^f$	0.159	0.155	0.004	17	0.868
C-ZSM-5(H)	0.519	0.488	0.031	17	0.868

<sup>a</sup>Determined by pyridine titration. <sup>b</sup>Measured by IPA titration. <sup>c</sup>Calculated by the difference between the total acidity and Brønsted acidity. <sup>d,e</sup>Determined by ICP-OES analysis. <sup>f</sup>Na<sup>+</sup> concentration is 1.35 wt %, equivalent to Si/Na = 28.

The C-ZSM-5(H) and C-ZSM-5(Na) zeolites have a Si/Al ratio of 17. The Na concentration in the C-ZSM-5(Na) support is 1.35 wt %, equivalent to a Si/Na ratio of 28. The

isomorphous substitution of a framework tetravalent Si by the trivalent Al atom introduces a negative charge onto the framework, which can be compensated to reach overall charge neutrality by the introduction of a cationic proton. This renders Brønsted acid (Si-O(H)-Al) sites in the M-ZSM-5 and C-ZSM-5(H) supports. The introduction of Na<sup>+</sup> cations neutralizes Brønsted acidity in zeolites. Because the Si/Na ratio is higher than the Si/Al ratio, C-ZSM-5(Na) maintains some Brønsted acidity, although it is lower than that of C-ZSM-5(H). The isomorphous substitution of lattice Si atoms with tetravalent Ti atoms does not bring local charge disbalance, so it generates the Lewis acid sites in the framework. Therefore, M-TS-1 and C-TS-1 supports contain mainly Lewis acidity. The siliceous M-Silicalite-1 does not have either Brønsted or Lewis acidity. Overall, these six zeolite supports allow us to compare the effects of support dimensionality (2D versus 3D), presence of acidity (M-Silicalite-1 versus others), and acidity type (Brønsted versus



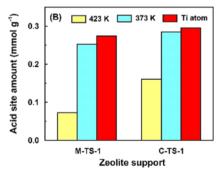


Figure 4. (A) Acid site concentrations of zeolite supports measured at 423 K and (B) Lewis acid site concentrations of M-TS-1 and C-TS-1 measured at different temperatures. Ti atom concentrations are included in (B) for comparison purposes.

Lewis) on Pt dispersion and the consequent NDE performance.

The organic base titrations using IPA and pyridine titrants quantified the concentrations of Brønsted and Lewis acid sites in the zeolite supports. In particular, IPA probes the Brønsted acidity, while the pyridine titrant can detect both types of acidities. The difference between both is accounted as the concentration of Lewis acid sites. The validity of the organic base titration for quantifying zeolite acidity has been confirmed by our previous work. 47,51 Figure 4A and Table 2 show that TS-1 (i.e., M-TS-1 and C-TS-1) zeolites mainly contain Lewis acid sites, while ZSM-5 zeolites (M-ZSM-5, C-ZSM-5(H), and C-ZSM-5(Na)) preferentially have Brønsted acidity. As expected, M-Silicalite-1 has neither Brønsed nor Lewis acid sites (data not shown). At a titration temperature of 423 K, the 2D M-TS-1 has almost two-fold lower Lewis acid site concentration than 3D C-TS-1, although they have very similar Ti atom concentrations (Table 2). The 2D M-ZSM-5 has similar Brønsted acidity concentration to Al atoms, which has been verified in our previous work. 44,55 The inclusion of Na+ in C-ZSM-5(Na) led to a decrease in Brønsted acid sites, compared with the parent C-ZSM-5(H).

The strength of Lewis acidity in the 2D M-TS-1 and 3D C-TS-1 zeolites was probed by measuring acid site quantities from pyridine uptakes at 373 K, in comparison to those obtained at 423 K in Figure 4A. Figure 4B shows that the measurable Lewis acid sites at 373 K are comparable to those of Ti atom concentrations, nearly independent of zeolite dimensionality. The increase in temperature to 423 K, however, resulted in lower detectable acid sites, especially for the 2D M-TS-1 zeolites. The ratios of acid sites measured at 423 K to that at 373 K are 56 and 29%, respectively, in C-TS-1 and M-TS-1. The lower Lewis acid sites at 423 K suggest that pyridine does not adsorb on all Lewis sites at this temperature, likely because a portion of the Lewis sites has a weaker strength. For instance, Fourier transform infrared spectroscopy (FTIR) studies of adsorbed pyridine on ZSM-5 zeolites have established that the pyridine adsorbs much more weakly on Lewis than Brønsted sites and, for this reason, the amount of pyridine adsorbed on Lewis sites decreases markedly as the adsorption temperature increases. 56-59 The acidity strength of Lewis acid sites in 2D M-TS-1 nanosheets is weaker compared to that enclosed in 3D C-TS-1 zeolites. The same trend has been observed by the FTIR studies of adsorbed pyridine on TS-1 zeolites by Shamzhy et al. 60,61

3.3. Silanol and Titanol Groups in Zeolite Supports. The properties of silanol (Si-OH) and/or titanol (Ti-OH) groups in 2D and 3D zeolite supports are analyzed by the hydroxyl vibration ( $\nu(OH)$ ) in the 3000–4000 cm<sup>-1</sup> region of their DRIFT spectra, as shown in Figure 5. Three bands centered at 3740, 3675, and 3520 cm<sup>-1</sup>, respectively, were observed. The band at 3740 cm<sup>-1</sup> corresponds to the stretching vibration of v(OH) in isolated Si-OH and Ti-OH groups, located at the external surface and within the zeolite micropores,<sup>62-65</sup> where they are not confined by either the shallow cavities on the external surface or micropores. Next, the peak at 3675 cm<sup>-1</sup> is assigned to the H-bonded Si-OH and Ti-OH groups that are partially confined in micropores and shallow cavities on external surfaces. 63-66 The broad band centered at 3520 cm<sup>-1</sup> is associated with Si-OH and Ti-OH groups with strong and mutual H-bonding that exist in micropores or on external surfaces. 63,66,67 The peak of 3601 cm<sup>-1</sup> in M-ZSM-5, C-ZSM-5(H), and C-ZSM-5(Na) supports

