Isolated Pt Species Anchored by Hierarchical-like Heteroatomic Fe-Silicalite-1 Catalyze Propane Dehydrogenation near the Thermodynamic Limit

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ABSTRACT: The atomic dispersion of precious metals accompanied by maximum atom utilization can provide specific chemical properties compared to nanoparticles and clusters that have attracted widespread interest. The selection of a suitable carrier to stabilize platinum atoms while maintaining high stability and propylene selectivity is of great challenge for propane dehydrogenation reactions operating at extremely high temperatures. Here, we report a conceptually designed catalyst comprising isolated Pt atoms stably bonded through skeleton O in a hierarchical-like heteroatomic ferrosilicate zeolite (H-Fe-S-1−3; denoted as “Fe-3”), capable of achieving high propane conversions at different temperatures and atmospheres close to the thermodynamic limit. No significant deactivation was observed for 3 days in a pure propane atmosphere at 580 °C, outperforming most of the cutting-edge Pt-based catalysts. The moderate acidity of Fe-3 and anchoring of hydroxyl species other than silanol nests were responsible for maintaining a suitable C−H break rather than an excessive C−C cleavage capacity and a high degree of Pt dispersion, respectively. X-ray absorption spectra and atomically resolved high-angle annular dark-field electron microscopy demonstrated major atomic dispersion of Pt species, along with complementary density functional theory calculations to determine the structure of Si−O−Pt−O−Fe corresponding to the T4 location as the key active site. Pt anchoring by sites other than the T4 site with analogous energies, such as T6, could be accountable for the observation that “cluster-like Pt species” are essentially composed of isolated Pt atoms not interacting with each other.

KEYWORDS: ferrosilicate zeolite, anchoring effect, isolated Pt sites, propane dehydrogenation, long-term stability

INTRODUCTION

The source of propylene, one of the key building blocks in the chemical industry, is slowly shifting from naphtha to light alkanes because of the advent of shale gas, which has led to the derivation of on-demand propane direct dehydrogenation (PDH) technology.1,2 The reaction is strongly endothermic; thus, increasing the reaction temperature (>500 °C) is the most effective strategy to achieve higher yields. However, sintering and carbon-coking at extreme temperatures may deactivate the catalytic system (i.e., Pt-based catalysts).3−5 Therefore, enhancing the structural stability of the active site of Pt-based catalysts can strategically improve performance stability and propylene selectivity in the PDH reaction by reducing the structure-sensitive side reactions (cracking, deep dehydrogenation, etc.) caused due to larger Pt ensembles.6−10 To address these challenges, plenty of intensive research has focused on constructing Pt-based intermetallic compounds, such as Pt-based nanoparticles, clusters, and single atoms. All reported Pt-based intergenic compounds achieved great reaction stability and propylene selectivity in the PDH reaction. For example, PtSn (Pt1Sn1) nanoparticles have been reported to operate as PDH catalysts at thermodynamically limited conversion levels with great stability and propylene selectivity.10 In addition, the specific contribution of the second metal in the PtZn and PtSn-based cluster catalysts for the PDH reaction has been demonstrated.11−13 Besides, Nakaya et al. proposed two construction strategies to achieve enhanced thermal stability of the single-atom Pt; the first included the introduction of Ca and Pb to simultaneously modulate the electronic and geometrical properties of Pt sites7 and the second illustrated Pt stabilization by synthesizing Pt-
based high entropy intermetallic compounds (HEIs). In another study, Chen et al. constructed stable single-site [PtZn] catalysts by assembling atomically ordered intermetallic alloy (IMA), achieving the highest propylene productivity of 83.2 mol\(\text{C}_3\text{H}_6\) g\(\text{Pt}\)\(^{-1}\) h\(^{-1}\). Furthermore, inert metals are essentially alloyed with Pt to dilute the Pt–Pt ensemble effect and thereby enhance catalyst stability and propylene selectivity against intermetallic compounds accompanied by a trade-off in initial intrinsic activity. Notably, conventional alloying-based methods are not the only ways to completely isolate Pt atoms; SiOZn-OH nests are also an effective tool for maximizing Pt dispersion primarily in the oxidized state. The materials were prepared to obtain the Fe-containing zeolites with the Pt loading method and contrasting materials (Pt/Fe-3-C1/2) are further described in the Supporting Information.

