Microwave-assisted catalytic fast pyrolysis of biomass for bio-oil production using chemical vapor deposition modified HZSM-5 catalyst

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A B S T R A C T

Chemical vapor deposition with tetra-ethyl-orthosilicate as the modifier was applied to deposit the external acid sites of HZSM-5, and the modified HZSM-5 samples were used for the microwave-assisted catalytic fast pyrolysis (MACFP) of biomass for bio-oil production. The experimental results showed that the external acid sites of HZSM-5 decreased significantly when SiO_2 deposited amount increased from 0 to 5.9%. For product distribution, the coke yield decreased, the oil fraction yield

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decreased at first and then increased, and the yields of water and gas first increased and then decreased over the range of SiO_2 deposited amount studied. For chemical compositions in oil fraction, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and oxygen-containing aromatic compounds first increased to maximum values and then decreased, while the relative content of oxygen-containing aliphatic compounds first decreased and then increased with increasing SiO_2 deposited amount.

Keywords:

Microwave

Catalytic fast pyrolysis

Biomass

Modified HZSM-5

Chemical vapor deposition

1. Introduction

Within the past decades, catalytic fast pyrolysis (CFP) of lignocellulosic biomass has become one of the most prevailing and promising methods to produce high-quality liquid fuels (termed bio-oil) and other high value-added chemicals (Lei et al., 2011; Budzianowski, 2012; Zhang et al., 2014). Among various studied catalysts, HZSM-5 aluminosilicate zeolite has shown attractive performance because of its excellent capacity for bio-oil deoxygenation and shape-selectivity for hydrocarbon production (Carlson et al., 2008; Zhang et al., 2015a; Czernik and Bridgwater, 2004). The 3-dimensional intersecting pore structure of HZSM-5 catalyst is characterized by

well-defined 10-membered rings with straight channels of 0.53 × 0.56 nm and sinusoidal channels of 0.51 × 0.55 nm, in which oxygenated organic compounds will be removed and hydrocarbons will be formed when biomass fast pyrolysis vapors pass through the catalyst layer (Olsbye et al., 2012; Zhang et al., 2015b).

However, it should be emphasized that some active compounds in the primary pyrolysis vapors can polymerize on the surface of acidic catalysts, resulting in the generation of coke. For HZSM-5 catalyst, coke can only be formed on its external surface, because coke is a kind of large-molecule aromatic compound and unable to be accommodated within the narrow inner micropores (Carlson et al., 2011). Coke will give rise to the blockage of pore mouth and the deactivation of HZSM-5 catalyst, so it is necessary to minimize the coke yield in CFP process. A useful technology to retard coke formation and obtain high yields of target products is to eliminate the external acid sites of HZSM-5 catalyst but meanwhile retain the internal acid sites (Matias et al., 2008). In this paper, selective inactivation of external acid sites of HZSM-5 catalyst is carried out by means of chemical vapor desopition of inert silica (SiO_2-CVD). The modifying agent used here is tetra-ethyl-orthosilicate (TEOS, $Si(OC_2H_5)_4$). Abbreviation in the bracket is used in the following description. As a bulky organosilicon compound, TEOS molecule is incapable of entering the intracrystalline void space. As the result, only acid sites on the outer surface of HZSM-5 are deposited by SiO_2 via TEOS degradation, whereas the internal acid sites are not altered. In this context, it is anticipated that external surface silylation of

HZSM-5 will inhibit coke formation and fine-tune catalytic performance.

Microwave-assisted catalytic fast pyrolysis (MACFP), which employs microwave and catalyst, is a relatively emerging technique. Recently, Ruan and his co-workers started to use MACFP process to processing biomass and prepare pyrolytic biofuels (Du et al., 2013; Xie et al., 2014; Borges et al., 2014). Compared to conventional heating method, microwave-assisted heating provides many advantages, including uniform fast internal heating, ease of operation and maintenance, no need for feedstock grinding, energy cost saving and so forth.

In this work, MACFP of biomass for bio-oil production using SiO_2-CVD modified HZSM-5 catalysts was conducted in a microwave reactor. Ammonia TPD and catalytic cracking of 1,3,5-tri-iso-propyl-benzene (1,3,5-TIPB) were carried out to determine the acidity characteristics of HZSM-5 catalysts. Besides, the effect of SiO_2 deposited amount on the production distribution, chemical compositions in oil fraction and aromatic production was studied and discussed.