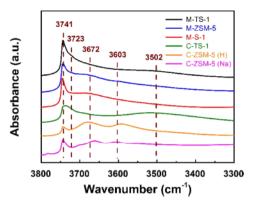


Figure 5. DRIFTS spectra of -OH groups in 2D M-TS-1, M-ZSM-5, and M-Silicalite-1 as well as 3D C-TS-1, C-ZSM-5(H), and C-ZSM-5(Na) zeolites.

is due to the Brønsted acid sites in these samples. It is clearly seen that 3D C-TS-1 and C-ZSM-5(H) have the highest concentrations of confined Si-OH and/or Ti-OH groups among all samples. 2D M-TS-1 and M-ZSM-5 have partially collapsed 2D zeolitic layers and therefore have higher concentrations of free isolated Si-OH and Ti-OH groups than the 3D analogues. The external surfaces on the 2D zeolite nanosheets are terminated by these Si-OH and Ti-OH groups. 68

To further understand the interdependence of the loaded Pt species and the associated three types of -OH groups, the variation in peak areas of the bands centered at 3741 cm<sup>-1</sup>  $(I_{3741}$ , free isolated -OH), 3723 cm<sup>-1</sup> and 3674 cm<sup>-1</sup>  $(I_{3723}$ and I<sub>3674</sub>, partially confined -OH groups), and 3502 cm<sup>-</sup>  $(I_{3500}, \text{ H-bonded } -\text{OH groups})$  were calculated for all the zeolite support samples after the peak deconvolution (Figure S13). We followed the procedure reported by Brauer et al. 69,7 to carry out the quantitative analysis without using the extinction coefficient. It is known that the determination of extinction coefficients is challenging due to a range of extinction coefficients reported in previous studies. 71,72 The DRIFTS spectra in the absorbance mode (Figure 5) were normalized to the overtone and combination Si-O-Si vibrations found between 1750 and 2100 cm<sup>-1</sup> ( $I_{1750-2100}$ ) in each spectrum that was used as an internal standard. Table S4 summarizes the values of peak intensities of each -OH species in each zeolite. The increase in mesoporosity in 2D zeolite nanosheets significantly improves free isolated -OH groups, compared to 3D zeolites since 2D M-TS-1 and 2D M-ZSM-5 zeolites have very high  $I_{3741}/I_{1750-2100}$  ratios compared to the 3D C-TS-1 and C-ZSM-5. These results suggest that -OH groups in 2D zeolite nanosheets should play a significant role as the anchoring sites for Pt species.

3.4. Platinum Loading on Zeolite Supports. To prepare the Pt/M-TS-1 catalysts, the Pt loading was explored by three methods: electrostatic adsorption (EA), solvent evaporation (SE), and wetness impregnation (WI). Figure 6 shows the morphology of Pt species on M-TS-1 prepared by these three methods. Clearly, the Pt particle sizes increase in the Pt/M-TS-1 samples when the synthesis method varied from IE (Pt/M-TS-1 (EA), Figure 6A) to SE (Pt/M-TS-1 (SE), Figure 6B) and then to WI (Pt/M-TS-1 (WI), Figure 6C). The difference of Pt particle size is also reflected by the Pt dispersion measured by the hydrogen chemisorption experiment (Figure 6F). The Pt dispersions are 90, 81, and 57% in Pt/M-TS-1

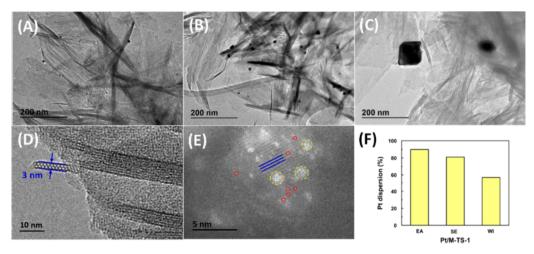


Figure 6. TEM images of Pt/M-TS-1 catalysts prepared by (A) electrostatic adsorption, (B) solvent evaporation, and (C) wetness impregnation approaches. (D and E) HR-TEM and HAADF-STEM images of the M-TS-1 support and Pt/M-TS-1 catalyst in image (A). (F) Pt dispersion in Pt/M-TS-1 catalysts made by different synthesis methods.

(EA), Pt/M-TS-1 (SE), and Pt/M-TS-1 (WI), respectively. No clear diffraction XRD peaks associated with Pt particles in these three samples were detected (Figure S2) due to the low Pt loading (0.088 wt %). It should be noted that the complexity in synthesis and difficulty of control of Pt concentrations decrease in the order of EA > SE > WI. Because Pt/M-TS-1 (SE) only has a slightly lower Pt dispersion than Pt/M-TS-1 (EA) but it is much easier to prepare, all the control Pt/zeolite catalysts (Table S2) were prepared by the SE method, as to be discussed below.