### RESULTS AND DISCUSSION

#### Synthesis, Morphological, and Textural Properties.
The Fe species were doped into the silicalite-1 zeolite through Fe-EDTA complexation during hydrothermal crystallization, hindering the formation of precipitates in a strongly alkaline environment. According to a previous study by Xiao and co-workers with slight modifications, Fe-EDTA was added to a gel containing tetraethyl silicate (TEOS), tetrapropylammonium hydroxide (TPAOH), and water for the crystallization of Fe-containing zeolites at a ratio of 1.0SiO\(_2\)/0.4TPAOH/\(x\)H\(_2\)O/\(y\)Fe/\(y\)EDTA \((x = 36–45, y = 0.006–0.045)\). After hydrothermal crystallization at 180 °C for 3 days, calcination was carried out to obtain the Fe-n carrier, which was then loaded with Pt to yield the final catalyst Pt/Fe-n. Detailed preparation of the hierarchical-like Fe-containing zeolites with the Pt loading method and contrasting materials (Pt/Fe-3-C1/C2) are further described in the Supporting Information.

All five catalysts exhibited a typical MFI structure, while no diffraction peaks belonging to the Pt metal were observed because of the low Pt loading. Additionally, peaks of Fe-related species were also not detected, indicating Fe incorporation into the skeleton or its good dispersion (Figure S1 and Table S1). The UV–vis and Raman spectra of these samples further confirmed that Fe in Pt/Fe-n got embodied into the zeolite framework, even at a Fe loading of up to 3 wt %; however, Pt/Fe-3-C1 had significantly larger Fe clusters as well as addition and exhibit over 95% propylene selectivity. Moreover, deactivation was insignificant in a pure propane atmosphere operating at 580 °C for 3 days, achieving propylene yields exceeding 400 mol\(\text{C}_3\text{H}_6\) g\(\text{Pt}\)\(^{-1}\) h\(^{-1}\) at a high weight hourly space velocity (WHSV), which is superior to most existing state-of-the-art Pt-based catalysts. Based on experimental and theoretical results, the structural elucidation of \(\equiv\text{Si}–\text{O}–\text{Pt}–\text{O}–\text{Fe}≡\) revealed the T4 location as a stable active site, where Pt anchoring through the zeolite diatomic linkage skeleton O is a pivotal factor for the stable atomic dispersion of Pt.
nanoparticles in addition to the skeletal Fe (Figures S2 and S3). N$_2$ adsorption–desorption isotherms of these samples depicted high and similar surface areas and pore volumes, which were not influenced by the Fe content (Figure S4 and Table S2). SEM images of these catalysts provided a visual indication of the average size of zeolite crystals that enlarged with an increasing Fe content (Figure S5), which was most evident at a Fe loading of 3% (Pt/Fe-4). Furthermore, the surface of Pt/Fe-3-C1 appeared less smooth compared to Pt/Fe-2, which could be related to the surface loading of Fe. Notably, a hierarchical-like morphology was observed at Fe contents of 0.96% and above; however, similar results were not obtained with EDTA addition without Fe complexation, suggesting that only the complexed form of Fe (EDTA-Fe) could influence zeolite crystallization, thus leading to morphological changes (Figure S6). To exclude the influence of water, since variable Fe contents corresponded to different concentrations of EDTA-Fe solution, Pt/Fe-3 was also synthesized in the presence of additional 3 mL of water, confirming that the simultaneous water increase did not affect the hierarchical-like morphology, given the apparent larger crystal size of Pt/Fe-4 (Figure S7).

