Article

Catalytic Cracking for Propylene Production over Au Catalyst Supported by External Surface-Modified ZSM-5 Zeolite

Lei Wu, Huijuan Su, Xun Sun, Libo Sun, Lijun Zhao and Caixia Qi *

Yantai Key Laboratory of Gold Catalysis and Engineering, Shandong Applied Research Center of Nanogold Technology (Au-SDARC), School of Chemistry & Chemical Engineering, Yantai University, Yantai 264005, China; wuleiwssf@163.com (L.W.); suhuijuan2012@ytu.edu.cn (H.S.); sunxun@ytu.edu.cn (X.S.); sunlibo@ytu.edu.cn (L.S.); zhaolijun0511@126.com (L.Z.)

* Correspondence: qicx@ytu.edu.cn; Tel./Fax: +86-0535-6911732

Abstract: To improve the yield of propylene in fluidized catalytic cracking, a series of different Au/ZSM-5-TOS catalysts were prepared by modifying ZSM-5, using an external surface modification method and Au nanoparticles. The modified catalyst maintained the MFI structure of ZSM-5, whereas the pore-opening size of the zeolite relatively decreased, without affecting its internal structure. The acidity of ZSM-5, especially the Brønsted acidity, reduced. Among the studied catalysts, the 0.2 wt% Au/ZSM-5-1%TOS catalyst exhibited the best feedstock conversion and propylene selectivity, along with a significant increase in propylene selectivity and a slight decrease in the conversion of light diesel oil, even after water vapor treatment at 800 °C for 4 h. Its catalytic activity at 360 °C exceeded that of ZSM-5 at 460 °C, showing great application potential in petrochemical processes.

Keywords: external surface modification; ZSM-5; gold; propylene; shape-selective catalyst

1. Introduction

Owing to the continuous changes in the global consumer culture, the demand for various types of processed propylene products continues to grow, particularly in the Asia-Pacific region, which is expected to use more than 100 million tons of propylene by 2023. Propylene is used to produce polypropylene, butyl alcohol, propylene oxide, acrylonitrile, phenol, and acrylonitrile [1]. As the main downstream product, the growing demand for polypropylene has greatly increased the demand for propylene [1]. Current propylene production is mainly divided into two main paths—steam cracking and catalytic cracking. The type of steam cracking feedstock and operating conditions significantly affect the product yield. As the highest energy-consuming process in the petrochemical industry, the reaction temperature can reach 800 °C, and large amounts of CO2 are released [2,3]. The temperature used in catalytic cracking is about 500 °C; the selectivity of propylene is high and the device has strong adaptability [4,5]. In catalytic cracking using solid acid catalysts, the product distribution can be controlled by adjusting the acid quantity, acid strength, acid type, and acid distribution to achieve high propylene selectivity [6].

Owing to its porous structure, ZSM-5 shows excellent shape-selective catalytic activity. The SiO2/Al2O3 ratio can be adjusted to endow different acidic properties. ZSM-5 also shows good hydrothermal stability and strong resistance to carbon deposition [7–12]. The modification method of ZSM-5 affects the physical and chemical properties of the resulting catalysts, affecting their catalytic performance. The methods include high-temperature water vapor treatment [13–15], alkali treatment [16,17], and element modification [18–32]. Our previous study showed that Au nanoparticle-modified ZSM-5 exhibited a positive contribution in a higher propylene selectivity and the feed conversion at a relatively lower reaction temperature, in the catalytic cracking of light diesel oil [19,26]. Shape-selective catalysis using zeolites plays an important role in catalytic cracking, aiming to increase the yield of the target products or inhibit side reactions. For the catalytic
cracking reaction over zeolites, the acidic sites on the external surface and mesoporous wall are located in a large space, which makes it easy to initiate bimolecular reactions, and it is not conducive to the production of low-carbon olefins and other target products. To further improve the propylene yield in fluidized catalytic cracking, a series of different Au/ZSM-5-TOS catalysts were prepared by modifying ZSM-5, using an external surface modification method and Au nanoparticles in this study.

External surface modification methods can decrease the pore-opening size of zeolites and cover the acidic sites of the external surface, without affecting their internal pores; however, the size of the modifier molecule must be larger than the zeolite pore size to prevent the modifier from entering the pores, so that they only interact with the outer surface of the zeolite. M. Niwa et al. first proposed this method [33–37], by using Si(OCH₃)₄ to modify mordenite, ZSM-5, H-mordenite, Pt-mordenite, and H-mordenite zeolites, using a chemical vapor deposition (CVD) method. However, this method requires a vacuum, large investment, and complex operation, making it difficult to apply industrially. Gao Zi et al. proposed the use of chemical liquid deposition (CLD), instead of CVD, to adjust the pore size of NaY, NaZSM-5, and HZSM-5 zeolites with silicon alkoxides and achieved ideal results [38]. Y.T. Cheng et al. adjusted the pore size of ZSM-5 zeolite successfully, using TEOS liquid deposition to produce p-xylene from lignocellulosic biomass, via catalytic fast pyrolysis [39].

In this study, trimethoxyoctadecylsilane (TOS) was used as a surface modification agent, to modify the external surface of ZSM-5 zeolite for an easier subsequent processing. Subsequently, nanogold particles were loaded onto the modified ZSM-5 to improve the catalytic cracking performance of octane and light diesel oil. Notably, not only the propylene selectivity and the conversion of the feed were enhanced significantly, but also the reaction temperature was considerably lowered [19,26,27].