To further understand Pt dispersion in the Pt/M-TS-1 (EA) sample, high-resolution TEM (HR-TEM) and sub-angstromresolution HAADF-STEM observations were collected, as shown in Figure 6D,E. The 2D M-TS-1 support contains platelike nanosheets, which is consistent with those visualized by the SEM image in Figure 1A. Some regions of the nanosheets still exhibit an ordered arrangement, and even the long-range ordering does not exist due to collapse caused by calcination. The lattice fringe can be clearly seen in Figure 6D. The isolated Pt species (indicated by red solid circles) and small Pt clusters (highlighted by yellow dashed circles) are clearly seen in the Pt/M-TS-1 catalyst since Pt has a higher atomic mass than Ti, Si, and O elements in the zeolite support (Figure 6E). This result suggests that the Pt species are well distributed on the 2D M-TS-1 support when the Pt/M-TS-1 catalyst is prepared by the electrostatic adsorption approach, which is consistent with the high Pt dispersion in Figure 6F.

3.5. Hydrogen Temperature-Programmed Reduction ( $H_2$ -TPR) Profiles. To probe the reducibility of Pt species and its interaction with the zeolite support, the  $H_2$ -TPR profile was collected for each of the Pt/zeolite catalysts. Figure 7A shows the  $H_2$ -TPR profiles of Pt/M-TS-1 prepared by different Pt loading methods. Two distinct peaks are observed in all three samples, in which the low temperature peak (at  $\sim$ 373 K) is assigned to the reduction of Pt-oxide (PtO<sub>x</sub>) species to metallic Pt<sup>73,74</sup> and the second peak appearing at a high temperature range (above  $\sim$ 673 K) is associated with the reduction of Pt species that interacts with the M-TS-1 support. For the Pt/M-TS-1 (SE) and Pt/M-TS-1 (WI), the high temperature reduction peaks are both located at  $\sim$ 723 K, but the peak area is larger in the former sample. Consequently, the area of the low temperature reduction peak in Pt/M-TS-1 (SE) is

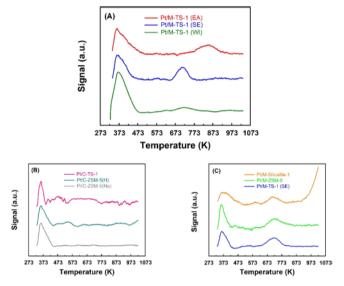


Figure 7. (A) H<sub>2</sub>-TPR profiles of Pt/M-TS-1 catalysts prepared by three different synthesis approaches. (B and C) H<sub>2</sub>-TPR profiles of Pt species supported on 3D and 2D zeolite supports, respectively. (Catalysts in (B) and (C) were prepared by the SE method.)

smaller than that of Pt/M-TS-1 (WI). The high temperature reduction peak in Pt/M-TS-1 (EA) shifts to 850 K, distinct from the peak positions in the other two samples in Figure 7A. The results suggest that the electrostatic adsorption process led to a stronger metal—support interface interaction between Pt and the M-TS-1 support, consistent with the high Pt dispersion in Pt/M-TS-1 (EA) discussed above. Accordingly, the WI method mainly resulted in aggregated PtO<sub>x</sub> particles, while the SE approach generated both PtO<sub>x</sub> particles and isolated Pt species on the 2D M-TS-1 support.

To examine the effects of support dimensionality (Figure 7B) and acidity (Figure 7C) on Pt anchoring in the catalysts, the  $\rm H_2$ -TPR profiles were obtained for Pt/C-TS-1, Pt/ZSM-5(H), and Pt/ZSM-5(Na) as well as Pt/M-ZSM-5 and Pt/M-Silicalite-1 catalysts. As shown in Figure 7B, the 3D Pt/C-TS-1 Pt/C-ZSM-5(H) and Pt/C-ZSM-5(Na) have similar  $\rm H_2$ -TPR profiles, all of which has one dominant low temperature reduction peak at ~353 K. This indicates that most Pt atoms

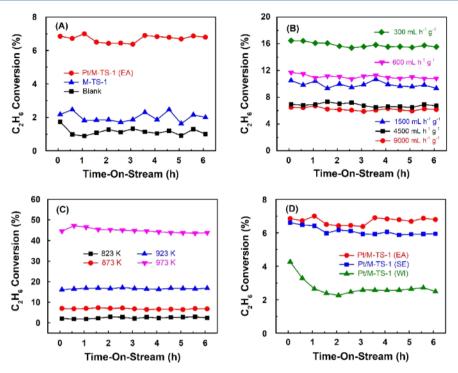


Figure 8.  $C_2H_6$  conversion over Pt/M-TS-1 catalysts. (A) Effect of catalyst usage (873 K, 103 kPa, space velocity of 9000 mL  $h^{-1}$  g<sup>-1</sup>, Ar internal standard, 0.088 wt % Pt loading by electrostatic adsorption). (B) Effect of space velocity (same conditions as (A) except for variation in space velocity). (C) Effect of temperature (same conditions as (A) except for temperature variation). (D) Effect of the Pt loading method (same conditions as (A) except for the Pt loading approach).