2. Materials and methods

2.1 Materials

Corn stover, which was collected from a farm field in the city of Yancheng in Jiangsu Province, China, was used as biomass feedstock in our experiments. Prior to experiment, all the feedstocks were pulverized mechanically and smashed to a particle

size of 0-0.5 mm in diameter. The proximate analysis of the air-dried corn stover was 7.27 wt.% moisture, 82.37 wt.% volatile, 4.06 wt.% ash, and 6.30 wt.% fixed carbon. The elemental composition of the dried corn stover was 41.77 wt.% carbon, 5.46 wt.% hydrogen, 42.34 wt.% oxygen, and 0.45 wt.% nitrogen.

HZSM-5 zeolite (Si/Al ratio = 50, particle diameter = 2-5 μm) purchased from the Catalyst Plant of Nankai University (China), was used as the parent catalyst in this study. The silicon alkoxide TEOS (analytical grade chemical) was purchased from Aladdin Company, and 1,3,5-TIPB (analytical grade chemical) was bought from Sigma-Aldrich Corporation.

2.2 SiO_2-CVD

The silanized HZSM-5 samples were obtained by SiO_2-CVD using the methodology described in Halgeri and Das (2002), which is described as below:

HZSM-5 catalyst was treated for silanization in a horizontal tubular reactor (15 mm i.d. and 1000 mm length), externally heated by an electric heater. 0.5 g HZSM-5 catalyst was placed in a heated section in the reactor. A 1.0 wt% TEOS solution in 50:50 (v/v) methanol and toluene was prepared, and then evaporated and passed through the HZSM-5 catalyst bed at 250 ^{o}C with a constant rate of 10 ml/h. In order to obtain uniform surface contact between the vapors and HZSM-5 catalyst, a constant volume of hydrogen flow (50 ml/min) was fed through the reactor and acted as the carrier gas. After treatment, HZSM-5 catalyst was collected carefully and then put

into a muffle furnace for calcination in air (550 °C, 10 h) for the decomposition of TEOS into SiO_2.

SiO_2 deposited amount was defined as the mass ratio of SiO_2 to HZSM-5 catalyst, which was determined by the weight difference before and after silanization treatment. HZSM-5 samples with different SiO_2 deposited amounts (1.3%, 2.5%, 3.7%, 5.1% and 5.9%) were obtained by adjusting and varying treatment time. The modified zeolites were referred as 1.3-SiO_2/HZSM-5, 2.5-SiO_2/HZSM-5, 3.7-SiO_2/HZSM-5, 5.1-SiO_2/HZSM-5 and 5.9-SiO_2/HZSM-5, respectively.

2.3 Determination of acid sites on the external surface

The catalytic cracking of 1,3,5-TIPB was carried out in a fixed bed to determine the extent of inactivation of the external acid sites of modified HZSM-5 catalysts (Kim et al., 1996). The molecule diameter of 1,3,5-TIPB is greater than the pore diameter of HZSM-5. Hence, 1,3,5-TIPB cannot enter the narrow inner channels, and its cracking can only take place on the external surface of HZSM-5.

0.1 g HZSM-5 catalyst was put in a horizontal tubular reactor (15 mm i.d. and 1000 mm length) and pretreated at 500 ^{o}C for 1 h in a continuous helium flow (30 ml/min). To start the cracking reaction, the reaction temperature was adjusted to 300 ^{o}C, and 1,3,5-TIPB was introduced into the catalyst fixed bed with a injection pump. During cracking reaction, the weight hourly space velocity (W/F) was kept at 4.0

$g \cdot h \cdot mol^{-1}$. Each experiment ran 25 min. After reaction, the products were collected by a condenser and analyzed by a gas chromatography / mass spectrometer (GC/MS) instrument (7890A/5975C, Agilent).

