catalysts

MDPI

Supplementary Material

Surface modification of Fe-ZSM-5 using Mg for a reduced catalytic pyrolysis temperature of low-density polyethylene to produce light olefin

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2. Results and discussion

2.1 Catalyst characterization

2.1.1 BET results

Table S1. The physical properties of catalysts.

Catalysts	Surface area (m^2/g)	Micro-pore surface area(m^2/g)	Pore volume of total(cm^3/g)	Pore volume of micro-pore(cm^3/g)	Average pore size(nm)
ZSM-5	328.9606	256.2448	0.1763	0.1330	2.8886
Fe-ZSM-5	293.1373	207.2026	0.1650	0.1114	3.3660
Fe-Mg-ZSM-5	307.9975	228.8373	0.1713	0.1191	3.2169

2.1.4 XRD analysis

Table S2. The crystallinity of different samples.

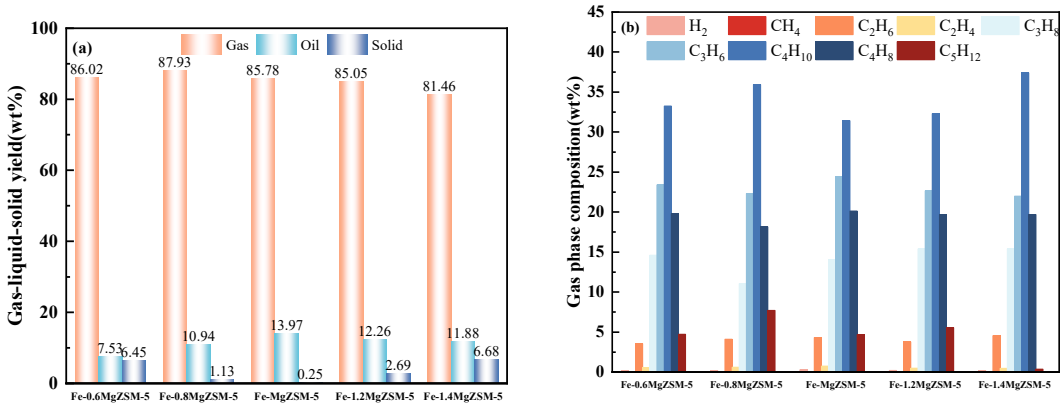
Catalysts	Crystallinity (%)
ZSM-5	99.87%
Fe-ZSM-5	81.63%
Fe-Mg-ZSM-5	73.27%

2.2.4 Catalytic performance of Fe-Mg-ZSM-5

The impact of Mg loadings on Fe-ZSM-5 catalyst was estimated by investigating the yield and distribution of light olefin. Varying the proportion of Mg-modified Fe-ZSM-5 catalyst from 0.6 wt.% to 1.4 wt.% lead to an initial increase and subsequent reduction in the yield of light olefin. In particular, the largest yield of light olefin was gained using 1 wt.% Mg-modified catalysts. **Fig.S1.** displays the effect of Fe-ZSM-5 with different Mg contents on the generation of light olefin. As presented in **Fig. S1a**, with the increase of Mg loading, the gaseous product firstly rose and then fell, and reached the maximum value (87.93%) at 0.8% of

Mg loading, while the liquid phase yield reached the maximum (13.97%) at 1.0 wt% of Mg loading. The gas is chiefly composed ofH_2, CH_4, C_2H_4, C_3H_6 C_4H_8, C_2H_6, C_3H_8, and C_5H_{12} (**Fig. S1b**), and the content of light olefin accounts for 45.31% of total gas product at 1.0 wt% of Mg loading.

The results from NH_3-TPD showed that the intensity distribution of acid sites on the catalyst was optimized by loading Mg on Fe-ZSM-5. The addition of Mg to Fe-ZSM-5 resulted in an improvement of the medium acid sites, which facilitated the transforming of volatiles to light olefin, with the highest yield (38.87%) at 1 wt% Mg addition (**Fig. S1c**). In addition, as the loading of Mg increased from 1.0 wt% to 1.4 wt%, the solid phase products increased, the gas phase products decreased, and the production of light olefin reduced, probably due to the blockage of molecular sieve pore channels as the metal loading increased, causing a decrease in catalyst activity. As seen from **Fig. S1d**, the light olefins are mainly propylene and butene, of which the amount of propylene is the most, the amount of ethylene is the least, with the increase of Mg loading, C_3H_6 and C_4H_8 are roughly at about 52.17% and 46.76% at 1.4 wt% of Mg loading, which may be due to the dominant role of Fe on the ZSM-5 catalyst, with Mg acting as a promoter and olefin methylation playing a dominant role in the reaction. At the same time, the increase of Mg load has little influence on the amount and selectivity of the three.