formed PtO, species on the 3D zeolite supports, whether it contains Lewis or Brønsted acidity. The high external surface area in the 2D M-TS-1 support and the resulting high density of free isolated terminal -OH groups promote Pt dispersion and stronger metal-support interaction. Figure 7C has both low (353 K) and high (723 K) temperature reduction peaks in the H<sub>2</sub>-TPR profiles of Pt species on the 2D M-ZSM-5 support, similar to those of Pt/M-TS-1 (SE). The variation in Lewis or Brønsted in the 2D zeolite supports did not influence the interaction between Pt and the support. The absence of acidity in the 2D zeolite support, however, led to a distinct H2-TPR profile. As shown in Figure 7C, Pt/M-Silicalite-1 has very small H<sub>2</sub> reduction peaks at 353 and 723 K. Instead, a very strong peak at temperature of >973 K is observed. By comparison to the H<sub>2</sub>-TPR profile of the M-Silicalite-1 support (Figure S3), this very high temperature peak (>973 K) should be resulted from the zeolite support. The lack of acidity in the pure siliceous M-Silicalite-1 support led to relatively serious agglomeration of metallic Pt particles. A similar phenomenon was observed in the Pt-Sn/SBA-15 catalyst. 75 In comparison to Pt-Sn loaded on the ZSM-5 and alumina, the H2-TPR of Pt-Sn/SBA-15 showed the least reduction peak among the samples. Overall, the low dimensionality of the zeolite support highly influences Pt dispersion and metal-support interaction. Although the acidity type does not show obvious impact on the Pt-support interaction, the presence of acidity is a necessity to enable strong metal-support interaction.

3.6. Non-oxidative Dehydrogenation of Ethane. To understand the synthesis-structure-performance relationships between zeolite-supported Pt catalysts and ethane conversion, we conducted the NDE tests on all the eight catalyst samples listed in Table S2. In these tests, the dependence of NDE on Pt dispersion, support acidity (Brønsted versus Lewis), and

support dimensionality (2D versus 3D) as well as long-term stability was elucidated in sequence. We first examined the NDE on the Pt/M-TS-1 (EA) catalyst and used this data as the basis to compare and understand the effects of Pt loading methods and reaction conditions as well as the performance of other catalyst samples.

3.6.1. Performance of Pt/M-TS-1 Catalysts. The physicochemical property characterizations above show that Pt/M-TS-1 (EA) has the highest Pt dispersion and the strongest metal-support interaction among the three Pt/M-TS-1 samples. We expect that it will enable the best NDE performances. Figure 8A shows that the ethane conversion was 1.5% in the absence of Pt/M-TS-1 catalysts at 873 K. The usage of the zeolite support (M-TS-1) promoted the ethane conversion by 25%, reaching 2.0% conversion. In the presence of Pt/M-TS-1 catalysts, ethane conversion reached 6.5%, nearly three-fold increase compared to the M-TS-1 support only catalyst. The reaction exclusively favored ethylene formation, as shown by the selectivity data in Figure S5 in the Supporting Information. Moreover, the Pt/M-TS-1 catalyst did not have any deactivation in the entire reaction period, i.e., a time-on-stream (TOS) of 6 h.

The effects of space velocity on the Pt/M-TS-1 (EA) catalyst in NDE are shown in Figure 8B. The  $\rm C_2H_6$  conversion at 873 K increased from 6.5 to 15.8% with the decrease in space velocity from 9000 to 300 mL  $\rm h^{-1}$  g<sup>-1</sup>, but the catalyst did not experience any deactivation in all these space velocities. The product was dominated by ethylene (>98%), even at the slowest velocity of 300 mL  $\rm h^{-1}$  g<sup>-1</sup>, as shown in Figure S6. Figure 8C illustrates that ethane conversion increased with an increase in the reaction temperature, reaching 44.5% at 973 K and 9000 mL  $\rm h^{-1}$  g<sup>-1</sup> space velocity. At temperatures of 823, 873, and 923 K, there were no noticeable catalyst deactivation.

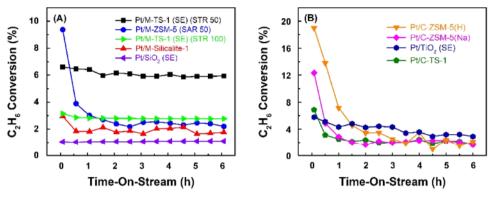


Figure 9.  $C_2H_6$  conversion over Pt loaded on (A) 2D and (B) 3D zeolite supports. Pt/SiO<sub>2</sub> (SE) in (A) and Pt/TiO<sub>2</sub> in (B) are included for comparison to metal oxide-supported Pt catalysts. (873 K, 103 kPa, space velocity of 9000 mL h<sup>-1</sup> g<sup>-1</sup>, Ar internal standard, 0.088 wt % Pt loading by SE).

The product at these temperatures was dominated by ethylene (>98.0%, Figure S7). At a temperature of 973 K, a slight drop (4% at a TOS of 6 h) in ethane conversion was observed. The products contain 92.5% ethylene, 4.3%  $CH_4$ , 0.1% acetylene ( $C_2H_2$ ), and 3.1% aromatics. The formation of  $CH_4$ ,  $C_2H_2$ , and aromatics byproducts should be caused by thermal cracking, dehydrogenation, and aromatization of  $C_2$  products at higher reaction temperature. The formation of aromatics products indicates coke deposition on the catalyst. As shown in Figure S4 in the Supporting Information, 1.7% coke was observed on Pt/M-TS-1 (EA) at a TOS of 6 h that was tested at 973 K. On the contrary, almost no detectable coke existed on Pt/M-TS-1 (EA) at 873 K. The gas phase conversion under each condition is listed in Table S7 in the Supporting Information.