2. Results

2.1. Catalytic Testing on N-Octane and Light Diesel Oil Cracking

Figure 1 shows the results obtained for the reaction temperatures of n-octane catalytic cracking over the catalysts 0.1%Au/ZSM-5-y%TOS and x%Au/ZSM-5-1%TOS, together with ZSM-5 and ZSM-5-1%TOS. The n-octane conversion and propylene selectivity of all the catalysts increased with increasing reaction temperature. Compared with the catalytic results obtained over ZSM-5, higher n-octane conversion, at all the tested temperatures, and propylene selectivity, at temperatures greater than 360 °C, were obtained over the two samples of ZSM-5-1%TOS and 0.1%Au/ZSM-5-1%TOS, when changing the TOS concentration and keeping the Au loading constant. The catalyst 0.1%Au/ZSM-5-1%TOS showed better performance with an increase in n-octane conversion and a slight enhancement in propylene selectivity. Subsequently, the effect of Au loading on the catalytic performance was investigated at a constant 1%TOS concentration. The catalyst 0.2%Au/ZSM-5-1%TOS showed the best n-octane conversion and propylene selectivity. Not only was there a continual enhancement in n-octane conversion even at the lower temperatures of 260 and 310 °C achieved, but also a great improvement in propylene selectivity at temperatures greater than 360 °C. The reproducible experimental results confirmed these phenomena.

Notably, at a reaction temperature of 360 °C, the conversion of n-octane increased from 92.0% to 100%, and the selectivity of propylene increased from 44.5% to 57.6%, compared with the parent ZSM-5. Furthermore, its catalytic performance at 360 °C even exceeded that of ZSM-5 zeolite at 460 °C (Conv.: 98.8%, Sel.: 53.7%), and the catalytic cracking reaction temperature reduced by more than 100 °C. This further reflects the unique feature that a gold catalyst works great under mild reaction conditions [40,41].

Catalytic cracking catalysts are often aged in water vapor at high temperatures in industrial application, to enhance their hydrothermal stability. Table 1 shows the catalytic cracking results of light diesel oil over ZSM-5 and the optimized 0.2%Au/ZSM-5-1%TOS catalysts, before and after water vapor treatment. Apparently, the modified 0.2%Au/ZSM-5-1%TOS catalyst had a more improved conversion rate, microreactivity, and propylene
selectivity than the parent ZSM-5 catalyst. After a high-temperature water vapor treatment at 800 °C for 4 h, although the activity of both catalysts was partially lost, the propylene selectivity improved, and the Au-modified ZSM-5 catalyst still showed a higher conversion rate, microreactivity, and propylene selectivity than the parent catalyst, especially at lower temperatures. These results indicate that the studied Au catalyst was supported on the modified ZSM-5 zeolite, using a suitable amount of TOS, and Au enhanced the catalytic performance and stability for the catalytic cracking reaction, at a much lower reaction temperature (such as 360 °C) than those reported so far [1–32]. This result indeed shows great potential in energy saving for the petrochemical process.

![Figure 1](image1.png)

**Figure 1.** Catalytic cracking of n-octane over the catalysts of 0.1 wt% Au/ZSM-5-y%TOS (A,B) and the catalysts of x%Au/ZSM-5-1wt%TOS (C,D), together with the parent catalyst of ZSM-5 and ZSM-5-1wt%TOS.

| Catalyst | Temperature (°C) | Product Distribution (%) | Conversion (%) | MAT (%) | Propylene Selectivity (%) |
|----------|------------------|--------------------------|----------------|---------|---------------------------|
|          |                  | Dry Gas+LPG a            | Gasoline       | Diesel Oil |                          |
| Z-before | 360              | 47.8                     | 6.6            | 45.6     | 53.5                      | 54.5 | 42.6 |
|          | 410              | 45.8                     | 5.8            | 48.4     | 50.6                      | 51.6 | 44.5 |
|          | 460              | 46.8                     | 5.7            | 47.5     | 51.5                      | 52.5 | 47.2 |
| 0.2Au/Z-1T | 360              | 44.7                     | 10.4           | 44.9     | 54.2                      | 55.1 | 42.9 |
|          | 410              | 46.8                     | 9.1            | 44.1     | 55.0                      | 55.9 | 46.6 |
|          | 460              | 47.9                     | 7.7            | 44.4     | 54.7                      | 55.6 | 48.7 |
| Z-after  | 360              | 34.0                     | 1.7            | 64.3     | 34.4                      | 35.7 | 46.4 |
|          | 410              | 34.0                     | 1.2            | 64.8     | 33.9                      | 35.3 | 57.2 |
|          | 460              | 36.2                     | 1.3            | 62.5     | 36.1                      | 37.5 | 56.8 |
| 0.2Au/Z-1T | 360              | 38.3                     | 3.7            | 58.0     | 40.8                      | 42.0 | 46.6 |
|          | 410              | 39.4                     | 1.8            | 58.8     | 39.9                      | 41.1 | 58.2 |
|          | 460              | 35.1                     | 2.3            | 62.6     | 36.1                      | 37.4 | 59.2 |

a LPG means liquefied petroleum gas. The calculations were done based on Equations (3) and (4) of Section 4.3.
2.2. X-ray Diffraction (XRD) Measurements

To understand the effect of the catalyst preparation process on the crystal structure of ZSM-5, the catalyst samples were characterized by powder XRD measurements. All the catalysts exhibited characteristic diffraction peaks of ZSM-5 with 2θ at 7.9, 8.8, 23.1, 23.9, and 24.3°, as shown in Figure 2. This proves that they all have a typical MFI topological structure [5,6,8,10,13,16], indicating that the crystal phase structure of ZSM-5 was maintained during the preparation. The diffraction peaks of Au (2θ = 38.2 and 44.4°) [42] were not detected in ZSM-5, probably due to the good dispersion or low loading of Au nanoparticles. In addition, as the concentration of loaded Au increases, the more heteroatoms (e.g., Cl) are introduced by the Au precursor Au(en)3Cl3 and the more severe the damage is to the zeolite structure, resulting in a weakening of the peak intensity.