Propane Dehydrogenation. The PDH performance of synthesized catalysts at 550 °C is shown in Figures 1a and S8. A high initial propane conversion value of 47.5% was obtained with Pt/Fe-3, which was higher than that of other Pt/Fe-1/2/4 and Pt/Fe-3-C1/C2. Moreover, Pt/Fe-3 exhibited a conversion of 46.3 and 96.2% propylene selectivity even after 20 h of operation. The lower performance of Pt/Fe-1 and Pt/Fe-4 compared with that of Pt/Fe-3 could be attributed to different reasons, mainly because of the sintering of Pt particles (Pt/Fe-1) and excessive coking caused by high Fe-4 acidity (Pt/Fe-4) (explained in more detail in the subsequent characterization section). Considering the effect of reaction temperature and atmosphere along with WHSV on the catalytic performance (Figure 1b,c), extreme H$_2$ pre-treatment and reaction temperature of 600 °C resulted in significant improvement in the propane conversion; however, the value decreased marginally with increasing reaction time. Noteworthy, the performance of Pt/Fe-3 did not degrade after 15 h in a pure propane atmosphere at 550 °C (26.3–27.1% conversion), and even raising the reaction temperature to 580 °C showed no significant deactivation after 3 days (39.2–36.5% conversion), demonstrating the high stability of the catalyst, to avoid the lack of deactivation perhaps due to excess activity and equilibrium limitations. This makes the stability test at equilibrium conversion not representative, so we further increased the WHSV (25.5 h$^{-1}$), making the conversion significantly lower than the equilibrium conversion value and the results showed significantly better stability (33.9–30.6% conversion). Despite an increase in WHSV by a factor of 10 (6–60 h$^{-1}$), the initial propane conversion was only reduced from 47.5 to 32.9% while obtaining higher propylene selectivity. Notably, the high propane conversion achieved at an extremely low Pt loading of 0.012 wt % at a WHSV of 60 h$^{-1}$ has not been previously reported in the literature. Furthermore, less than 2% propane conversion by Fe-3 alone at 550–600 °C indicated its minimal contribution to the PDH reaction performance, acting only as a carrier under such operating conditions (Figures S9a). Considering the inherent acidity of Fe-3 and elevated WHSV conditions, propane conversion by Fe-3 was also performed at a reduced WHSV of 2 h$^{-1}$, resulting in approximately 10% conversion; however, propylene selectivity was unsatisfactory. With further WHSV reduction, a corresponding increase in propane conversion values could be anticipated. The actual propane conversion to propylene was not high (Figures 9b), illustrating the need for conducting conversion reactions at higher WHSV. Figure 1d shows that Pt/Fe-3 achieved improved propylene yields (over 400 mol$_{C_3H_6}$ g$_{Pt}$$^{-1}$ h$^{-1}$ at high WHSV) and deactivation rates than most frontier catalysts owing to the lower Pt loading and high PDH performance (Table S3). Moreover, Pt/Fe-3 outperformed Pt/Fe-3-C1 and Pt/Fe-3-C2 counterparts with essentially equal Pt and Fe loadings, demonstrating the importance of all Fe species in Fe-3 skeletal iron, which mediated the dramatic improvement in PDH performance.

To monitor the influence of the alkali metal Na and water in the EDTA-Fe solution, the corresponding samples were prepared and compared with Pt/Fe-3 for PDH performance, revealing that these factors had no effect on the catalytic activity (Figures S10 and S11). For better comparison, Pt/Fe-3-catalyzed experimental propane conversion and conversion at thermodynamic equilibrium limits were studied as a function of temperature (Figures 1e and S12). Interestingly, the experimental conversion values at different temperatures and reaction atmospheres were similar to the thermodynamic equilibrium conversion values, further emphasizing the efficient PDH performance of Pt/Fe-3. Moreover, the comparison was made during the initial stage, in which side reactions usually contribute slightly; consequently, the actual reaction deviates more from the equilibrium conversion. A related analysis has been presented later while discussing the induction period of propane selectivity. Despite the evident stability of Pt/Fe-3, the catalytic activity slowly reduced with the accumulation of coke, indicating oxidative regeneration as an essential part of the process. The efficient regeneration stability was further confirmed by achieving 44% propane conversion and 97% selectivity even after three regeneration cycles compared to the initial run (Figure 1f). Concomitantly, the regeneration performance was tested at a high WHSV of 67 h$^{-1}$ to evaluate stability. After two regenerations, the performance dropped significantly, and the conversion rate essentially remained at around 22%; however, the deactivation observed was justified considering the extremely low Pt loading of below 0.01 wt % under these conditions (Figures S13). Apart from PDH reactions, Pt/Fe-3 was also applied to ethane dehydrogenation reactions, exhibiting efficient performance (Figure S14).