Figure 8D shows the ethane conversion in NDE over the catalyst prepared by the solvent evaporation (Pt/M-TS-1 (SE)) and wetness impregnation (Pt/M-TS-1 (WI)) methods, in comparison to that of Pt/M-TS-1 (EA) at 873 K and a space velocity of 9000 mL h<sup>-1</sup> g<sup>-1</sup>. Under the same reaction conditions, Pt/M-TS-1 (WI) had an initial ethane conversion of 4.3%, which dropped to 2.2% at a TOS of 1.5 h and was kept at this conversion till a TOS of 6 h. This represents nearly 2.5-fold decrease in ethane conversion compared to that of Pt/ M-TS-1 (EA). The Pt/M-TS-1 (SE) catalyst, however, only has a slight inferior performance to Pt/M-TS-1 (EA). The initial ethane conversion was similar to that of Pt/M-TS-1 (EA) (6.6%). It decreased to 6.2% at a TOS of 1.5 h and very slowly dropped to 5.9% at a TOS of 6 h. The product selectivity was not impacted by the Pt loading approaches (Figure S8). The differences in NDE performance (ethane conversion and catalyst deactivation) across these three catalysts can be attributed to the differences in Pt dispersion and Pt-support interaction. Apparently, Pt/M-TS-1 (EA) had the highest Pt dispersion and strongest Pt-support interaction, which led to the highest catalyst activity and durability.

3.6.2. Effects of Zeolite Support Acidity and Dimensionality. As noted above, Pt/M-TS-1 (SE) has only slightly inferior NDE performance to Pt/M-TS-1 (EA), but the precise Pt concentration is much easier to control than that in the electrostatic adsorption process. Therefore, we selected the solvent evaporation approach to load the same amount (0.088 wt %) of Pt onto other 2D (M-ZSM-5, M-Silicalite-1, and M-TS-1 with a Si/Ti ratio of 100) and all 3D (C-TS-1, C-ZSM-5(H), and C-ZSM-5(Na)) zeolite supports to study the effects of support acidity and dimensionality on the NDE. This adversely assisted us to understand why Pt/M-TS-1 (EA) has

the excellent stability, activity, and selectivity in NDE. Since M-TS-1 contains both  $SiO_2$  and  $TiO_2$  compositions, we prepared  $Pt/TiO_2$  (SE) and  $Pt/SiO_2$  (SE) catalysts to understand the NDE performance on metal oxide-supported Pt catalysts in the study.

Figure 9A shows the ethane conversion versus TOS over Pt/ M-Silicalite-1 and Pt/M-ZSM-5 catalysts. In comparison with Pt/M-TS-1 (SE), ethane conversion (after a TOS of ~1.0 h) over Pt/M-Silicalite-1 was ~3 times lower accompanied with deactivation at a TOS < 0.5 h. For NDE over the Pt/M-ZSM-5 catalyst, the ethane initial conversion was 1.5 times higher than that of Pt/M-TS-1 (SE), which dropped to  $\sim$ 2.2% after a TOS of 2.0 h. As a siliceous zeolite, 2D M-Silicalite-1 does not have a heteroatom that generates Brønsted or Lewis acidity. The interaction between Pt and the M-Silicalite-1 support is weak, as reported for Pt residence on the silica support.<sup>20</sup> Therefore, although the support has a high external surface area similar to that of the M-TS-1 support, ethane conversion drops slightly due to deactivation. When the Si/Ti ratio decreased from 100 to 50, the Pt/M-TS-1 (SE) catalyst nearly doubled the ethane conversion. Clearly, the increase in Lewis acidity of the support promoted the anchoring of Pt species and their dispersion, leading to high conversion in the NDE reaction. The Pt loading onto the pure siliceous SiO2 support did not show very good NDE performance either. As shown in Figure 9A, Pt/SiO<sub>2</sub> (E) showed ~1.0% ethane conversion, almost 6 times lower than that of the Pt/M-TS-1 (SE) catalyst.

The presence of Brønsted acidity in Pt/M-ZSM-5 enables strong metal—support interaction, but the strong acidity catalyzed side reactions such as aromatization of C<sub>2</sub> products to form benzene, naphthalene, and even coke, as evidenced by the product selectivity in Figure S9.<sup>76–78</sup> This in fact caused catalyst deactivation for NDE over the Pt/M-ZSM-5 catalyst. In contrast, the presence of Lewis acidity in the M-TS-1 support renders strong metal—support interaction and Pt dispersion, but the weak acidity does not enable acid-catalyzed side reactions. All these characteristics enabled the stable and active NDE performance in the Pt/M-TS-1 (SE) catalyst.

Figure 9B presents the NDE performance over the 3D zeolite-supported Pt catalysts. Similar to the Pt/M-ZSM-5 catalyst, Pt/C-TS-1, Pt/C-ZSM-5(Na), and Pt/C-ZSM-5(H) all had high initial conversions but underwent a fast deactivation before a TOS of 3 h. Although C-TS-1 has Lewis acidity, the absence of sufficient external surface areas and terminal —OH groups did not enable high Pt dispersion and strong Pt—support interaction. The fast deactivation of the

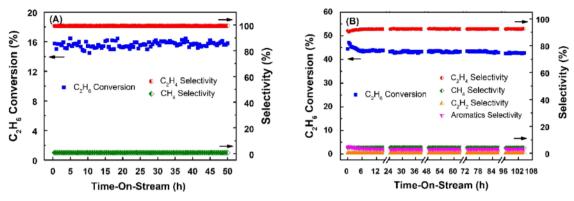


Figure 10. Long-term stability test for the Pt/M-TS-1 (EA) catalyst in the NDE reaction at (A) 873 K (103 kPa, space velocity of 300 mL  $h^{-1}$   $g^{-1}$ , Ar internal standard) and (B) 973 K (103 kPa, space velocity of 9000 mL  $h^{-1}$   $g^{-1}$ , Ar internal standard).