![Figure 2. XRD patterns of catalysts. (A) 0.1wt%Au/ZSM-5-y%TOS and (B) x%Au/ZSM-5-1wt%TOS with ZSM-5 and ZSM-5-1wt%TOS.](image)

2.3. N2 Adsorption–Desorption Isotherms

The changes in the specific surface area and pore size distribution of the modified zeolites were investigated by N2 adsorption–desorption isotherms. The N2 adsorption–desorption isotherms of the Au/ZSM-5-TOS series catalysts are shown in Figure 3A,C. All the samples displayed type IV isotherms with an H4 hysteresis loop, indicating a microporous structure containing some slit mesopores, according to the IUPAC classification [5,6,8,10,13,16,43]. The corresponding NLDFT pore size distribution curves in Figure 3B,D support this conclusion. Interestingly, another small peak appeared at a relatively higher position in the micropores range of 0.5–0.6 nm, after the modification of TOS and Au nanoparticles, indicating that the pore-opening sizes of ZSM-5 micropores were, therefore, narrowed. Because the molecular size of TOS is much larger than that of a ZSM-5 pore, it cannot enter the deep pores and mainly interacts with the external surface. Based on the results obtained for ZSM-5-1%TOS, most of the silica particles decomposed by TOS are probably mainly embedded in the external surface and some silica particles entered the pore-opening area and effectively narrowed the pore openings.

By carefully observing the difference in the change in micropores in the range of 0.5–0.6 nm after the modification, it was found that the peak obtained for the sample of 0.2%Au/ZSM-5-1%TOS exhibited the highest conversion and propylene selectivity among all the catalysts, with a minor revision to the micropores of the parent ZSM-5 at 0.5–0.6 nm. This means that more regular micropores of ZSM-5 lead to a higher propylene selectivity, consistent with our previous study [26].
2.4. Transmission Electron Microscopy (TEM) Observations and EDS Measurements

The distribution situation of Au nanoparticles on ZSM-5 was studied using TEM analysis and EDS measurements over the (0.1–0.5%)Au/ZSM-5-1%TOS catalysts. Figure 4 shows the TEM image of the representative catalyst of 0.2%Au/ZSM-5-1%TOS; the size distribution of the Au nanoparticles is very wide, regardless of the Au loading, from a few nanometers to nearly a hundred nanometers. Figure 4D is a partial enlargement of Figure 4B. The nanoparticles also showed different shapes (flat, spherical, etc.) and exhibited different contact modes with ZSM-5. Some nanoparticles simply adhered to the surface of ZSM-5. Some of the Au nanoparticles were mixed in the spaces between the ZSM-5 particles, while other nanoparticles were embedded in the zeolite. Figure 5 shows the elemental mapping of Au, Si, and Al for the 0.2%Au/ZSM-5-1%TOS catalyst. This shows that the Au nanoparticles were homogeneously dispersed on ZSM-5, indicating that the existence of much smaller Au particles were not observed by the TEM images shown in Figure 4. The same observations and EDS elemental mapping images were also obtained over the other four Au/ZSM-5-1%TOS catalysts. Combining with the irregular change in the pore-opening size range of 0.5–0.6 nm micropores of the modified catalysts (Figure 3B,D), it is difficult to say that none of the small Au particles entered the micropores of ZSM-5.

2.5. NH₃ Temperature-Programmed Desorption (TPD) Measurements

The acidity, one of the dominant factors in the catalytic cracking reaction, was characterized by NH₃-TPD measurements. Figure 6 shows the TPD of ammonia of the Au/ZSM-5-TOS series of catalysts. All the catalysts exhibited three ammonia desorption peaks, with weakly acidic sites at around 120 °C, medium acidic sites at around 215 °C, and strong acidic sites at around 440 °C. Table 2 shows the specific acid content of the Au/ZSM-5-TOS catalysts.
Figure 4. TEM images of 0.2%Au/ZSM-5-1%TOS catalyst at four different spots (A–D).

Figure 5. Element mapping of Au, Si, and Al in 0.2%Au/ZSM-5-1%TOS catalyst.

Compared with ZSM-5, the strong acid content of all the modified catalysts clearly decreased, while the weak acid content slightly increased. When loaded with 0.1 wt% Au, the strong acid content of the modified catalysts continually decreased with an increase in the TOS amount, while the contents of medium and weak acidity first increased and then decreased. When maintaining a constant 1%TOS concentration with increasing Au loading, the contents of strong and weak acidity continually increased, except for the samples with 0.1 and 0.2 wt% Au loading, which exhibited the same change trend with TOS modification. Taking account of the catalytic data in Figure 1, the largest decrease in strong acid content, moderate decrease in medium acid content, and moderate increase in weak acid content occurred at the optimal catalyst 0.2%Au/ZSM-5-1%TOS, among all the samples. Its strong acid content decreased by 54.9%, from 0.051 to 0.023 mmol·g⁻¹, and its medium acid content decreased by 25.4%, from 0.074 to 0.058 mmol·g⁻¹. Its weak acid content also increased by 25.4%, from 0.067 to 0.084 mmol·g⁻¹.
The absorption peak at 1450 cm\(^{-1}\) from pyridine adsorption infrared spectroscopy. Figure 7 shows their Py-IR spectra, along with Table 2.

Generally, SiO\(_2\) (originated from TOS modification), mainly located on the external surface and mesoporous wall, significantly reduced the strong acid content of the parent ZSM-5. Gold modification simply increased both strong and weak acid contents, but a small amount of gold (0.1 wt% and 0.2 wt% nominal loading) did not make a further positive contribution in the total acid content. From the catalytic results in this study, we may conclude that the acidity of the catalyst has no linear relationship with the catalytic activity, although this is an acid-dominant reaction and strong acidity was acclaimed to be good for hydrocarbon catalytic cracking [43,44].

### 2.6. Pyridine Adsorption Fourier Transform Infrared (Py-IR) Measurements

In addition to the TPD of ammonia, the effects of external surface modification and Au nanoparticles on the distribution of Lewis acids and Brønsted acids in two representative catalysts, 0.1%Au/ZSM-5-1%ZSM-5 and 0.2%Au/ZSM-5-1%TOS, were evaluated, using pyridine adsorption infrared spectroscopy. Figure 7 shows their Py-IR spectra, along with those of ZSM-5 and ZSM-5-1%TOS, at desorption temperatures of 150, 300, and 450 °C. The absorption peak at 1450 cm\(^{-1}\) is the characteristic peak of the Lewis acid sites and the absorption peak at 1540 cm\(^{-1}\) is the characteristic peak formed by the adsorption of pyridine molecules on the Brønsted acid sites of ZSM-5. Table 3 shows the distribution of Brønsted and Lewis acids for these two catalysts, along with a comparison with those of the ZSM-5 and ZSM-5-1%TOS catalysts. The amount of Brønsted and Lewis acids was obtained using the extinction coefficient method.

