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Transformation of Propane over ZnSnPt Modified Defective HZSM-5 Zeolites: The Crucial Role of Hydroxyl Nests Concentration

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Abstract: A series of ZnSnPt supported defective MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (30, 110, 700, and ∞) and hydroxyl nests concentration were prepared and characterized by multiple techniques including scanning electron microscopy (SEM), nitrogen physisorption, NH_3 -TPD, transmission electron microscopy (TEM), hydrogen temperature programmed reduction (H_2 -TPR), and Fourier transform infrared spectrometer (FT-IR). It was found that Brønsted acid sites ($\text{Si}(\text{OH})\text{Al}$) with strong acid strength and the hydroxyl nests with weak acid strength coexisted over the defective ZSM-5 zeolites and ZnSnPt Lewis acid sites preferentially located on the hydroxyl nests. The increase in the concentration of hydroxyl nests and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios apparently improved the distribution of ZnSnPt Lewis acid sites. The hydroxyl nest incorporated ZnSnPt Lewis acid sites showed extraordinary dehydrogenation ability. Specially, *operando* dual beam Fourier transform infrared spectrometer (DB-FTIR) was applied to characterize the propane transformation under reaction conditions. At low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the propane efficiently transforms into propene and aromatics (total selectivity of 93.37%) by the cooperation of Brønsted acid sites and ZnSnPt Lewis acid sites. While at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the propane mainly transforms into propene (selectivity of above 95%) and hydrogen. This study provides guidance for the preparation of highly efficient propane dehydrogenative transformation catalyst.

Keywords: defective MFI; hydroxyl nests; ZnSnPt Lewis acid sites; $\text{Si}(\text{OH})\text{Al}$; *operando* dual beam FT-IR spectroscopy

1. Introduction

Environmentally friendly and non-corrosive, solid acid catalysts (zeolites and zeolite-based catalysts) have been widely applied in numerous petrochemical processes [1]. A “hydroxyl-nest defect” over the silica–alumina zeolites was first produced by progressively removing the aluminum from the frameworks and substituting with nests of four hydroxyls [2]. Although the hydroxyl nests possess mild acidic properties [3–5], the catalytic function of the hydroxyl nests are seldom reported and merely testified to be effective in the Beckmann rearrangement [6–8]. The HZSM-5 zeolite with MFI topology has been widely employed in applications such as cracking, dehydrogenation, oligomerization, and aromatization due to their large surface area, excellent reactivity and stability, unique pore structure, and shape selectivity [9,10]. Usually, the upgrading of its catalytic performance depends on the posttreatments to adjust the acidic properties [11–14]. On account of the weak acidity of the hydroxyl nests, it provides another way for the designing of novel catalysts in heterogeneous reactions by regulating the ratio of hydroxyl nests to $\text{Si}(\text{OH})\text{Al}$ groups.

High-efficiency transformation of light alkanes is one of the greatest challenges of the present catalysis research. The introduction of Zn, Ga, and Pt species into HZSM-5 improved the dehydrogenative aromatization performance and inhibited the cracking of side-reactions [13,15–18]. The Cyclar process was jointly developed by BP and UOP using Ga–Pt modified ZSM-5 zeolite as the catalyst [19]. When propane was used as a feedstock, the aromatics yield announced was 63.1 wt% and the dry gas yield was 31 wt%. Nevertheless, the extremely high selectivity of the by-products and high cost of Ga–Pt modification catalysts hampered its further development. According to literature and our previous work, Zn modified HZSM-5 zeolites are effective catalysts for the dehydrogenative aromatization of light alkanes and exhibit comparable catalytic performance to Ga–Pt loaded ZSM-5 zeolite [20–31]. However, the generation of substantial amounts of dry gas (methane and ethane) by-products has inhibited the large-scale application of the light alkanes dehydrogenative aromatization over the Zn supported HZSM-5 zeolite [32–35]. According to our previous study [36], the addition of SnPt into Zn/HZSM-5 apparently improved the propane dehydrogenative aromatization performance. However, due to the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of HZSM-5, the Brønsted acidity and metal dispersion were not at the optimal status. Moreover, we found that Zn modified defective HZSM-5 catalysts obtained better performance than regular HZSM-5 catalysts in hexane aromatization, and the hydroxyl group stabilized Zn species exhibited better dehydrogenative performance [37].