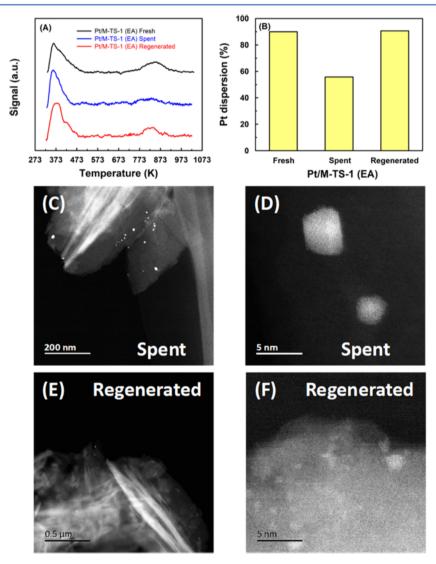


Figure 11. (A) H<sub>2</sub>-TPR profiles, (B) Pt dispersion, and HAADF-STEM images of (C and D) spent and (E and F) regenerated Pt/M-TS-1 (EA) catalysts.

Pt/C-TS-1 catalyst should be caused by Pt sintering since no byproduct was formed, as shown in Figure S10. The  $Pt/TiO_2$  sample showed a similar trend to that of the Pt/C-TS-1 sample. An obvious decrease in ethane conversion due to catalyst deactivation was observed within a TOS of 6 h. Besides the low external surface area and low Pt dispersion, 3D

Pt/C-ZSM-5 has Brønsted acidity, both of which led to Pt thermal sintering and acid-catalyzed coke formation (Figure S16 and Table S10) and thus fast catalyst deactivation. The neutralization of a portion of Brønsted acidity by introducing Na<sup>+</sup> cations into 3D C-ZSM-5 slowed down the deactivation; however, Pt/C-ZSM-5(Na) still had NDE performance decay

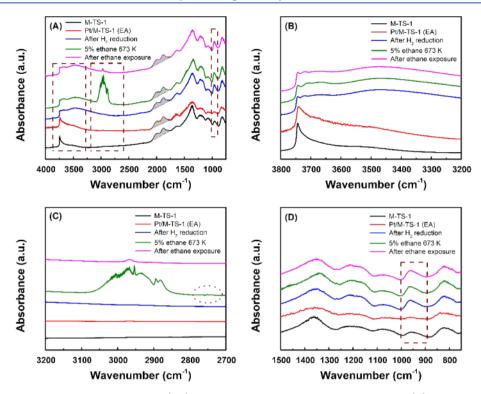


Figure 12. In situ DRIFTS spectra of the Pt/M-TS-1 (EA) catalyst under different treatment conditions. (A) Spectra in a frequency range of 4000–750 cm<sup>-1</sup>. (B–D) Adsorption bands of stretching vibrations of –OH groups, –CH groups, and Si-O-Ti groups in sequence.

with TOS due to the residue Brønsted acidity in the zeolite support. The H<sub>2</sub> chemisorption was done on the 3D Pt/C-TS-1, Pt/C-ZSM-5(H), and Pt/C-ZSM-5(Na) catalysts, showing 73, 68, and 73% Pt dispersion in sequence (Figure S14), lower than that of the Pt/M-TS-1 catalyst. Clearly, the high external surface area, high concentration of terminal —OH groups, and Lewis acidity of 2D M-TS-1 are key characteristics to enable Pt anchoring with high dispersion and strong metal—support interaction. Consequently, Pt/M-TS-1 (EA) has the highest stability, activity, and selectivity among all zeolite-supported Pt catalysts in this study. The equilibrium conversion and TOF in each case are listed in Tables S8 and S9 in the Supporting Information.

3.6.3. Catalyst Durability Test. Figure 10 shows the longterm stability performance of the Pt/M-TS-1 (IE) catalyst in NDE. At a reaction temperature of 873 K (Figure 10A), the ethane conversion was kept at 15.7% with >99.0% ethylene product selectivity at a TOS up to 50 h. When the reaction temperature was increased to 973 K, ethane conversion was increased to 47.2%, accompanied with a slight decrease in ethylene selectivity (92.5%) (Figure 10B). The NDE had a slight decrease (~4%) in ethane conversion before a TOS of 6 h. Afterward, it was stable with a TOS of 100 h. The ethane conversion remained at 43.0% with the selectivity toward byproducts being less than 8.0%, i.e., 4.3% CH<sub>4</sub>, ~0.1% C<sub>2</sub>H<sub>2</sub>, and ~3.0% aromatics. As discussed above, the slight catalyst deactivation at 973 K should be caused by gas phase reactions. The NED reaction in the blank reactor in the absence of catalysts had 9.5 and 34.0% ethane conversions at 873 and 973 K, respectively. The low space velocity in Figure 10A and high temperature in Figure 10B promoted the gas phase reaction. As discussed in the Section 3.6.1 above, the ethane conversion in the blank reactor at 873 K and 9000 mL h<sup>-1</sup> g<sup>-1</sup> space velocity was 1.5%, much lower compared to the 9.5% at the same

temperature and a space velocity of 300 mL  $h^{-1}$  g<sup>-1</sup>. After subtraction of the blank run conversion from the total conversion in each case, the TOFs are 0.02 and 0.81 s<sup>-1</sup> in Figure 10A,B, respectively. Although gas phase reactions are present that could cause coke formation and catalyst deactivation, the 2D M-TS-1 nanosheet support has a high external surface area and large mesoporosity that should facilitate fast mass transport to mitigate coke accumulation. Therefore, we did not see significant catalyst deactivation in these long-term stability tests. The M-TS-1 nanosheet-supported Pt catalyst stays in the forefront in terms of  $C_2H_6$  conversion,  $C_2H_4$  selectivity, and long-term stability after comprehensive evaluation and comparison to various catalyst systems reported previously (Table S5).