### Table 2. NH\(_3\)-TPD data of Au/ZSM-5-TOS catalysts.

| Sample      | Total Acidity /mmol g\(^{-1}\) | Strong Acidity /mmol g\(^{-1}\) | Medium Acidity /mmol g\(^{-1}\) | Weak Acidity /mmol g\(^{-1}\) |
|-------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------|
| Z-5-1T      | 0.192                           | 0.051                           | 0.074                           | 0.067                       |
| 0.1Au/Z-0.5T| 0.179                           | 0.035                           | 0.069                           | 0.075                       |
| 0.1Au/Z-1T  | 0.190                           | 0.032                           | 0.078                           | 0.080                       |
| 0.1Au/Z-2T  | 0.207                           | 0.026                           | 0.084                           | 0.097                       |
| 0.1Au/Z-3T  | 0.155                           | 0.019                           | 0.053                           | 0.083                       |
| 0.1Au/Z-4T  | 0.145                           | 0.015                           | 0.053                           | 0.077                       |
| 0.2Au/Z-1T  | 0.165                           | 0.023                           | 0.058                           | 0.084                       |
| 0.3Au/Z-1T  | 0.237                           | 0.042                           | 0.081                           | 0.114                       |
| 0.4Au/Z-1T  | 0.218                           | 0.039                           | 0.071                           | 0.108                       |
| 0.5Au/Z-1T  | 0.235                           | 0.040                           | 0.078                           | 0.117                       |

Figure 6. NH\(_3\)-TPD profiles of catalysts 0.1 wt% Au/ZSM-5-y%TOS (A) and x%Au/ZSM-5-1wt%TOS (B), with ZSM-5 and ZSM-5-1wt%TOS.
Compared with ZSM-5, the concentrations of the Brønsted and Lewis acids of the modified catalysts decreased at different temperatures, and the $C_B/C_L$ also decreased, especially the contents of the strong and moderate Brønsted acids, which decreased more than that of the Lewis acids. When the Au loading was 0.2 wt%, the contents of the Lewis acids did not change much; however, the strong Brønsted acid content further decreased by about 50%, with a relatively significant increase in the weak Brønsted acid. As a result, the ratio of Brønsted acid sites to Lewis acid sites (B/L) clearly decreased after the modification. Especially, the ratio of strong Brønsted acid sites to strong Lewis acid sites ($S_B/S_L$, for $C_B/C_L$ at 450 °C) sharply decreased. The results are consistent with the conclusion of the NH$_3$-TPD measurements.

### 3. Discussion

As shown in Figure 1, a modified ZSM-5 catalyst with 0.2 wt% Au and 1 wt% TOS exhibited excellent performance in the catalytic cracking of n-octane and light diesel oil. Up to now, a variety of modification methods have been developed to make ZSM-5 with good catalytic cracking performance. For example, Ai Sha et al. [27] used a Au-Zn-modified HZSM-5 catalyst for the catalytic cracking of n-butane at 550 °C. The conversion increased from 33.9% to 70.9%, but the selectivity decreased from 14.8% to 10.4%. Xu Hou et al. [22] modified ZSM-5 with Zr and found that it had a certain promoting effect on the cracking of n-pentane at 500 °C. Notably, almost all the current catalytic cracking reactions are carried out above 500 °C, and the high activity achieved at a much lower temperature of 360 °C in this study has never been obtained before [19,26,27].

Clearly, both TOS and nanogold particles, of suitable amounts, play positive roles in improving the catalytic cracking performance, as observed from the data corresponding to the comparison of the ZSM-5, ZSM-5-1%TOS and 0.2 wt% Au/ZSM-5-1%TOS catalysts, indicating a slight increase in the conversion of octane and propylene selectivity at temperatures greater than 360 °C, over a 1%TOS modified ZSM-5 catalyst and significant improvement in both values when 0.2 wt% gold was loaded onto the sample of ZSM-5-1%TOS.

Brønsted acid sites are usually considered as the active sites for hydrocarbon catalytic cracking and the pore structure plays a key role in the improvement of the selectivity of light olefins [44]. Jung et al. found that a high conversion and a high yield of alkenes were

---

**Table 3.** Py-IR data of ZSM-5, ZSM-5-1%TOS and 0.1 and 0.2%Au/ZSM-5-1%TOS catalysts.

| Sample     | $C_B$/umol g$^{-1}$ | 150 °C | 300 °C | 450 °C | 150 °C | 300 °C | 450 °C | 150 °C | 300 °C | 450 °C |
|------------|---------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Z          | 176.1               | 129.4  | 67.2   | 260.6  | 112.4  | 34.3   | 0.68   | 1.15   | 1.96   |
| Z-1T       | 303.4               | 191.1  | 111.3  | 251.6  | 121.7  | 30.4   | 1.21   | 1.57   | 3.72   |
| 0.1Au/Z-1T | 210.6               | 81.8   | 48.3   | 205.9  | 79.4   | 28.2   | 1.02   | 1.02   | 1.96   |
| 0.2Au/Z-1T | 242.9               | 99.2   | 23.8   | 206.3  | 88.6   | 30.1   | 1.18   | 1.12   | 0.79   |

---

**Figure 7.** Py-IR spectra of the samples at 150, 300, and 450 °C, respectively.
obtained over ZSM-5 zeolite, with a large amount of strong acid sites [16]. However, a clear decrease in the number of Brønsted acid sites was detected over the modified ZSM-5 in this study, using Py-IR (Figure 7), mainly caused by TOS external surface modification. From the point of view of the contribution of acidity to catalytic cracking activity, less TOS and more Au particles (not nominal 2 wt% in the optimal catalyst) could obtain a very active catalyst in this work. However, this was not the case. Wang et al. found a synergistic effect between the acid properties and pore structures in the propylene production process of biomass-derived glycerol to aromatics, over hierarchical HZSM-5 zeolites [45]. As suggested by our N\textsubscript{2} adsorption–desorption analysis in Figure 3B,D, some of the SiO\textsubscript{2}, decomposed from TOS, and Au particles near the pore openings and internal micropores may make a space confinement that causes an increase in the propylene selectivity. Therefore, the optimal catalytic performance of the modified catalyst resulted from the moderate acidity and suitable pore size distribution.