2.4 Apparatus

MACFP experiments were conducted in a microwave oven (MAX, CEM Corporation; 750 W & 2450 MHz). The experimental setup (see Fig. 1) was composed of: (1) semi-continuous biomass feeder; (2) biomass feedstocks; (3) quartz inlet connector (length: 140 mm; diameter: 24.6 mm); (4) microwave oven; (5) microwave control panel; (6) quartz reactor with two necks (specially made with fused quartz; length: 128 mm; diameter: 127 mm); (7) microwave absorbent (SiC) bed; (8) fixed bed with SiC and HZSM-5 catalyst mixer; (9) quartz wool; (10) quartz outlet connector (length: 148 mm; diameter: 24.6 mm); (11) thermocouple to measure the temperature of (7) and (8); (12) quartz connector; (13) bio-oil collector; (14) condenser; (15) connection to a vacuum pump to draw the pyrolysis vapors out of quartz reactor. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

During experiments, SiC particles (particle size: 30 grit) were used as the microwave absorbent. SiC can be easily heated using microwaves because of its excellent absorption property for microwaves. Use of SiC can significantly enhance the heating rate. When biomass is fed onto the heated SiC in a microwave reactor, it

will be heated through two heating mechanisms simultaneously: (1) the direct microwave irradiation; (2) the thermal conduction from heated SiC (Borges et al., 2014). As a result, fast microwave-assisted pyrolysis conditions will be achieved, and biomass can be instantaneously heated to the desired CFP temperature. 500 g of SiC particles were placed in the quartz reactor to form a layer of microwave absorbent bed. Then the quartz reactor was put into the cavity of the microwave oven. After connecting the quartz inlet and outlet tubes, some SiC particles and 0.25 g HZSM-5 catalyst were fully mixed and put into the bottom of quartz outlet connector to form another fixed bed. This fixed bed was expected to upgrade primary pyrolysis vapors. Then the microwave oven was turned on for heating processing. When the first and second fixed beds ((7) and (8)) were heated to the desired temperature (500 ^{o}C), 5 g corn stover was introduced onto the hot SiC bed (7) semi-continually through the biomass feeder. Pyrolysis reactions occurred in the quartz reactor and the primary pyrolysis vapors were upgraded when they passed through the fixed bed (8). In this set of experiments, the pyrolysis temperature and upgrading temperature were exactly the same (500 ^{o}C). A pulse width modulation (PWM) control was applied to keep the microwave oven on and off every 15 s to maintain the desired reaction temperature of (7) and (8). The vacuum degree of the experimental system was kept at 250 mm Hg to maintain an inert atmosphere in the reactor. Each experiment ran 45 min.

2.5 Products analysis

At the end of each experiment, the solid residue (coke & char) was cooled to

room temperature. The spent HZSM-5 catalyst sample was collected carefully and dried at 120 ^{o}C for 1 h in a drying oven. Then the dried sample was put into a muffle furnace for combustion (650 ^{o}C, 2 h) so that the coke yield was determined. Besides, the char yield was calculated by the weigh difference of the quartz reactor with and without char. The bio-oil (oil fraction & water) yield was determined by the weigh difference of the bio-oil collector before and after each experiment, while the gas yield was determined by difference according to mass balance (Gas yield = 100% - Coke yield - Char yield - Bio-oil yield). The water content in bio-oil was determined using a method of Karl Fischer Titration. The yield of oil fraction in bio-oil was determined by difference (Oil fraction yield = Total bio-oil yield - Water content in bio-oil × Total bio-oil yield). Each experiment was repeated at least twice under the same conditions, and their average values were calculated and used for discussion.

The chemical compositions of oil fraction were also identified using the gas chromatography / mass spectrometer (GC/MS) instrument (7890A/5975C, Agilent). High-purity helium was employed as the carrier gas (1.2 mL/min). The oven temperature was 40 ^{o}C, which was held for 3 min initially and then increased to 290 ^{o}C with a heating rate of 5 ^{o}C/min. It was held at 290 ^{o}C for 5 min. The GC/MS injector temperature of 250 ^{o}C and detector temperature of 230 ^{o}C were held. The GC separation was carried out using a capillary column named HP-5 MS. A split ratio of 1:10 was used with the injection size of 1 μL. The chromatographic peaks were discriminated and analyzed by means of the National Institute of Standards and

Technology (NIST) mass spectral data library. Relative content of each component in the bio-oil was determined by calculating its chromatographic area percentage. Gaseous products were analyzed using a Varian CP4900 gas chromatography (GC)/thermal conductivity detector (TCD) with a 5A molecular sieve column and a PPQ column.