3.6.4. Characterization on Spent and Regenerated Catalysts. To study metal dispersion after the NDE reaction and regeneration, the spent and regenerated Pt/M-TS-1 (EA) catalysts were characterized by H2-TPR, chemisorption, and HAADF-STEM measurements. Specifically, the spent catalyst was prepared by running the NDE reaction over fresh Pt/M-TS-1 (EA) at 873 K and 9000 mL  $h^{-1}$   $g^{-1}$  space velocity for a TOS of 6 h. After reaction, one portion of the spent catalyst was collected for physicochemical property characterization and the other portion was exposed to a flow air (100 mL min<sup>-1</sup>) at 823 K for 4 h with a ramp rate of 3 K min<sup>-1</sup>. As shown in Figure 11A, both the low temperature peak (at ~373 K) assigned to the reduction of Pt-oxide (PtO<sub>x</sub>) species to metallic Pt $^{73,74}$  and the high temperature peak (at  $\sim$ 723 K) associated with the reduction of Pt species bonded onto the M-TS-1 support are observed in spent and regenerated Pt/M-TS-1 (EA). A close comparison among the H2-TPR profiles show that the low temperature peak position and intensity are similar among the fresh, spent, and regenerated samples, while the high temperature peak intensity is reduced in the spent catalyst

and is restored after catalyst regeneration. The Pt dispersion measured from the chemisorption in Figure 11B shows that the spent Pt/M-TS-1 (EA) has a dispersion of 56%, 34% lower than that of the fresh Pt/M-TS-1 (EA). The regenerated sample has 90% Pt dispersion, comparable to that of the fresh catalyst. These results suggest that the reductive NED environment led to a slight transformation of Pt species bonded on the M-TS-1 support to smaller clusters or particles. The oxidative environment, however, restored the Pt dispersion. The HAADF-STEM images in Figure 11C-F further evidenced the interconversion between small Pt single atoms/clusters and larger Pt clusters/small particles in changing the reducing and oxidizing environments. The catalyst maintained crystallinity in both the NDE reaction and regeneration process since similar XRD patterns of fresh, spent, and regenerated Pt/M-TS-1 (EA) were observed (Figure S11). The reversible transformation between aggregation and redispersion of Pt species on the M-TS-1 support is consistent with the Pt/CHA zeolite catalyst reported previously. 79,80 We would like to note that Pt is confined in the micropores of CHA that is prepared by mixing the Pt precursor in the CHA synthesis mixture prior to crystallization. The Pt/M-TS-1 catalyst in our work was prepared by the electrostatic adsorption approach after M-TS-1 was hydrothermally synthesized.

The Pt/M-TS-1 (EA) catalyst was further characterized by in situ DRIFTS measurement under both pretreatment and reaction conditions. Figure 12 shows the DRIFTS spectra of the M-TS-1 support before Pt loading, Pt loaded on M-TS-1 (EA), Pt/M-TS-1 (EA) after H<sub>2</sub> reduction at 673 K, Pt/M-TS-1 (EA) after ethane exposure at 673 K, and Pt/M-TS-1 (EA) after cooling down to 393 K in a flow N2 gas. A comparison among these spectra indicates the physiochemical property change of the Pt/M-TS-1 catalyst in the NDE reaction. Figure 12A shows the spectra spanning the frequency range of 4000— 750 cm<sup>-1</sup>. Three regions show spectra differences across the sample under different conditions, which corresponds to the stretching vibrations of -OH groups ( $\nu(O-H)$ ), C-H groups (v(C-H)), and Si-O groups in Si-O-Ti bonds in M-TS-1 zeolite. A closer look of the absorption bands at each region is presented in Figure 12B-D. A quantitative analysis for the absorption bands in Figure 12B-D was done by using the procedure reported by Bräuer et al. 69,70 The DRIFTS spectra in the absorbance mode were normalized to the overtone and combination Si-O-Si vibrations found between 1750 and 2100 cm<sup>-1</sup> ( $I_{1750-2100}$ , shaded regions in Figure 12A) in each spectrum that was used as an internal standard.

Figure 12B shows the stretching vibration frequencies of -OH groups ( $\nu(O-H)$ ), which are sensitive to the H-bonding environment of silanols and titanols in the catalysts. The  $\nu$ (O– H) bands in the region 3750-3200 cm<sup>-1</sup> of DRIFTS spectra are observed for the catalysts at different treatment statuses. Four distinct bands centered at 3742, 3723, 3675, and 3502 cm<sup>-1</sup> are observed. It is well accepted that the band at ~3742 cm<sup>-1</sup> corresponds to free and isolated lattice termination hydroxyls (denoted as "free -OH") and the other three bands correspond to hydroxyls perturbed by hydrogen bonding, which causes a redshift in  $\nu(O-H)$  relative to the "free -OH" bonds. In particular, the  $\nu(O-H)$  band at ~3502 cm<sup>-1</sup> is often assigned to the mutually H-bonded hydroxyls. Discrepancies exist on the assignments for bands at ~3723 and ~3675 cm<sup>-1</sup> in the literature, 63,66,67,81,82 but in all scenarios, both of them stand for weakly H-bonded -OH groups (defined as "partially