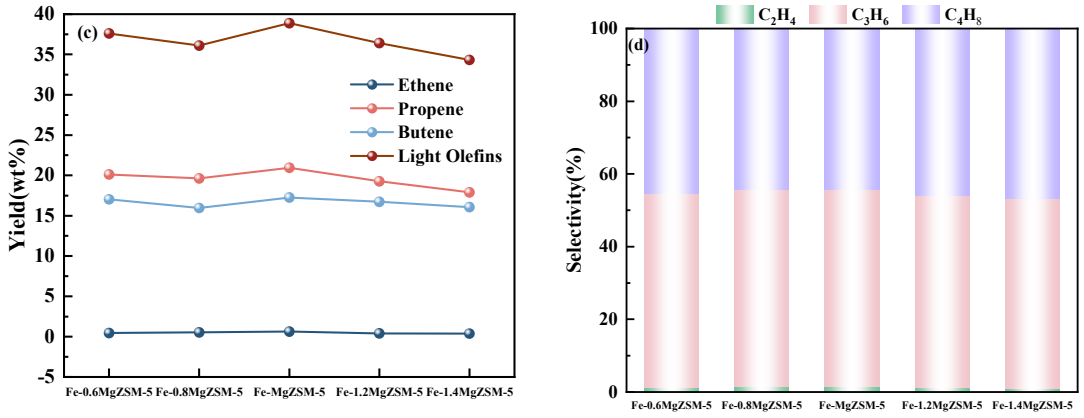


Figure S1. Influence of Fe-ZSM-5 with various Mg contents on the yields of light olefin. (a) Mass percentages of solids, gases, and liquids; (b) Mass percentages of H_2, CH_4, light olefin, and C_2-C_5 alkanes; (c) Weight yield of light olefin; (d) Olefins selectivity of C_2H_4, C_3H_6, and C_4H_8.

3. Materials and methods

3.2 Experimental setup

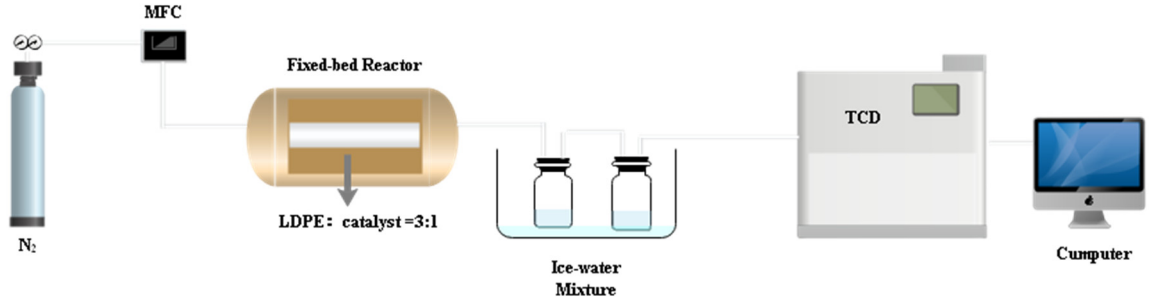


Figure S2. The pyrolysis experimental setup.

3.3 Characterization of sample

The N_2 adsorption-desorption isotherm of the adsorbent was measured at 77 K using the ASAP 2020 volume adsorption analyzer. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area. The pore size distribution map is calculated by the Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) patterns were recorded by Rigaku D/MAX-2500/PC X-ray diffractometer using Cu-Ka (λ=0.5406 nm, 50 KV, 300 mA) radiation with step sizes of $2°\cdot min^{-1}$ in the range of 5°-85°. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI 5000C ESCA spectrometer equipped

with MgKα (1253.60 eV) radiation. Analyze the element mapping image by energy dispersive X-ray spectrometer (EDS, JEOL, JXA-8230). The morphology and structure of catalysts were examined by scanning electron microscope (SEM, JEOL, JSM-6700F, Japan) and transmission electron microscope (HRTEM, JEOL, JEM-2100F, Japan). The thermogravimetric analysis (TGA) of the Fe-Mg-ZSM-5 was carried out using a LECO TGA 701 (LECO Co., USA) thermogravimetric analyzer. For the analysis, 5.26 mg of the sample was heated to 900℃ at a heating rate of 10℃/min in a nitrogen atmosphere.

3.4 Products analysis

Standard gases are used for calibration and analysis. The area normalization method was employed to calculate the mass percentage of each gas component using the following formula 4.

$$C_i\% = \frac{f_i A_i}{\sum f_i A_i} \times 100\% \quad (4)$$

where C_i represents the mass percentage of each gas component, f_i represents the mass correction factor for different gas components, A_i represents the peak area of different gas component.