Therefore, in this study, a series of ZnSnPt modified defective MFI zeolites (ZSM-5 and silicalite-1) with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (30, 110, 700 and ∞) and hydroxyl nests concentration are systematically studied. It is found that ZnSnPt Lewis acid sites are preferentially located on the hydroxyl nests with weak acidity rather than on the $\text{Si}(\text{OH})\text{Al}$ groups with strong acidity, and the size of metal particles is smaller and much more uniform at higher concentration of the hydroxyl nests. These ZnSnPt Lewis acid sites located on the hydroxyl-nest defects show superior propane dehydrogenation performance. For the ZnSnPt modified HZSM-5 zeolite with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30, the selectivity of propylene and BTX (benzene, toluene, xylene) is 52.92% and 40.45%, respectively, while the selectivity of C_1 – C_2 alkanes is only 6.63%. For the ZnSnPt modified HZSM-5 zeolite with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ∞ , propane mainly transforms into propene (above 95% selectivity) and hydrogen. *Operando* dual beam Fourier transform infrared spectrometer (FTIR) study unravels that the acidity of neighboring active sites over ZnSnPt Lewis acid sites located hydroxyl nests determines the transformation paths.

2. Results and Discussion

2.1. Defective MFI Zeolites Supported by Zn–Sn–Pt with Different $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratios

As shown in the scanning electron microscopy (SEM) images in Figure 1, the introduction of Zn, Sn, Pt into HZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios by impregnation has little influence on the crystal size and morphology (Figure 1). According to the XRD (X-ray diffraction) patterns shown in Figure S1, five characteristic diffraction peaks of the MFI structure are preserved [5] and no diffraction signals for metal species are observed, indicating that the metal species are highly dispersed.

Figure 1. Scanning electron microscopy (SEM) images of defective MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. (a) HZ30, (b) HZ110, (c) HZ700, (d) S-1.

According to the nitrogen physisorption results (Table 1), some important specifics related to the locations of Zn, Sn, and Pt on the ZnSnPt/MFI catalysts are found. The external surface area and the mesoporosity of ZnSnPt modified defective MFI catalysts obviously decreased compared with that of the parent zeolites. The external surface of the parent nano-MFI crystals in the aggregates formed the inter-crystal mesopores as revealed by the pore size distribution (Figure 2). After the modification with Zn, Sn and Pt species, the inter-crystal mesopores apparently decreased. Based on the abovementioned results, it is assumed that parts of the metals are located on the external surface of the catalysts. Moreover, it can be seen that the specific surface area and pore capacity of micropores also decrease after loading ZnSnPt. It is reasonable to deduce that some of the ZnSnPt metal particles are located inside the zeolite channels.

Table 1. Textural properties of the parent and Zn–Sn–Pt modified defective MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

Sample	HZSM-5				ZnSnPt/HZSM-5			
SiO ₂ /Al ₂ O ₃	30	110	700	∞	30	110	700	∞
S _{BET} ^a	425	342	380	443	364	291	293	354
S _{micro} ^b	334	232	232	364	310	212	196	324
S _{extern} ^b	91	110	148	79	54	79	97	30
V _{pores} ^b	0.35	0.27	0.28	0.30	0.24	0.23	0.21	0.22
V _{micro} ^b	0.23	0.14	0.14	0.16	0.18	0.13	0.13	0.12
V _{meso} ^c	0.12	0.13	0.14	0.14	0.06	0.10	0.08	0.10

^a BET method applied to the N_2 isotherm. ^b t -Plot method applied to the N_2 isotherm. ^c $V_{\text{meso}} = V_{\text{pore}} - V_{\text{micro}}$. V_{pore} was determined from the amount of N_2 adsorbed at $p/p^0 = 0.99$.

Figure 2. Pore size distribution of defective MFI zeolites (a) and Zn–Sn–Pt modified defective MFI zeolites (b) with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

2.2. Metallicity of ZnSnPt Lewis Acid Sites over Defective MFI Zeolites with Different $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratios

TEM was carried out to obtain the direct information about metal dispersion on ZnSnPt/MFI catalysts. As shown in Figure 3, the average size of metal particles is larger than 4 nm over the ZnSnPt/HZ30 catalyst. Moreover, it was found that the metal dispersion further enhanced with increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Over ZnSnPt/S-1, the metal particles decreased to 0–3 nm centering at less than 2 nm. These results suggest that small-sized metal particles are obtained at a high concentration of hydroxyl nests, as seen in Figure 3d. H_2 -TPR is performed to illustrate the interaction between the metals. In Figure S2, SnPt/HZ30 catalyst has only one hydrogen consumption peak at 645 K that is between Pt/HZ30 and Sn/HZ30 catalysts. This phenomenon suggests the formation of SnPt alloy particles on the SnPt/HZ30 catalyst. Based on our previous work [38], there is no hydrogen consumption peak on the Zn/HZ30 catalyst, and a hydrogen consumption peak at a high temperature attributed to strong interaction between the zinc and platinum species of $\text{Zn}_{1.0}\text{Pt}_{0.1}/\text{HZ30}$ catalyst. As shown in Figure 4, there are two hydrogen consumption peaks over the ZnSnPt modified defective MFI zeolites: One at around 633 K, which is associated with the formation of SnPt alloys; and the other at a high temperature, which shows strong interaction between zinc and platinum species. Thus, the H_2 -TPR characterization provided more convincing evidences for the formation of SnPt alloys and the interaction between platinum and small ZnO cluster.

Figure 3. TEM images and particles size distribution of Zn–Sn–Pt modified defective MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. (a) ZnSnPt/HZ30, (b) ZnSnPt/HZ110, (c) ZnSnPt/HZ700, (d) ZnSnPt/S-1 catalysts.

Figure 4. H_2 -TPR profiles of ZnSnPt modified defective MFI zeolites. (a) ZnSnPt/HZ30; (b) ZnSnPt/HZ110; (c) ZnSnPt/HZ700; (d) ZnSnPt/S-1.

2.3. Acidity of ZnSnPt Lewis Acid Sites over Defective MFI Zeolites with Different SiO₂/Al₂O₃ Ratios

The acidity of these samples is characterized by the FTIR spectra of the surface hydroxyl (OH-FTIR), NH₃-TPD (Figures 5 and 6), and pyridine adsorbed FTIR spectra (Py-FTIR) (Figure S3). OH-FTIR spectra suggested that the defective ZSM-5 contained Brønsted acid groups (3610 cm⁻¹) associated with framework aluminum (Si(OH)Al), isolated external silanol groups (3740 cm⁻¹), free internal silanol groups (3720 cm⁻¹), and hydroxyl nests (at around 3500 cm⁻¹) that consist of a number of silanol groups interacting through extended hydrogen bonding [3,34,39]. The modification of the MFI zeolites with Zn, Sn and Pt species led the Brønsted acid sites and hydroxyl nests to simultaneously decrease. However, the decreasing of hydroxyl nests is much more significant suggesting that the ZnSnPt is mainly located in the hydroxyl nests. Moreover, with increase in the SiO₂/Al₂O₃ ratios, the relative distance between the acid sites and ZnSnPt active sites also increased.

Figure 5. OH-FT-IR spectra of parent and Zn–Sn–Pt modified defective MFI zeolites with different SiO₂/Al₂O₃ ratios. (a) HZ30 and ZnSnPt/HZ30; (b) HZ110 and ZnSnPt/HZ110; (c) HZ700; ZnSnPt/HZ700; (d) S-1 and ZnSnPt/S-1.

Figure 6. (a) The NH₃-TPD profiles of defective MFI zeolites with different SiO₂/Al₂O₃ ratios; (b) Zn–Sn–Pt modified defective MFI zeolites with different SiO₂/Al₂O₃ ratios.

Generally, the NH₃-TPD profiles of defective HZSM-5 zeolites have two typical desorption peaks: one centered at about 230 °C and the other at 400 °C. The low temperature peak is associated with acid sites obtaining weak acidity [40,41]. The high temperature peak is associated with acid sites obtaining strong acidity. Due to the existence of Si(OH)Al groups with strong acid strength, the Zn modification also converts these Si(OH)Al groups with strong acidity into acid sites with medium and weak acidity. Thus, the overall amount of weak acid sites obtained by NH₃-TPD profiles shows no decrease. Only a slight signal of NH₃ desorption is obtained over the S-1 zeolite, demonstrating its weak acidic character.

Over ZnSnPt/S-1 catalyst, the signals of NH_3 desorption of the samples with ZnSnPt modification are strong that shows the stability of the Zn species on the hydroxyl nests can enhance the acidity of the ZnSnPt/S-1 zeolite.