Construction of Pt/Fe-n Catalysts. Figure 2a shows a schematic representation of the hierarchical-like Fe-based zeolite (shown for Pt/Fe-3 here) synthesis process along with the Pt loading method. Furthermore, the hierarchical-like structure with stacking along the b-axis has been depicted, as shown in Figure 2b–d; this structural arrangement facilitates a reduction in diffusion limitations and allows a certain degree of PDH performance optimization. To better illustrate this point, a probe molecule 2,3-dimethylpyridine (DMPyr) containing two methyl groups showed slow diffusion in the MFI 10-MR channel, allowing time-resolved comparisons of the titration of acid sites within the bulk and hierarchical-like phase catalysts (Pt/Fe-1 vs Pt/Fe-3). Additionally, peaks at around 1635 cm$^{-1}$ were observed for both Pt/Fe-1 and Pt/Fe-3 during titration attributed to the Lewis acid site, with higher L acid amounts obtained in the first 10 min because of the larger surface area of Pt/Fe-1 (Figure S15). Moreover, a pronounced increase in the L acid amount with Pt/Fe-3 was noticed as time progressed, suggesting better diffusion properties of the
To explore Pt dispersion in Pt/Fe-3, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images at different resolutions are presented in Figure 2e–i. At an initial 10 nm resolution, small white Pt spots marked with yellow circles were observed, mainly occurring as clusters accompanied by a few nanoparticles. However, the spots consisted of numerous isolated Pt atoms, visible at a higher resolution (1 nm). The homogeneity of the Fe skeleton and its significant Pt dispersion ability as a carrier was reflected by the uniform appearance of Pt and Fe in the same position throughout the zeolite (Figure 2j). On comparing the HAADF-STEM images of the remaining samples (Figure S16), a clear association between an increase in the Fe content of the skeleton and prominent Pt anchoring, with no Pt nanoparticle formation, was observed except for Pt/Fe-1. In contrast, the Pt/Fe-3-C1 and Pt/Fe-3-C2 catalysts (Figures S16e and S17), with a combination of skeletal and exoskeletal Fe and entirely exoskeletal Fe, respectively, showed considerably larger Pt nanoparticles. This approach of stabilizing Pt species through incorporation into heteroatomic zeolites could also be extended partially to other catalysts, such as Pt/Co-3 and Pt/Ni-3, with Pt/Ni-3 exhibiting PDH performance relatively similar to Pt/Fe-3 (Figure S18). However, both catalysts did not show a hierarchical-like morphology and possessed fewer nanoparticles (Figure S19), again demonstrating the importance of skeletal Fe in Pt dispersion at the atomic level.

To gain insight into the skeletal Fe-mediated high Pt dispersion, several structural characteristics were explored. The $^{29}$Si and $^1$H MAS NMR spectra confirmed the presence of skeletal iron, and both isolated Si-OH and Si-(OH)-Fe exerted significant fixation effects on Pt species (Figures S20 and S21). Subsequent OH-FT-IR spectra delineated different OH species present in Pt/Fe-n catalysts in detail, with the H-bonded-OH groups having similar abilities (Figure S22). The current approach to isolating Pt atoms is different from Pt

Figure 2. (a) Schematic representation of the synthesis of a hierarchical-like Fe-based zeolite and Pt loading (taking Pt/Fe-3 as an example). Characterization of the Pt/Fe-3 sample: (b) high-resolution TEM imaging; (c, d) HAADF-STEM and AC-HAADF-STEM imaging on the [010] plane; (e–i) AC-HAADF-STEM imaging of the Pt distribution in Pt/Fe-3 and the corresponding enlarged images; (j) AC-HAADF-STEM imaging and elemental mappings for Si, O, Na, Fe, and Pt.

Figure 3. (a, b) Pt L$_{III}$-edge XANES and EXAFS spectra of Pt/Fe-3 and Pt/Fe-3-r. (c, d) Fe K-edge XANES and EXAFS spectra of Fe-3 and Pt/Fe-3. (e, f) Wavelet transform (WT) plots of Fe-3 and Pt/Fe-3. (g, h) Fe K-edge XANES and EXAFS spectra of Pt/Fe-3 and Pt/Fe-3-r. (i) In situ CO-DRIFTS spectra of various samples (r represents the sample after 4 h of PDH reaction).
anchoring to silanol nests reported by Qi et al.\textsuperscript{16} Besides, the H\textsubscript{2}-TPR test illustrated a clear difference between the nonskeletal and skeletal Fe, with skeletal Fe being stable because of its strong resistance to reduction (Figure S23). The anchoring of hydroxyl groups generated strong metal—support interactions after calcination, making the reduction of Pt species difficult, one of the evident reasons for high Pt dispersion. In addition to H-bonded-OH and isolated Si—OH, Si—(OH)—Fe increased with the skeletal Fe content, which could be another crucial factor in atomic Pt dispersion. Furthermore, XPS was employed to monitor the electronic states of the Pt/Fe-n catalysts. As shown in Figure S24a, Fe was essentially present in the +3 valence state without the formation of PtFe alloys. The Pt species in Pt/Fe-1 and Pt/Fe-3-C1, mainly embodied as nanoparticles, were not present in the 0 valence state after reduction but in the oxidation state because of strong metal—support interactions (Figure S24b). In contrast, no Pt 4f signal was detected in Pt/Fe-3 and Pt/Fe-4, indicating the stable bonding of Pt species within these zeolites through H atom replacement within the Si-OH group and interaction with the O atom.\textsuperscript{14}