2.6 Data Processing

The conversion efficiency of 1,3,5-TIPB was used in the paper to measure the inactivation extent of the external acid sites of modified HZSM-5 catalysts, and defined as

$$\eta = 1 - \frac{m_p}{m_T} \tag{1}$$

where η is the conversion efficiency of 1,3,5-TIPB, m_p is the mass of 1,3,5-TIPB in the collected products, and m_T is the total mass of 1,3,5-TIPB fed in.

The selectivity of aromatics in oil fraction was also calculated. The selectivity of a certain kind of aromatics was defined and calculated as follows

$$S_{aromatic} = \frac{c_{aromatic}}{\sum c_{aromatic}} \tag{2}$$

where $S_{aromatic}$ is the selectivity of a certain kind of aromatics, such as benzene or toluene; $c_{aromatic}$ is the relative content of a certain kind of aromatics; $\sum c_{aromatic}$ is the relative content of all aromatics.

3. Results and discussion

3.1 Porosity and acidity characteristics of HZSM-5 catalysts

The porosity characteristics of parent and modified HZSM-5 samples were analyzed by N_2 porosimetry (BET method). The results are shown in Fig. 2(a). Obviously, the BET surface area and pore size of HZSM-5 catalyst decreased with increasing SiO_2 deposited amount. The acidity characteristics of parent and modified HZSM-5 samples were analyzed by ammonia TPD, and the results are shown in Fig. 2(b). As could be seen, the total acid sites (both weak acid sites and strong acid sites) of HZSM-5 catalyst decreased with increasing SiO_2 deposited amount.

On the other hand, 1,3,5-TIPB was selected as probe molecule in our present study as its catalytic cracking conversion over HZSM-5 took place only on the external surface. Hibino et al. (1993) carried out experiments to investigate the adsorption of 1,3,5-TIPB on parent and silanized HZSM-5, and their results showed that no adsorption of 1,3,5-TIPB was observed, proving that 1,3,5-TIPB was converted by HZSM-5 rather than adsorbed. Namba et al. (1986) also reported that the conversion of 1,3,5-TIPB corresponded to the relative amount of acid sites on the external surface of HZSM-5 crystallites. Fig. 2(c) shows the conversion efficiencies of 1,3,5-TIPB over parent and modified HZSM-5 catalysts as a function of SiO_2 deposited amount. As could be seen, conversions of 1,3,5-TIPB decreased significantly with inceasing SiO_2 deposited amount, indicating that SiO_2-CVD method could selectively inactivate the external surface.

3.2 Product distribution

The product yields of MACFP of corn stover over silylated HZSM-5 with different SiO_2 deposited amount are shown in Fig. 3. A steady decrease in coke yield was observed when the SiO_2 deposited amount increased from 0 to 5.9%. The oil fraction yield tended to decrease at first and then increase over the range of SiO_2 deposited amount studied, and the oil fraction yields in this study were from 15.6 to 22.6 %. It could also be seen that the yields of water and gas increased first and then decreased. Besides, the char yield remained almost constant. Besides, we also conducted additional experiments to investigate the biomass microwave assisted pyrolysis without catalyst (microwave assisted non-catalytic fast pyrolysis, non-MACFP) at 500 ^{o}C (also see Fig. 3). Compared to non-MACFP process, MACFP process can reduce the yield of oil fraction and increase the yields of water and gas. For MACFP process, when the primary product vapors passed through the HZSM-5 catalyst layer, some of them will be cracked and upgraded, forming water and light gas. As a result, MACFP process led to a decrease in the yield of oil fraction and increase in the yields of water and gas.