In addition, Py-FTIR spectroscopy was carried out to follow the transformation of Brønsted and Lewis acid sites during the catalysts preparation. According to the Py-FTIR spectra of HZ110 and ZnSnPt/HZ110 in Figure S3, it can be seen that the absorbance at 1435 cm^{-1} attributed to the Lewis acid sites of the hydroxyl nests disappeared and a new peak that was attributed to the Zn Lewis acid sites appeared at 1450 cm^{-1} . Similar phenomenas were also observed for the other samples. The absorbance at 1540 cm^{-1} attributed to the Brønsted acid sites, still existed after loading the metals over these samples. Therefore, according to the OH-IR and Py-IR results, the metals preferentially located on the hydroxyl nests showed weak acidity.

2.4. Catalytic Performance of Zn–Sn–Pt Modified Defective MFI Zeolites with Different $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratios

The catalytic performance of parent and ZnSnPt modified defective MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios was tested by propane transformation. In Figure 7, it is obvious that the ZnSnPt modified defective MFI zeolites exhibit better catalytic performance than the parent zeolites. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of parent defective MFI zeolites have little significant effect on the propane product distribution. The selectivity in propane transformation over MFI zeolites is highly affected by the conversion degree and by the extension of consecutive reactions. The conversion of propane over the parent MFI zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios is low. At low conversion levels, propane undergoes cracking reaction with large amount of methane, ethane, and ethylene as main products. These results suggest that the ability of the ZSM-5 parent zeolites to activate propane is poor. At higher conversion levels, the activation by the hydride transfer mechanism predominates due to the formation of BTX [42]. The conversion of propane is enhanced significantly after the incorporation of Zn, Sn, and Pt species. The hydroxyl nest incorporated ZnSnPt Lewis acid sites showed extraordinary dehydrogenation ability. Over ZnSnPt/MFI catalysts, the decrease in the propane conversion with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios is caused by the reduction in the number of Brønsted acid sites, which weakens the interaction between Brønsted acid sites and the metal Lewis acid sites. The selectivity of propylene increases with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of MFI zeolites. For ZnSnPt/HZ700, the propane conversion and propylene selectivity is 24.35% and 98.51%, respectively. Moreover, for ZnSnPt/S-1, the propane conversion and propene selectivity is 19.05% and 96.43%, respectively. For ZnSnPt/HZ30, the selectivity of propylene and aromatics is 40.45% and 52.92%, respectively, and the selectivity of $\text{C}_1\text{--C}_2$ alkanes is only 6.63%, suggesting that when Brønsted acid sites are in close proximity to the high dispersion of metal clusters that are stably located on the hydroxyl nests, propane dehydrogenative aromatization occurred by synergistic catalysis between them.

In the propane aromatization process, the Brønsted acid sites are responsible for the oligomerization and cyclization, while Lewis acid sites catalyze the dehydrogenation of alkanes and cycloalkene intermediates. It is indicated that the difference in the propane transformation of ZnSnPt/MFI zeolites with various hydroxyl nests concentration should be not only attributed to their different acidity, but also sensitive to the relative positions of different active centers. Regardless of this, an appropriate ratio between Brønsted acid sites and hydroxyl nests concentration of ZnSnPt/MFI catalysts can improve the selectivity of aromatics. However, a significant decrease in proximity between the Brønsted acid sites and the other active species inhibits the oligomerization and aromatization of olefins, conversely increasing the propylene selectivity.

Figure 7. The performance of defective MFI zeolites (a,a') and Zn-Sn-Pt modified defective MFI zeolites (b,b') with different SiO₂/Al₂O₃ ratios in propane transformation with a fixed-bed reactor. (T = 610 °C, GHSV = 1800 h⁻¹, atmospheric pressure).

In order to further investigate the stability of ZnSnPt/MFI catalysts, a 30 h continuous propane transformation was performed. Figure 8 suggests that the conversion of propane and the selectivity of products over ZnSnPt/MFI catalysts with different SiO₂/Al₂O₃ ratios are stable during 30 h test.

Figure 8. Stability test on ZnSnPt/MFI catalyst with different SiO₂/Al₂O₃ ratios. T = 610 °C, atmospheric pressure, GHSV = 1800 h⁻¹. (a) The conversion of propane; (b) the selectivity of C₃H₆; (c) the selectivity of aromatics.