Furthermore, the improved conversion in the optimized catalyst was partially attributed to the possibility of nanogold in dehydrogenation [46], along with the contribution of mesopores in cracking [17]. The dehydrogenation of alkane could form olefin and initiate, or at least enhance the cracking reaction [47]. It has been reported that Au-based catalysts work well for ethanol [48] and benzyl alcohol dehydrogenation [49] at low temperatures. Further investigation into the dehydrogenation of alkane and the studied catalysts is under way.

4. Materials and Methods

4.1. Catalyst Synthesis

In this study, all the chemicals were obtained from commercial suppliers (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and Xiya Reagent, Chengdu, China) and used as received, without further purification.

Au(en\textsubscript{2})Cl\textsubscript{3} preparation included the following steps: The Au(en\textsubscript{2})Cl\textsubscript{3} precursor was prepared by adding 0.09 mL of ethylenediamine dropwise to 2 mL (0.1 g/mL) of HAuCl\textsubscript{4} solution with stirring. The obtained mixture was stirred for another 30 min at room temperature, and then 14 mL of ethanol was added dropwise under stirring. The material was recovered by centrifugation with ethanol, after stirring continuously for 30 min. The sample was denoted as Au(en\textsubscript{2})Cl\textsubscript{3}, after being vacuum-dried at 40 °C for more than 12 h.

Au/ZSM-5 catalysts were prepared using the following steps: ZSM-5 (Si/Al = 37.3) was calcined at 550 °C in the air for 4 h, before further treatment. TOS was dissolved in methylbenzene, and then ZSM-5 powder was added to the solution with stirring. The suspension was completely mixed by vigorous stirring at 90 °C for 6 h. The resulting solid was collected by centrifugation, washed with anhydrous ethanol, and then dried in a vacuum drying oven at 80 °C for 12 h. The loading of gold onto ZSM-5, with or without TOS modification, was carried out using an isovolumic impregnation method, with the final calcination step at 550 °C, at a heating rate of 5 °C·min\textsuperscript{−1} in static air for 4 h. The obtained catalysts were denoted as x%Au/ZSM-5-y%TOS (x is the Au concentration, and y is the TOS concentration. All the concentrations were normal mass percents). To simplify the nomenclature of the catalysts in all the figures and tables for clarity of presentation, x%Au/ZSM-5-y%TOS is denoted as xAu/Z-yT, with Z denoting ZSM-5 and T denoting TOS.

In addition, the deposition of SiO\textsubscript{2} on the surface of ZSM-5 was demonstrated by the XPS measurement. The surface Si, O, and Al contents of the three representative catalysts are shown in Table 4.
Table 4. The surface elemental contents, measured by XPS analysis.

| Sample   | Si2p Atomic (%) | Al2p Atomic (%) | O1s Atomic (%) |
|----------|-----------------|-----------------|---------------|
| Z        | 25.95           | 2.75            | 55.92         |
| Z-1T     | 26.60           | 2.69            | 57.47         |
| Z-4T     | 26.75           | 2.43            | 57.29         |
| 0.2Au/Z-1T | 27.14       | 2.30            | 57.34         |

4.2. Catalyst Characterization

The powder XRD patterns were obtained using a Shimadzu XRD-6100 diffractometer, utilizing Cu Kα monochromatic radiation (λ = 0.154 nm) and operating at 40 kV and 100 mA. An inductively coupled plasma-atomic emission spectroscopy (ICP-AES; PerkinElmer ICP 2100) was used to determine the quantity of Au on the catalysts predissolved in hydrofluoric acid (HF) and aqua regia.

The TEM images were obtained using an FEI Talos F200X microscope, working at 200 kV. The chemical elements present on the surface of the catalyst were analyzed using a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer (XPS, Thermo Scientific, Waltham, MA, USA) with the following parameters: monochromatic Al Kα radiation (hv = 1486.6 eV), power 150 W and 400 µm beam spot.

The surface areas and pore size distributions of samples were analyzed using an Autosorb-iQ apparatus, via low-temperature nitrogen physical adsorption. The samples were first dehydrated at 200 °C for 8 h. The surface area and microporous area, external surface, and micropore volume were calculated using the Brunauer–Emmett–Teller (BET) equation and t-plot method. The pore size distribution was obtained using nonlocal density functional theory (NLDFT).

The NH₃-TPD analysis of the catalysts was performed using a TP-5080 multifunctional adsorption instrument at a heating rate of 10 °C·min⁻¹ and a thermal conductivity detector (TCD). A Py-IR analysis was used to characterize the Brønsted and Lewis acids in the samples, using a Bruker Vertex 70 instrument. The samples were pretreated under vacuum conditions at 200 °C for 1 h, and then pyridine was adsorbed. Finally, the pyridine adsorption IR spectra of the samples were measured at 150, 300, and 450 °C.

4.3. Catalyst Evaluation for the Catalytic Cracking of N-Octane and Light Diesel

The catalytic activity measurements for n-octane conversion over the Au/ZSM-5-TOS catalysts were performed in a small, confined fluidized bed reactor. The catalysts were reduced in situ with pure H₂ (25 mL·min⁻¹) at 300 °C for 3 h, followed by N₂ purging. Then, n-octane or light diesel was introduced, and the catalytic performance was evaluated from 260 to 460 °C.