Since the Pt 4f signal was not observed in Pt/Fe-3, detailed information on the electronic and coordination structures of Fe and Pt in Pt/Fe-3 was obtained through XAS recorded at Fe K and Pt L\textsubscript{III}-edges. The intensity of the white line for Pt/Fe-3 laid between Pt foil and PtO, indicating the presence of Pt species in Pt/Fe-3 in an oxidized state between 0 and +4 valence (Figure 3a).\textsuperscript{19,20} The corresponding FT \(k^4\)-weighted EXAFS profile in R space is shown in Figure 3b, where only a significant peak contributed by the Pt—O scattering pathway was examined. Moreover, the Pt foil standard was not detected in Pt/Fe-3 for the Pt—Pt peak, demonstrating the formation of isolated Pt atoms and stabilization by oxygen atoms in the zeolite. EXAFS fitting (Figure S25 and Table S4) provided the approximate quantitative chemical conformation of Pt coordinated to two oxygen atoms in Pt/Fe-3, which was further confirmed by DFT calculations (Figure S26). Specifically, the two O atoms were derived from Si—O—Fe and Si—O—Si, respectively. The Fe K-edges X-ray absorption near-edge structure (XANES) energies of Fe-3 and Pt/Fe-3 were similar to those of the reference Fe\textsubscript{2}O\textsubscript{3} (Figure 3c), indicating that Fe species consisted of isolated Fe\textsuperscript{3+} sites. This was further confirmed by extended X-ray absorption fine structure (EXAFS) and wavelet transform (WT) results, detecting only a strong peak attributed to Fe—O coordination without any Fe—Fe scattering path (Figure 3d-f). In addition, the XANES and EXAFS spectra of both Fe-3 and Pt/Fe-3 samples indicated the absence of PtFe alloys and were in general agreement, further demonstrating the stabilization of isolated Pt atoms through interactions with O atoms. Interestingly, the electronic structures and coordination environments concerning Pt and Fe remained essentially unchanged after 4 h of reaction, elaborating the stability of the isolated Fe and Pt sites (Figure 3a,b,g,h) accounting for stable PDH performance properties. Subsequently, in situ DRIFTS with CO adsorption was carried out to further acquire information on surface Pt ensembles in different catalyst samples (Figure 3i). For Pt/Fe-1, a prominent peak at 2077 cm\textsuperscript{-1} accompanied by a sharp peak at 2088 cm\textsuperscript{-1} was observed, which could be attributed to the CO adsorption on single Pt\textsuperscript{4+} atoms and well-coordinated Pt metal nanoparticles.\textsuperscript{21–23} Comparatively, Pt/Fe-3, Pt/Fe-4, and Pt/Fe-3-C1 showed only the CO adsorption peaks of single Pt\textsuperscript{4+} atoms and Pt nanoparticles. Moreover, CO adsorption peaks detected only at 2077 cm\textsuperscript{-1} in Pt/Fe-3 after regeneration tests further supported the presence and stability of the isolated Pt\textsuperscript{4+} atoms. These results are consistent with the atomic-level Pt dispersion observed in AC-HAADF-STEM, again illustrating the great stability of isolated Pt species.

The stability of Pt-based catalysts can also be interpreted through STEM visualization of the Pt state after the PDH reaction. After 20 h of reaction at 550 °C in a 25% propane atmosphere, the Pt state of catalysts essentially matched that of the reduced samples, except for the apparent appearance of large nanoparticles in Pt/Fe-2 (Figure S27). Subsequent visualization of Pt/Fe-3 under different temperatures and atmospheric conditions revealed that the Pt size appeared mainly dominated by “ultra-small clusters” without further magnifying resolution (Figures S28 and S29). Therefore, Pt/Fe-3 was visualized at high resolution under exposure to extreme reaction conditions for longer intervals (Figure 4). Figure 4a shows that PDH reactions carried out at higher temperatures compared to those in zeolite preparation did not destroy the zeolite skeleton. AC-HAADF-STEM imaging showed that the ultra-small spots were composed of isolated Pt atoms (Figure 4b–d). Significant Pt dispersion was further illustrated through elemental mapping (Figure 4e). Together, the high stability of the atomically dispersed O-bonded Pt atoms was confirmed by the combined results of XAS, in situ CO-DRIFTS, and AC-HAADF-STEM imaging.