As the 1,3,5-TIPB catalytic conversion results shown in Fig. 2, SiO_2-CVD method made SiO_2 deposited on the external surface of HZSM-5 and inactivated the external acid sites dramatically. The external acid sites decreased significantly with increasing SiO_2 deposited amount. As the result, coke formation was restrained and

coke yield tended to decrease gradually when the SiO_2 deposited amount increased from 0 to 5.9%. Besides, as mentioned above, the deactivation and aging of HZSM-5 catalyst was caused by pore opening blockage with generated coke, so the inactivation of external surface and decrease of coke yield also improved the catalyst life and promoted the subsequent conversion reactions. Thus, more primary product vapors would diffuse into the internal pores and be converted when they passed through the HZSM-5 catalyst layer, forming more water and light gas (CO, CO_2 and other light noncondensable gases). Therefore, the yields of water and gas increased and the yield of oil fraction decreased with increasing SiO_2 deposited amount. However, larger SiO_2 deposited amount gave rise to the pore opening blockage and prevented relative cracking reactions. Consequently, the further increase of SiO_2 deposited amount led to a decrease in the yields of water and gas and increase in oil fraction yield. This result was in good agreement with previous literatures (Zheng et al., 2004; Cheng et al., 2012).

3.3 Chemical compositions in oil fraction

The chemical compositions in oil fraction discriminated and analyzed by GC/MS could be classified into several groups as aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds and others (nitrogen-containing compounds and unidentified compounds). Fig. 4(a) gives the relative contents of different groups in oil fraction. As could be seen, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and

oxygen-containing aromatic compounds first increased to maximum values and then decreased, while the relative content of oxygen-containing aliphatic compounds decreased with the SiO_2 deposited amount from 0 to 5.1 %, but increased at higher SiO_2 deposited amount. As shown in Fig. 4(b), a steady increase in relative content of hydrocarbons was observed at the lower SiO_2 deposited amounts (< 3.7%), and a decrease of relative content of hydrocarbons was observed when the SiO_2 deposited amount increased from 3.7% to 5.9%. Besides, the relative content of oxygenates showed the same tendency to that of oxygen-containing aliphatic compounds. The SiO_2 deposited amount of 3.7% was considered the optimum condition for maximum relative content of hydrocarbons. The bio-oil components from non-MACFP process are also shown in Fig. 4(a). It was found that there were almost no aliphatic hydrocarbons and aromatic hydrocarbons in the oil fraction from non-MACFP process, and there were various oxygenates in the oil fraction.

When the primary product vapors passed through the HZSM-5 catalyst, serious deoxygenation reactions (including dehydration, decarboxylation, decarbonylation and so forth) occurred inside the internal structure, thereby removing oxygen as H_2O, CO and CO_2 and converting the carbon and hydrogen into hydrocarbons (Zhang et al., 2015a; Zhang et al., 2015b; Zhang et al., 2012). For parent HZAM-5 catalyst without SiO_2 deposition, coke could be easily formed, thus blocking the pore opening and preventing the subsequent catalytic reactions. For 1.3-SiO_2/HZSM-5, 2.5-SiO_2/HZSM-5 and 3.7-SiO_2/HZSM-5 catalysts, SiO_2-CVD treatment process led

to the inactivation of external acid sites, reducing the coke yield and improving the pore opening blockage. Therefore, these three catalysts showed better catalytic effect than parent catalyst. Besides, the higher SiO_2 deposited amount was more conducive to the inactivation of more external acid sites. Hence, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and total hydrocarbons increased and the relative content of oxygen-containing aliphatic compounds decreased with increasing SiO_2 deposited amount from 0 to 3.7%. However, when the SiO_2 deposited amount further increased from 3.7% to 5.9%, the pore openings of HZSM-5 catalyst were blocked by SiO_2 deposition, thus preventing the catalytic reactions. As a result, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and total hydrocarbons decreased and the relative content of oxygen-containing aliphatic compounds increased with the further increase of SiO_2 deposited amount. Besides, the relative content of oxygen-containing aromatic compounds also first increased and then decreased. The oxygen-containing aromatic compounds were mainly from the pyrolysis of lignin. 1.3-SiO_2/HZSM-5, 2.5-SiO_2/HZSM-5 and 3.7-SiO_2/HZSM-5 catalysts increased the relative content of oxygen-containing aromatic compounds because they could promote the catalytic pyrolysis of lignin derivatives.