Operando DB-FTIR was employed to reveal the catalytic functions of ZnSnPt/MFI zeolites with different SiO₂/Al₂O₃ ratios (30, 110, 700, and ∞) and hydroxyl nests concentration under propane reaction conditions. In order to get more detailed information, the selected FT-IR profiles (1350–1650, 2800–3050, and 3300–3800 cm⁻¹) are displayed in Figure 9. Note that, in contrast to ZnSnPt modified defective MFI zeolites of high SiO₂/Al₂O₃ ratios, propane is more strongly adsorbed over ZnSnPt/HZ30 catalyst. As the temperature of propane adsorption enhanced, the absorbance of Si(OH)Al group at 3610 cm⁻¹ obviously decreased (Figure 9a (1)), which indicated that the Brønsted acid sites participated in the propane transformation. However, the initial step on metal clusters through propane dissociative

adsorption resulted in an obvious increase in surface C_xH_y species (Figure 9a (2)–(3)). The absorbance of CH_3 and CH_2 bending vibrations was at 1375, 1453 and 1395, 1471 cm^{-1} , respectively [34]. In addition, the absorbance at 1560 cm^{-1} could most likely be attributed to the precursors of aromatic compounds, and the absorbance at 1585 cm^{-1} attributed to $C=C$ double bond linked to Zn species [34,43,44]. In the presence of large number of Brønsted acid sites, the propane aromatization reaction was catalyzed by the cooperation between ZnSnPt metal sites and Brønsted acid sites. Over ZnSnPt/HZ110 catalyst, the ZnSnPt stably located on the hydroxyl nests and the absorbance of Brønsted acid sites slightly decreased with the increase in reaction temperature (Figure 9b (1)). This reveals that the amount of Brønsted acid sites involved in propane transformation is much lower than that of ZnSnPt Lewis acid sites. Therefore, only propylene is observed in the bending modes region (Figure 9b (3)). Abovementioned results suggest that the aromatization reaction is very sensitive to the location of the active center. When the Brønsted acid sites are far away from the other active site, the oligomerization and later aromatization of olefin intermediates are inhibited. Over ZnSnPt/S-1 catalyst, without the participation of Brønsted acid sites, the highly dispersed active species locating on the higher content of hydroxyl nests mainly catalyzed propane dehydrogenation. However, due to the weak adsorption and activation capacity of ZnSnPt/S-1 catalyst in propane transformation, the absorbance of CH_3 and CH_2 bending vibrations were not detected. This *operando* dual beam FTIR study suggests that the acidity of the neighboring active sites over the hydroxyl nest incorporated ZnSnPt Lewis acid sites determines the transformation paths of propane.

Figure 9. The *operando* DB-FT-IR spectra of propane transformation over (a) ZnSnPt/HZ30, (b) ZnSnPt/HZ110, (c) ZnSnPt/HZ700; (d) ZnSnPt/S-1 catalysts. The feeding GHSV of propane was about 8 h^{-1} .

3. Experimental Section

3.1. Materials

Nano-sized silicalite-1(S-1) and defective H-ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios of 30, 110, and 700 were supplied by Dalian Ligong Qiwangda Chemical Technology (DQ-TECH), Dalian, China.

Zn/MFI catalysts were prepared using the impregnation method at 353 K for 4 h. The catalysts were dried at 383 K for 12 h and calcined at 813 K for 6 h. The ZnSnPt/MFI catalysts were impregnated by successively loading stannum and platinum on the Zn/MFI catalysts. The modification catalysts were dried and calcined by the same method to obtain the ZnSnPt/MFI catalysts. Catalysts modified by three metals with different SiO₂/Al₂O₃ ratios were represented by ZnSnPt/HZ30, ZnSnPt/HZ110, ZnSnPt/HZ700, and ZnSnPt/S-1, respectively. Metal loadings measured by ICP are shown in Table S1.

3.2. Characterization

The amount of Zn, Sn, and Pt over ZnSnPt modified MFI zeolites was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an optima 2000DV instrument. The SiO₂/Al₂O₃ ratios were determined by X-ray fluorescence (XRF) measurements with a Bruker S8 TIGER spectrometer (Bruker, Madison, WI, USA). The surface morphology of zeolites was characterized by the scanning electron microscopy (SEM) on a Quanta 450 scanning electron microscope.

Nitrogen adsorption–desorption measurements were carried out with a Micrometrics ASAP 2020 instrument (Micromeritics, Atlanta, GA, USA) at 77 °C. Prior to measurements, the samples were pretreated in vacuum at 350 °C for 6 h. The classical Brunauer–Emmett–Teller (BET) model was used to calculate the specific surface area, while the t-plot method was used to discriminate the pore volume, the BJH method was applied to calculate the pore distribution.