The catalyst-associated acidity has a crucial effect on the PDH reaction; therefore, FT-IR spectra of all catalysts for

Figure 4. Characterization of spent Pt/Fe-3 (reaction conditions: 0.1 g of catalyst was mixed with 0.9 g of quartz sand, atmospheric pressure, pure C\textsubscript{3}H\textsubscript{8}, WHSV = 17 h\textsuperscript{-1}, 580 °C, 72 h). (a) AC-HAADF-STEM imaging on the [010] plane; (b–d) AC-HAADF-STEM imaging of the Pt distribution in Pt/Fe-3 and the corresponding enlarged images; (e) AC-HAADF-STEM imaging and elemental mapping for Si, O, Na, Fe, and Pt.
pyridine adsorption were determined (Figure 5a). The peaks at 1446 and 1597 cm\(^{-1}\) were assigned to Py-H, while the peak corresponding to the L acid site appeared at 1607 cm\(^{-1}\). The peaks at 1491 and 1545 cm\(^{-1}\) were attributed to the L&B acid and B acid sites, respectively.\(^{24,25}\) The B acid site peaks were observed to be weakened in all samples, suggesting a weak acidity that prevents pyridine from being well-protonated. In contrast, the position of the \(\nu_{8a}\) vibrational mode in the spectrum was highly sensitive to the intensity of the L acid site. Therefore, the variation in the L acid peak intensity suggests high acidity of the L acid site in Pt/Fe-\(n\), which becomes more pronounced with increasing Fe content (Figure 5b). Notably, Pt loading also exerted a similar effect, probably due to the O atom protonation that stabilized the small number of Pt atoms. This is consistent with a previous report by Zhang et al., wherein the amount of L acid increased following Hf loading.\(^{25}\)

The pyridine adsorption results were further verified by the NH\(_3\)-TPD curve; the first two peaks within 400 °C could be attributed to the skeletal Fe site involvement in the weak acidity of B acid and stronger L acid, respectively (Figure 5c).\(^{26,27}\) The excessive skeletal Fe content in Pt/Fe-4 resulted in higher acidity and acid content, which can lead to side reactions similar to those observed with large Pt ensembles. Furthermore, the increased coke production because of side reactions initiated by the overly acidic carrier (Pt/Fe-4) and the large size of the Pt ensemble (Pt/Fe-3-C1) was also demonstrated through O\(_2\)-TPO, TG, and Raman spectroscopy (Figure 5d–f). This indicates the requirement of a suitable carrier (Fe-3) for the atomic-level dispersion of Pt for the significant reduction in coke generation. The coke content produced by Pt/Fe-3 in a pure propane atmosphere at 580 °C within 3 days was barely higher than that produced by Pt/Fe-3-C1 (20 h). The first run of Pt/Fe-3 and subsequent air regeneration treatment showed that nearly 100% coke removal could be achieved at lower temperatures, as illustrated by TG and Raman spectroscopy results, with additional photographs of the used and regenerated catalyst (Figures S30 and S31).

The inherent acidity of Fe-\(n\) carriers and the activity of Fe-3 in the PDH reaction at low WHSV with poor propylene selectivity could be related to the induction period of propylene selectivity. Therefore, the PDH reaction was carried out for variable time intervals using different carriers in a pure propylene atmosphere; the estimation of the coke content of the reacted catalysts through O\(_2\)-TPO and TG analysis also...

Figure 5. Characterizations of synthesized catalysts. (a) Pyridine-adsorbed FT-IR spectra, (b) numbers of acid sites, (c) NH\(_3\)-TPD curves, (d) O\(_2\)-TPO curves, (e) TG profiles, and (f) Raman spectra. Reaction conditions (Pt/Fe-1, Pt/Fe-3, Pt/Fe-4, and Pt/Fe-3-C1): C\(_3\)H\(_8\)/N\(_2\) = 25/75, WHSV = 6 h\(^{-1}\), 550 °C, 20 h. Reaction conditions (Pt/Fe-3-pure propane): pure C\(_3\)H\(_8\), WHSV = 17 h\(^{-1}\), 580 °C, 72 h.