bonded -OH groups") compared to the "free -OH" and "mutually H-bonded -OH" groups. As shown in Figure 12B, the "free -OH" groups are dominant in the M-TS-1 nanosheets prior to Pt loading. After Pt loading and calcination in flowing air, the DRIFTS of Pt/M-TS-1 show a slight decrease in the "free -OH" groups, accompanied with an increase in partially and mutually H-bonded -OH groups. The reduction of Pt/M-TS-1 in the flowing H<sub>2</sub>/N<sub>2</sub> mixture (5% H<sub>2</sub>) at 673 K and then in flowing N<sub>2</sub> upon cooling down to 393 K further decreased the "free -OH" and increased the other three types of -OH groups. Afterward, the exposure of the catalyst to flowing ethane gas (5% C<sub>2</sub>H<sub>6</sub>/N<sub>2</sub> at 673 K) and then flowing N2 (back to 393 K) did not cause obvious changes in the -OH speciation compared to those after the H<sub>2</sub> reduction treatment. Table S3 summarizes the peak intensity after the absorption bands centered at 3742 cm<sup>-1</sup> ( $I_{3742}$ ), 3723 cm<sup>-1</sup> ( $I_{3723}$ ), 3675 cm<sup>-1</sup> ( $I_{3675}$ ), and 3502 cm<sup>-1</sup> ( $I_{3502}$ ) were deconvoluted (Figure S12), integrated, and normalized to the overtone and combination Si-O-Si vibrations found between 1750 and 2100  $\mathrm{cm}^{-1}$  (  $I_{1750-2100}$  , shaded regions in Figure 12A) in each spectrum.

Figure 12C shows the DRIFTS spectra in the band centered around 3000 cm<sup>-1</sup> frequency. All the spectra do not have obvious absorption except for the one measured from Pt/M-TS-1 (EA) upon exposure to ethane gas. The strong and broad band ranging from 2800 to 3100 cm<sup>-1</sup> in this spectrum is believed to be attributed to the stretching vibrations of the CH<sub>3</sub> groups. It is believed that these C-H bands should be from ethane molecules adsorbed in zeolite and on the supported Pt species. 83,84 In addition, the spectrum of ethane absorbed on the Pt/M-TS-1 catalyst exhibits a very small band with a frequency of ~2750 cm<sup>-1</sup>, ~200 cm<sup>-1</sup> lower than those of the C-H stretching vibrations of physically adsorbed ethane. The presence of this band might indicate a polarizability of the stretching vibrational mode. It has been concluded that the polarized vibration is connected with the subsequent heterolytic dissociation of ethane, resulting in the catalytic activation of adsorbed molecules. A similar phenomenon has been reported for Cu<sup>+</sup>- and Zn<sup>2+</sup>-loaded ZSM-5 zeolite materials. 84,85 The absence of any absorption peaks in the 1500-1640 cm<sup>-1</sup> range suggests that no aromatics or oligomerized products are formed on the catalyst surface, which is different from those of ZSM-5-supported Pt catalysts. 86 A small amount of ethane existed on the catalyst after its exposure to ethane followed by flowing N2 gas for 3 h.

Figure 12D shows that the absorption happened around 960 cm<sup>-1</sup> in M-TS-1, after Pt loading, and then exposure to  $\rm H_2$  reduction and ethane gas. This band is defined as the stretching vibration of Si–O groups in Si-O-Ti bonds in TS-1 zeolite. The loading of Pt precursors onto the M-TS-1 support followed by calcination treatment led to a decrease in peak intensity of  $\nu(\rm Si-O)$ , as shown in Table S2. After  $\rm H_2$  reduction treatment, the peak intensity was increased, even slightly higher than the one in the original M-TS-1 support prior to Pt loading. This peak intensity change might suggest that Pt has some degree of interaction with the Ti sites in the M-TS-1 support, although the detailed coordination structure remains unknown.

# 4. CONCLUSIONS

In summary, an active, selective, and highly stable catalyst was created for non-oxidative dehydrogenation of ethane. The catalyst contains subnanometric Pt species that resided on the 2D multilamellar TS-1 zeolite nanosheet support. The ultrathin (~3 nm) nanosheets have high external surface areas and terminal silanol/titanol groups in addition to the Lewis acidity generated from isomorphous substitution of lattice Si with tetravalent Ti atoms, a high dispersion of Pt, and strong Pt—support interaction achieved. The loading of Pt species by the electrostatic adsorption method, in comparison to solvent evaporation and wetness impregnation, brought close and strong Pt—support interaction. All these features enable the Pt/M-TS-1 (EA) catalyst to overcome the deactivation mechanisms from either coke deposition side reactions or thermal sintering of Pt species. The as-prepared Pt/M-TS-1 nanosheet catalyst exhibited unpresented durability, catalytic activity, and ethylene selectivity in NDE among all zeolite-supported catalysts studied in this work.

#### ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c02676.

Preparation of zeolite supports; preparation of Pt/zeolite catalysts; assessment of Brønsted and Lewis acidity; lowangle XRD patterns of 2D zeolite supports before and after calcination; high-angle XRD patterns of Pt/M-TS-1 catalysts; H2-TPR profiles of the Pt/M-Silicalite-1 catalyst and M-Silicalite-1 support; TGA profiles of spent catalysts; selectivity performance; quantification for -OH groups and peak deconvolution for in situ DRIFTS spectra in the Pt/M-TS-1 (EA) catalyst in different treatment statuses; quantification for -OH groups and peak deconvolution for in situ DRIFTS spectra in zeolite supports; comparison of NDE performances over Pt/M-TS-1 (EA) to NDE catalysts used in the literature; carbon and hydrogen balance analysis; Pt dispersion of 3D catalysts; gas phase conversion, and equilibrium conversion and TOF under different reaction conditions (PDF)

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#### Notes

The authors declare no competing financial interest.

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