The acidity of catalysts were characterized by OH-FTIR, Py-FTIR, and NH₃-TPD methods. The FTIR spectra of the surface hydroxyl groups (-OH) were recorded with a Nicolet is10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in the region of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. The catalysts were pretreated at 673 K under vacuum (10⁻³ Pa) for 4 h. After the cell was cooled down to 303 K, the spectrum of OH-FTIR was recorded. Pyridine adsorbed FTIR spectra (Py-FTIR) were measured by a Nicolet 6700 spectrometer, and the background spectra were recorded in the region of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ after pretreated in vacuum at 673 K for 4 h. The catalysts were exposed to pyridine at room temperature for 0.5 h. The wafers of catalyst samples containing chemisorbed pyridine were subjected to thermal treatment at 423 K in vacuum and cooled to room temperature, and then the IR spectra were recorded. NH₃-TPD was performed to characterized the overall acidity of the catalysts with a Quantachrome ChemBET 3000 chemisorb instrument. First, 150 mg catalysts were pretreated in He at 873 K for 1 h. Then the catalysts were cooled down to 373 K to absorb NH₃ for 0.5 h. In order to remove physically adsorbed NH₃, the catalyst samples were purged in He for 0.5 h with the flow rate of 50 mL min⁻¹. The NH₃-TPD profiles were recorded from 373 to 873 K with a rate of 16 K min⁻¹.

Transmission electron microscopy (TEM) images of the modified MFI zeolites were recorded on a microscopy (Tecnai F30 G2, FEI, Eindhoven, Netherlands).

The hydrogen temperature programmed reduction (H₂-TPR) measurements were performed to study the interaction of metals by Quantachrome ChemBET Pulsar TPR/TPD Automated Chemisorption Analyser (Shimadzu, Kyoto, Japan). The samples were pretreated in He flow at 673 K for 0.5 h, then cooled down to 303 K. H₂-TPR was performed by temperature programmed reduction in a mixture of 5% H₂ and Ar from 373 K to 1073 K at a rate of 10 K min⁻¹.

Operando DB-FT-IR study was applied to unravel the role of Zn, Sn, and Pt in propane transformation under real reaction conditions [28,38,45]. The catalysts were pressed into thin wafers, then pretreated in vacuum (10⁻³ Pa) at 673 K for 4 h. After the cell was cooled down to 303 K, the background spectra were recorded in the region of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

After that, the dual beam IR-cell reactor was filled with diluted propane (1% propane in N₂). Propane transformation was performed from 323 K to 673 K under the pressure of 0.1 MPa. Finally, the spectra were recorded by subtracting the background spectrum from the sample spectra.

3.3. Propane Transformation

The propane transformation was performed in a fixed-bed reactor. The reaction tube with an inner diameter of 10 mm was filled with 1 g catalyst. The propane transformation was carried out at 883 K, 0.1 Mpa, and GHSV was 1800 h^{−1}. The mass balance was obtained by weighing the gross weight of feedstock and products. Coke deposits over samples were ignored. The reaction products were analyzed with an online GC-14C gas chromatography.

4. Conclusions

Hydroxyl nest incorporated ZnSnPt Lewis acid sites showed extraordinary dehydrogenation ability over the defective MFI zeolites. The increase in the concentration of hydroxyl nests and SiO₂/Al₂O₃ ratios apparently improved the distribution of ZnSnPt Lewis acid sites. *Operando* dual beam FTIR study showed that the acidity and distance of neighboring active sites over the hydroxyl nest incorporated ZnSnPt Lewis acid sites determines the propane transformation paths. At low SiO₂/Al₂O₃ ratios, the propane efficiently transformed into aromatics by the cooperation of the neighboring Brønsted acid sites and ZnSnPt Lewis acid sites. While at high SiO₂/Al₂O₃ ratios, the propylene is mainly generated by cooperation of neighboring hydroxyl nests and ZnSnPt Lewis acid sites.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/7/571/s1>, Figure S1: XRD profiles of ZnSnPt/MFI zeolites with different SiO₂/Al₂O₃ ratios. Figure S2: H₂-TPR profiles of Sn or Pt modified defective MFI zeolites.

Author Contributions: J.L. and H.G. supervised the work; W.Z. and J.L. conceptualized and designed the experiments, analyzed the results, and wrote the manuscript; W.Z. performed the catalyst preparation, characterization and catalytic tests; L.L. and X.Z. performed the NH₃-TPD measurement; N.H. performed the argon physisorption measurements.

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