Figure 6. Calculated energy profiles along the minimum energy pathways and the optimized intermediates (side views, A–E) upon PDH reaction with the reduced Pt/Fe-3 (blue) and Pt/Fe-3-C1 (red, Pt(111)). Navy blue, pink, red, gray, yellow, and white spheres represent Pt, Fe, O, C, Si, and H atoms, respectively.
reflected the induction period as a critical issue for propylene selectivity (Figure S32). As shown in Figure 5, the carrier acidity increased markedly with increasing skeletal Fe content, which further corresponded to the simultaneous rise in coke content after 5 h of reaction with Fe-n (n = 1, 3, and 4) in a pure propylene atmosphere. In addition, the difference in the coke content after 1 h and 5 or 10 h of reaction was insignificant for Fe-3, indicating that the coke production mainly occurs at the beginning of the reaction and coincides with the induction period of propylene selectivity. Therefore, the actual true activity could be considered slightly lower because of coke generation in the initial stage. Accordingly, propane conversion after a reaction time of 20 h or more probably represents the true performance accurately. The value was more off the equilibrium conversion but still very high.

The production of coke precursors was further examined using in situ C\textsubscript{3}H\textsubscript{8}-DRIFT spectra (Figure S33). Compared to Pt/Fe-3-C1, Pt/Fe-3 showed a clear contribution to propylene desorption, resulting in less coke precursor generation from deep dehydrogenation. This was also verified by the C\textsubscript{3}H\textsubscript{8}-TPD profiles (Figure S34), thus obtaining over 96% propylene selectivity. Propane activation was also detected in real-time by in situ C\textsubscript{3}H\textsubscript{8}-DRIFT spectra (Figure S35). The higher intensity of the peaks corresponding to intermediate reaction species (\textit{Pt}=C\textsubscript{3}H\textsubscript{7}\textsuperscript{+} and \textit{Pt}=C\textsubscript{3}H\textsubscript{5}\textsuperscript{+}) in Pt/Fe-3 confirmed its enhanced initial propane conversion capacity, in agreement with subsequent kinetic analysis. The C\textsubscript{3}H\textsubscript{8}-TPS profiles (Figure S36), with the lowest response temperature for H\textsubscript{2} production by Pt/Fe-3, indicated an elevated initial C–H cleavage rate. Additionally, the reduced activation energy of Pt/Fe-3 (61.9 KJ/mol) compared to Pt/Fe-3-C1 (66.1 KJ/mol) also justified the highest PDH performance of Pt/Fe-3 (Figure S37).

DFT calculations were carried out to understand the reaction mechanism for the significant improvement in Pt/Fe-3 over Pt/Fe-3-C1 (Figures 6, S38, and S39). Silicalite-1 possesses 12 crystallographically distinct T-sites at 8(d) position within the unit cell; therefore, a 12 Fe substitution MFI model was constructed by replacing one of the eight positions (Figure S37). Here, out of the 12 models, T4 was selected as a more stable model with the site for Pt anchoring in Pt/Fe-3, as previously reported by Mayoral et al.\textsuperscript{28} Similar reports on the identification of Ti sites in TS-1 zeolites have shown the T4 site to be of higher priority.\textsuperscript{29} Based on the structural characterization, the corresponding optimized structures and energies of only Pt-coordinated O atoms from the Si–O–Si or Si–O–Si and Si–O–Fe bridges were compared (Figures S41 and S42). The interaction between Pt and O atoms from Si–O–Si and Fe–O–Si bridges was much stronger than that from the single Si–O–Si bridge, allowing proper anchoring of Pt atoms and successful fabrication of isolated Pt atoms in Pt/Fe-3. However, Pt/Fe-1 with minimal Si–O–Fe bridges more likely formed nanoparticles, in line with a previous study.\textsuperscript{30} Accordingly, PDH activity could be described by the first dehydrogenation barrier, which is the rate-determining step. A comparison of the dehydrogenation barriers from C\textsubscript{3}H\textsubscript{3} to C\textsubscript{3}H\textsubscript{2} in Pt/Fe-3 confirmed a higher priority for methyl dehydrogenation (2.32 eV) over methylene dehydrogenation (2.46 eV) (Figure S43). The corresponding dehydrogenation barrier for Pt/Fe-3 was marginally increased by about 0.24 eV compared to Pt(111), resulting in a relatively maximized pass propane conversion. In addition, propylene selectivity was determined by the difference between the third dehydrogenation barrier and the propylene desorption barrier.\textsuperscript{31} The binding strength of \pi\textsubscript{ads} adsorbed propylene on Pt/Fe-3 (–0.82 eV) was also weaker than that of di-\sigma on Pt(111) (–1.07 eV), further promoting the desorption of propylene on Pt/Fe-3 and thus leading to less coke generation (Table S5). Furthermore, C\textsubscript{3}H\textsubscript{2} produced by C\textsubscript{3}H\textsubscript{3} dehydrogenation existed in both n- and iso-propenyl forms, with both Pt/Fe-3 and Pt(111) showing a greater barrier to the production of iso-propenyl than n-propenyl (Figures 6 and S44–S47). C\textsubscript{3}H\textsubscript{2} produced by deep dehydrogenation, attributed to the isolated Pt atom in Pt/Fe-3, was considered a model precursor for coke formation, which could only interact with the Pt/Fe-3 surface through single bonds rather than forming more stable interactions with the three Pt–C as in the case of the corresponding Pt nanoparticles at a three-fold hollow site on Pt(111). The deep dehydrogenation of propylene on Pt/Fe-3 with a little higher free energy barrier (0.82 eV) was more heat-absorbing compared to the same step (0.80 eV) on Pt(111), resulting in a higher propylene selectivity for Pt/Fe-3.