3.4 Production of aromatic hydrocarbons

It should be pointed out that the pore diameter of HZSM-5 is similar to the dynamics diameters of benzene, toluene and xylene, so the HZSM-5 catalyst has a significant shape-selective effect on the formation of aromatic hydrocarbons (Zhang

et al., 2015c; Zhang et al., 2014). When the vapors of fast pyrolyzed corn stover passed through the HZSM-5 catalyst layer, they would diffuse into the internal pores of HZSM-5 catalyst and form aromatic hydrocarbons via an aromatics carbon pool in the HZSM-5 framework (Ilias and Bhan, 2013).

The relative contents and detailed selectivities of aromatic hydrocarbons are shown in Fig. 5. In this study, aromatic hydrocarbons included benzene, toluene, ethylbenzene, xylene, indene and naphthalene. As could be seen, the relative contents of benzene, toluene, xylene and naphthalene tended to increase first and then decrease (see Fig. 5(a)). Among all the aromatic hydrocarbons, xylene and toluene accounted for the largest fraction (see Fig. 5(b)). The maximum selectivity of xylene was achieved at the SiO_2 deposited amout of 3.7%, while that of toluene was obtained at the SiO_2 deposited amout of 1.3%.

3.5 Composition of non-condensable gas

The non-condensable gas was mainly composed of 4 compositions: H_2, CO, CO_2 and CH_4. The results were shown in Fig. 6. Compared to non-MACFP process, MACFP process could promote the production of H_2, CO, CO_2 and CH_4. The highest concentration of syngas (H_2+CO) found was 32.94%, and it could be used as high quality fuel.

4. Conclusion

MACFP of biomass for bio-oil production was conducted over SiO_2-CVD modified HZSM-5 in this work. When SiO_2 deposited amount increased from 0 to 5.9%, the external acid sites of HZSM-5 decreased significantly. For product distribution, the coke yield decreased, the oil fraction yield first decreased and then increased, and the yields of water and gas first increased and then decreased. For chemical compositions in oil fraction, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and oxygen-containing aromatic compounds first increased and then decreased, whereas the relative content of oxygen-containing aliphatic compounds first decreased and then increased.

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Figure captions

Fig. 1. Schematic diagram of MACFP experimental setup.

Fig. 2. Porosity and acidity characteristics of HZSM-5 catalysts: (a) BET surface area and pore size; (b) NH_3-TPD; (c) External acidity characteristics - conversion efficiencies of 1,3,5-TIPB.

Fig. 3. Product distribution.

Fig. 4. Compositions in oil fraction: (a) Relative contents of different groups; (b) Relative contents of hydrocarbons and oxygenates.

Fig. 5. Production of aromatic hydrocarbons: (a) Relative contents; (b) Selectivities.

Fig. 6. Compositions in non-condensable gas.