The conversion of n-octane and the selectivity of the target products were calculated using Equations (1) and (2), which are as follows:

\[
\text{Conversion} = 1 - \frac{(C₈H₁₈)_{\text{out}}}{(C₈H₁₈)_{\text{in}}} \quad (1)
\]

\[
\text{Selectivity} = \frac{m}{[(C₈H₁₈)_{\text{in}} - (C₈H₁₈)_{\text{out}}]} \quad (2)
\]

where \((C₈H₁₈)_{\text{in}}\) and \((C₈H₁₈)_{\text{out}}\) refer to the mass of n-octane in the feed and products, and \(m\) refers to the mass of the target product.

The microactivity index (MAT) and the conversion of light diesel were calculated using Equations (3) and (4), which are as follows:

\[
\text{Conversion} = \frac{(W \times D₀\% - D\% \times W₁)}{(W \times D₀\%)} \quad (3)
\]

\[
\text{MAT} = 1 - (1 - G\%) \times W₁/W \quad (4)
\]
where D₀% is the proportion of diesel components in the light diesel feed; W and W₁ are the mass of liquids before and after the reaction, respectively; D% and G% are the relative contents of diesel and gasoline in the liquid product, respectively.

5. Conclusions

The catalytic performance of ZSM-5 zeolite, subjected to external surface modification and Au nanoparticle loading, was studied in the catalytic cracking of n-octane and light diesel. The modified catalyst maintained the MFI structure of ZSM-5, whereas the pore-opening size of the zeolite relatively decreased, without affecting its internal structure. Taking the advantage of the high catalytic activity of Au nanoparticles at a low temperature and the modification of pore-opening size by SiO₂, obtained from TOS decomposition, the catalytic cracking reaction temperature decreased with an improved conversion of feedstock and propylene selectivity, although the acidity of ZSM-5, especially the Brønsted acidity, decreased. The best catalytic performance was achieved over the modified catalysts with 0.2 wt% Au loading. Its catalytic activity at 360 °C even exceeded the activity of ZSM-5 at 460 °C. In addition, after water vapor treatment at 800 °C for 4 h, the propylene selectivity significantly increased, with a slight decrease in the conversion of light diesel oil.

Author Contributions: Conceptualization, L.W. and C.Q.; methodology, L.W.; software, L.W.; validation, L.W. and C.Q.; formal analysis, L.S. and X.S.; investigation, L.W.; resources, C.Q.; data curation, H.S. and L.S.; writing—original draft preparation, L.W.; writing—review and editing, C.Q.; supervision, H.S. and L.Z.; funding acquisition, C.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Nos. 21773202, 21802117).

Data Availability Statement: Date are contained within the article.

Acknowledgments: We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (Nos.21773202 and 21802117). We also appreciate the Key Research and Development Plan of Yantai (Grants: 2019JRC140 and 2021XDHZ068).

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Kohei, K.; Hajime, I.; Seitaro, N.; Akira, I. Comparison of steaming stability of Cu-ZSM-5 with those of Ag-ZSM-5, P/H-ZSM-5, and H-ZSM-5 zeolites as naphtha cracking catalysts to produce light olefin at high temperatures. Appl. Catal. A-Gen. 2015, 489, 272–279. [CrossRef]
2. Alipour, S. Recent advances in naphtha catalytic cracking by nano ZSM-5: A review. Chin. J. Catal. 2016, 37, 671–680. [CrossRef]
3. Wei, Y.; Liu, Z.; Wang, G.; Qi, Y.; Xu, L.; Xie, P.; He, Y. Production of light olefins and aromatic hydrocarbons through catalytic cracking of naphtha at lowered temperature. Stud. Surf. Sci. Catal. 2005, 158, 1223–1230. [CrossRef]
4. Lin, L.F.; Qiu, C.F.; Zhuo, Z.X.; Zhang, D.W.; Zhao, S.F.; Wu, H.H.; Liu, Y.M.; He, M.Y. Acid strength controlled reaction pathways for the catalytic cracking of 1-butene to propene over ZSM-5. J. Catal. 2014, 309, 136–145. [CrossRef]
5. Rahimi, N.; Karimzadeh, R. Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. Appl. Catal. A-Gen. 2011, 398, 1–17. [CrossRef]
6. Konno, H.; Tago, T.; Nakasaka, Y.; Ohnaka, R.; Nishimura, J.; Masuda, T. Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha. Microporous Mesoporous Mater. 2013, 175, 25–33. [CrossRef]
7. Panya, W.; Prasert, R.; Naoki, M.; Osamu, S.; Aritomo, Y. Effect of carbon number on the production of propylene and ethylene by catalytic cracking of straight-chain alkanes over phosphorus-modified ZSM-5. Fuel Process. Technol. 2020, 202, 106367. [CrossRef]
8. Isabelle, B.; Alexander, S. Determination of the exact microporous volume and BET surface area in hierarchical ZSM-5. J. Phys. Chem. C. 2019, 123, 4235–4242. [CrossRef]
9. Wang, C.F.; Zhang, L.; Huang, X.; Zhu, Y.F.; Li, G.; Gu, Q.F.; Chen, J.Y.; Ma, L.G.; Li, X.J.; He, Q.H.; et al. Maximizing sinusoidal channels of HZSM-5 for high shape-selectivity to p-xylene. Nat. Commun. 2019, 10, 1–8. [CrossRef]
10. Dong, X.L.; Shaikh, S.; Vittenet, J.R.; Wang, J.J.; Liu, Z.H.; Bhatte, K.D.; Ali, O.; Xu, W.; Osorio, I.; Saib, Y.; et al. Fine tuning the diffusion length in hierarchical ZSM-5 to maximize the yield of propylene in catalytic cracking of hydrocarbons. ACS Sustain. Chem. Eng. 2018, 6, 15832–15840. [CrossRef]
11. Inagaki, S.; Sato, K.; Hayashi, S.; Tatami, J.; Kubota, Y.; Wakahara, T. A mechnanochemical approach for selective deactivation of external surface acidity of ZSM-5 zeolite catalyst. *ACS Appl. Mater. Interfaces* 2015, 7, 4488–4493. [CrossRef] [PubMed]