The white spots observed in AC-STEM imaging consisted of isolated Pt atoms, consistent with the results of XAS and in situ CO-DRIFTS. However, the anchoring of Pt atoms only by the T4 site indicates further isolation of these atoms and more pronounced atomic dispersion, which in turn suggests the presence of other sites besides T4. Rietveld refinement of the synchrotron X-ray diffraction (SXRD) data enabled the direct visualization of heteroatom doping in the zeolite framework and the grafting of other species in the extra framework.\textsuperscript{31,32} Figure 7a,b shows the optimized crystal structures of Fe-3 and Pt/Fe-3; the corresponding atomic and structural parameters are summarized in Tables S6–S8. The Fe position was more likely located at the T6 site, while the Pt species were more stable in the 10-membered ring. Subsequent DFT calculations further confirmed the better stability of isolated Pt atoms in a 10-membered ring than other small rings (Figures 7c and S48). However, the calculated energy of Pt anchoring for the T4 site
in the five-membered ring was lower than that for the T6 site. Although some specific sites possessed lower energies than others (e.g., T4), these minor energy differences were insufficient to draw a definite conclusion about Pt atom location at specific sites. Hence, other sites besides T4, such as T6, might have a Pt anchoring effect, resulting in a “clustered-like Pt species” appearance in low-resolution AC-STEM imaging observed as white spots, which actually comprised isolated Pt atoms.

**CONCLUSIONS**

In this study, we have reported a conceptually designed catalyst composed of Pt species anchored via hydroxyl groups other than silanol nests. The isolated Pt atoms were stably bonded through the O framework in a hierarchical-like heteroatomic silicalite zeolite with a suitable acidity after subsequent calcination and reduction, which could achieve high propane conversions at different temperatures and atmospheres close to the thermodynamic limit. Moreover, no significant deactivation was observed for 3 days in a pure propane atmosphere at 580 °C, outperforming most of the cutting-edge Pt-based catalysts.

The introduction of Fe increased the stability of O interactions in the Fe—O—Si bridge compared to the Pt—O interaction in the Si—O—Si bridge, leading to the formation of an active site (≡Si—O—Pt—O—Fe≡). The Fe-doped T4 site expressed a stronger Pt anchoring effect, and the Rietveld refinement of the SXRD data indicated the presence of other anchoring sites, such as T6. However, the calculated energy for the T6 site was a little higher, which caused the Pt species at the isolated site to form “cluster-like shapes”, as observed in the AC-STEM imaging. The involvement of ≡Si—O—Pt—O—Fe≡ as a reaction center in the PDH reaction represented a specific mode, which induced the first dehydrogenation of the methyl group in C3H8 with a slightly higher energy barrier than Pt(111), ensuring an unparalleled initial propane conversion. The subsequent deep dehydrogenation of C3H6 at the ≡Si—O—Pt—O—Fe≡ active site also possessed a higher energy barrier. Moreover, the presence of isolated Pt atoms allowed C3H6 interactions only through a single bond, accelerating propylene desorption and leading to a higher propylene selectivity. These findings provide a promising route for the preparation of efficient Pt-based alkane dehydrogenation catalysts by isolating Pt ensembles into single sites using heteroatomic zeolites and hints toward the potential exploitation of other isolated site-anchored metal catalysts, such as Pd, for specific reactions.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c05042.

Experiments; characterization results (XRD, SEM, HAADF-STEM, UV–vis, Raman, OH-FITR, in situ C3H6/C2H4-DRIFTS, TPR/TPD/TPSR); DFT calculations; and other supplementary results and discussion of the PDH reaction and spectroscopy (PDF)

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**Notes**

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