12. Knöll, J.; Singh, U.; Nicolic, J.; Gonzalez, R.; Ziebarth, M.; Fougeret, C.; Brandt, S. Unit cell volume as a measure of dealumination of ZSM 5 in fluid catalytic cracking catalyst. *Ind. Eng. Chem. Res.* 2014, 53, 16270–16274. [CrossRef]

13. Zhang, N.; Liu, C.L.; Ma, J.H.; Li, R.F.; Jiao, H. Determining the structures, acidity and adsorption properties of Al substituted HZSM-5. *Phys. Chem. Chem. Phys.* 2019, 21, 18758–18768. [CrossRef] [PubMed]

14. Zhao, L.; Gao, J.S.; Xu, C.M.; Shen, B.J. Alkali-treatment of ZSM-5 zeolites with different SiO2/Al2O3 ratios and light olefin production by heavy oil cracking. *Fuel Process. Technol.* 2011, 92, 414–420. [CrossRef]

15. Wan, J.L.; Wei, Y.X.; Liu, Z.M.; Li, B.; Qi, Y.; Li, M.Z.; Xie, P.; Meng, S.H.; He, Y.L.; Chang, F.X. A ZSM-5-based catalyst for efficient production of light olefins and aromatics from fluidized-bed naphtha catalytic cracking. *Catal. Lett.* 2008, 124, 150–156. [CrossRef]

16. Jing, J.; Park, J.; Seo, G. Catalytic cracking of n-octane over alkali-treated MFI zeolites. *Appl. Catal. A-Gen.* 2005, 288, 149–157. [CrossRef]

17. Su, L.L.; Liu, L.; Zhuang, J.Q.; Wang, H.X.; Li, Y.G.; Shen, W.J.; Xu, Y.D.; Bao, X.H. Creating mesopores in ZSM-5 zeolite by alkali treatment: A new way to enhance the catalytic performance of methane dehydroaromatization on Mo/HZSM-5 catalysts. *Catal. Lett.* 2003, 91, 155–167. [CrossRef]

18. Feng, R.; Yan, X.L.; Hu, X.L.; Zhang, Y.X.; Wu, J.J.; Yan, Z.F. Phosphorus-modified b-axis oriented hierarchical ZSM-5 zeolites for enhancing catalytic performance in a methanol to propylene reaction. *Appl. Catal. A-Gen.* 2020, 594, 117464. [CrossRef]

19. Liu, Q.; Zhang, M.; Sun, L.B.; Su, H.J.; Zou, X.H.; Qi, C.X. The performance of catalytic conversion of ZSM-5 comodified with gold and lanthanum for increasing propylene production. *Ind. Eng. Chem. Res.* 2019, 58, 14695–14704. [CrossRef]

20. Zhang, C.D.; Kwak, G.; Lee, Y.J.; Jun, K.W.; Gao, R.X.; Park, H.G.; Kim, S.; Min, J.E.; Chang Kang, S.; Guan, G.F. Light hydrocarbons to BTEX aromatics on Zn-modified hierarchical ZSM-5 combined with enhanced catalytic activity and stability. *Microporous Mesoporous Mater.* 2019, 284, 316–326. [CrossRef]

21. Chu, Y.Y.; Gao, X.Z.; Zhang, X.; Xu, G.T.; Li, G.C.; Zheng, A.M. A theoretical study the effective phosphorous species over modified P-ZSM-5 zeolite. *Phys. Chem. Chem. Phys.* 2018, 20, 11702–11712. [CrossRef] [PubMed]

22. Hou, X.; Qiu, Y.; Tian, Y.J.; Diao, Z.H.; Zhang, X.W.; Liu, G.Z. Reaction pathways of n-pentane cracking on the fresh and regenerated Sr, Zr and La-loaded ZSM-5 zeolites. *Chem. Eng. J.* 2018, 349, 297–308. [CrossRef]

23. Dai, W.L.; Yang, L.; Wang, C.M.; Wang, X.; Wu, G.J.; Guan, N.J.; Obenaus, U.; Hunger, M.; Li, L.D. Effect of n-butanol cofeeding on the methanol to aromatics conversion over Ga-modified nano H-ZSM-5 and its mechanistic interpretation. *ACS Catal.* 2018, 8, 1352–1362. [CrossRef]

24. Long, L.; Lan, Z.Z.; Han, Z.X.; Qiu, Y.F.; Zhou, W.X. Co3O4 nanosheet wrapped commercial HZSM-5 for promoting catalytic cracking of n-decane and antiicting activities. *ACS Appl. Energy Mater.* 2018, 1, 4130–4139. [CrossRef]

25. Li, F.W.; Ding, S.L.; Wang, Z.H.; Li, Z.X.; Li, L.; Gao, C.; Zhong, Z.; Lin, H.F.; Chen, C.J. Production of light olefins from catalytic cracking bioil model compounds over La2O3-modified ZSM-5 zeolite. *Energy Fuel* 2018, 32, 5910–5922. [CrossRef]

26. Qi, C.X.; Wang, Y.X.; Ding, X.T.; Su, H.J. Catalytic cracking of light diesel over Au/ZSM-5 catalyst for increasing propylene production. *Chin. J. Catal.* 2016, 37, 1747–1754. [CrossRef]

27. Ai Sha, N.L.H.; Liu, J.X.; He, N.; Guo, H.C. Catalytic conversion of n-butane over Au-Zn-modified nano-sized HZSM-5. *Chin. J. Catal.* 2013, 34, 1262–1266. [CrossRef]

28. Sami, M.; Brahim, M.; Pieter, C.; Evgeny, A.; Emiel, J. Structure and reactivity of Zn-modified ZSM-5 zeolites: The importance of clustered cationic Zn complexes. *ACS Catal.* 2012, 2, 71–83. [CrossRef]

29. Corma, A.; Mengual, J.; Miguele, P. Stabilization of ZSM-5 zeolite catalysts for steam catalytic cracking of naphtha for production of propene and ethene. *Appl. Catal. A-Gen.* 2012, 421–422, 121–134. [CrossRef]

30. Siddiqui, M.; Aitani, A.; Saeed, M.; Al-Yassir, N.; Al-Khattaf, S. Enhancing propylene production from catalytic cracking of Arabian Light VGO over novel zeolites as FCC catalyst additives. *Fuel* 2011, 90, 459–466. [CrossRef]

31. Xue, N.H.; Liu, N.; Nie, L.; Yu, Y.; Gu, M.; Peng, L.M.; Guo, X.F.; Ding, W.P. 1-Butene cracking to propene over P/HZSM-5: Effect of lanthanum. *J. Mol. Catal. A-Chem.* 2010, 327, 12–19. [CrossRef]

32. Wang, X.N.; Zhao, Z.; Xu, C.M.; Duan, A.J.; Zhang, L.; Jiang, G.Y. Effects of light rare earth on acidity and catalytic performance of HZSM-5 zeolite for catalytic cracking of butane to light olefins. *J. Rare Earths* 2007, 25, 321–328. [CrossRef]

33. Niwa, M.; Murakami, Y. CVD zeolites with controlled pore-opening size. *J. Phys. Chem. Solids.* 1989, 50, 487–496. [CrossRef]

34. Niwa, M.; Kota, M.; Hattori, T.; Murakami, Y. Fine control of the pore-opening size of zeolite ZSM-5 by chemical vapor deposition of silicon methoxide. *J. Phys. Chem.* 1986, 90, 6233–6237. [CrossRef]

35. Niwa, M.; Kawashima, Y.; Murakama, Y. A shape-selective platinum-loaded mordenite catalyst for hydrocracking of paraffins by the chemical vapour deposition of silicon alkoxide. *J. Chem. Soc. Faraday. Trans. 1* 1985, 81, 2757–2761. [CrossRef]

36. Niwa, M.; Kato, S.; Hattori, T.; Murakami, Y. Fine control of the pore-opening size of the zeolite mordenite by chemical vapour deposition of silicon alkoxide. *J. Chem. Soc. Faraday. Trans. 1* 1984, 80, 3135–3145. [CrossRef]

37. Niwa, M.; Itoh, H.; Kato, S.; Hattori, T.; Murakami, Y. Modification of H-mordenite by a vapour-phase deposition method. *J. Chem. Soc. Chem. Commun.* 1982, 245, 819–820. [CrossRef]

38. Yue, Y.H.; Tang, Y.; Gao, Z. Zeolite pore size engineering by chemical liquid deposition. *Stud. Surf. Sci. Catal.* 1997, 105, 2059–2065. [CrossRef]
39. Cheng, Y.T.; Wang, Z.P.; Gilbert, C.J.; Fan, W.; Huber, G.W. Production of p-xylene from biomass by catalytic fast pyrolysis using ZSM-5 catalysts with reduced pore openings. *Angew. Chem. Int. Ed.* 2012, 51, 11097–11100. [CrossRef]

40. Hayashi, T.; Tanaka, K.; Haruta, M. Selective vapor-phase epoxidation of propylene over Au/TiO₂ catalysts in the presence of oxygen and hydrogen. *J. Catal.* 1998, 178, 566–575. [CrossRef]

41. Qi, C.X.; Zheng, Y.H.; Lin, H.; Su, H.J.; Sun, X.; Sun, L.B. CO oxidation over gold catalysts supported on CuO/Cu₂O both in O₂-rich and H₂-rich streams: Necessity of copper oxide. *Appl. Catal. B-Environ.* 2019, 253, 160–169. [CrossRef]

42. Qi, C.X.; Zhu, S.D.; Su, H.J.; Lin, H.; Guan, R.G. Stability improvement of Au/Fe-La-Al₂O₃ catalyst by incorporated with a FeOₓ layer in CO oxidation process. *Appl. Catal. B-Environ.* 2013, 138–139, 104–112. [CrossRef]

43. Sing, K.S.W.; Everett, D.H.; Haul, R.A.W.; Moscou, L.; Pierotti, R.A.; Rouquerol, J.; Siemieniewska, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* 1985, 57, 603–619. [CrossRef]

44. Tian, Y.J.; Zhang, B.F.; Liang, H.R.; Hou, X.; Wang, L.; Zhang, X.W.; Liu, G.Z. Synthesis and performance of pillared HZSM-5 nanosheet zeolites for n-decane catalytic cracking to produce light olefins. *Appl. Catal. A-Gen.* 2019, 572, 24–33. [CrossRef]

45. Wang, F.; Chu, X.Z.; Zhao, P.S.; Zhu, F.X.; Li, Q.Q.; Wu, F.Y.; Xiao, G.M. Shape selectivity conversion of biomass derived glycerol to aromatics over hierarchical HZSM-5 zeolites prepared by successive steaming and alkaline leaching: Impact of acid properties and pore constraint. *Fuel* 2020, 262, 116538. [CrossRef]

46. Zhang, M.; Liu, Q.; Long, H.A.; Sun, L.B.; Murayama, T.; Qi, C.X. Insights into Au nanoparticle size and chemical state of Au/ZSM-5 catalyst for catalytic cracking of n-octane to increase propylene production. *J. Phys. Chem. C* 2021, 125, 16013–16023. [CrossRef]

47. Corma, A.; Orchilles, A.V. Current views on the mechanism of catalytic cracking. *Microporous Mesoporous Mater.* 2000, 35–36, 21–30. [CrossRef]

48. Wang, C.Y.; Garbarino, G.; Allard, L.F.; Wilson, F.; Busca, G.; Flytzani-Stephanopoulos, M. Low-temperature dehydrogenation of ethanol on atomically dispersed gold supported on ZnZrOₓ. *ACS Catal.* 2016, 6, 210–218. [CrossRef]

49. Zheng, J.W.; Qu, J.; Lin, H.Q.; Zhang, Q.; Yuan, X.; Yang, Y.H.; Yuan, Y.Z. Surface composition control of the binary Au–Ag catalyst for enhanced oxidant-free dehydrogenation. *ACS Catal.* 2016, 6, 6662–6669. [CrossRef]