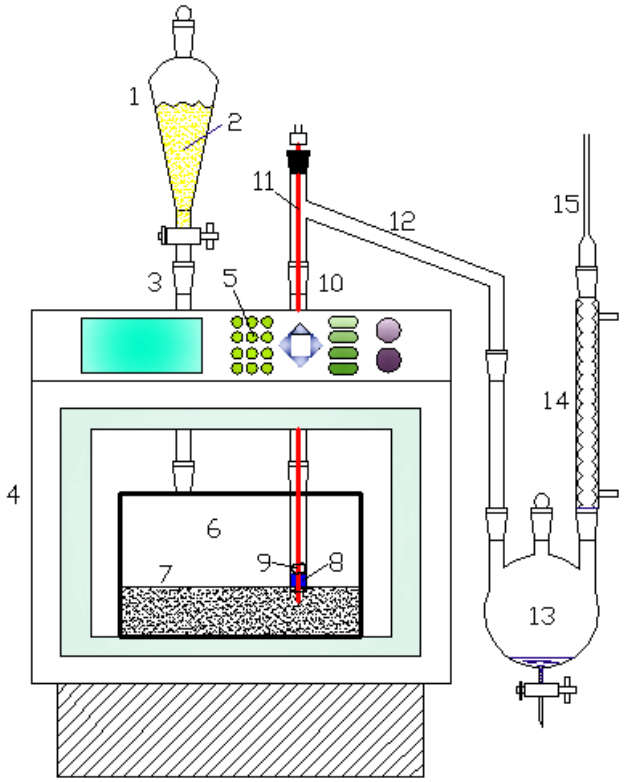
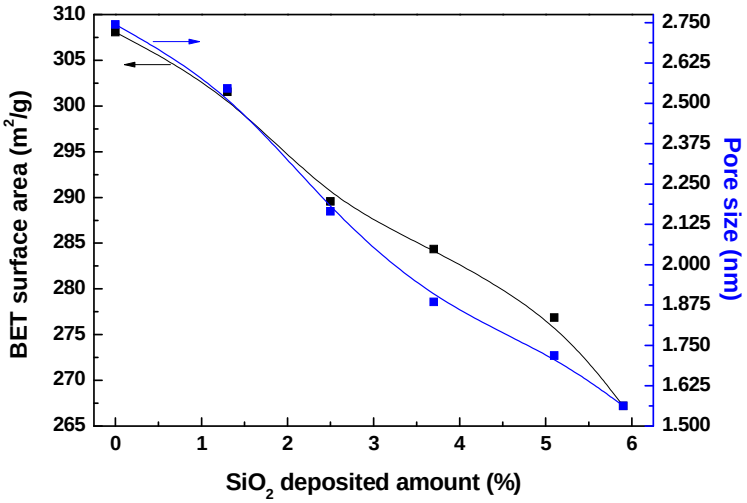
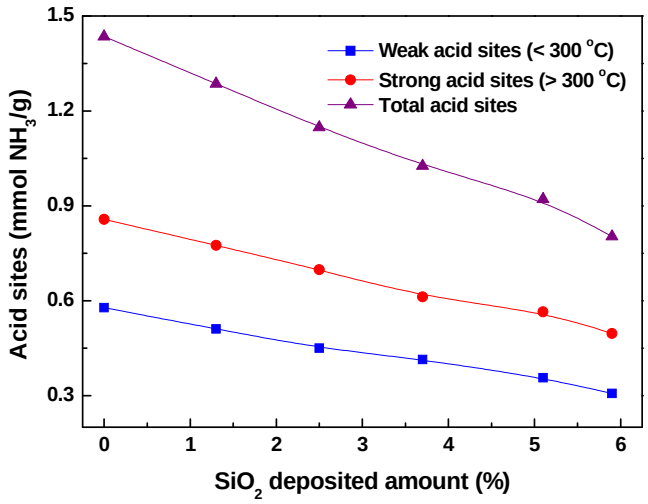


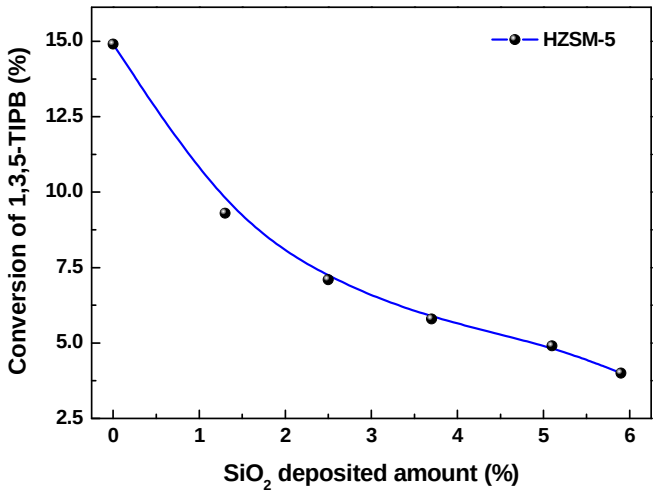
Fig. 1. Schematic diagram of MACFP experimental setup.


BET surface area (m2/g)
Pore size (nm)
SiO2 deposited amount (%)
310
305
300
295
290
285
280
275
270
265
2.750
2.625
2.500
2.375
2.250
2.125
2.000
1.875
1.750
1.625
1.500
0
1
2
3
4
5
6

(a)


Weak acid sites (< 300 °C)
Strong acid sites (> 300 °C)
Total acid sites
Acid sites (mmol NH3/g)
SiO2 deposited amount (%)
1.5
1.2
0.9
0.6
0.3
0
1
2
3
4
5
6

(b)



(c)

Fig. 2. Porosity and acidity characteristics of HZSM-5 catalysts: (a) BET surface area and pore size; (b) NH_3-TPD; (c) External acidity characteristics - conversion efficiencies of 1,3,5-TIPB.

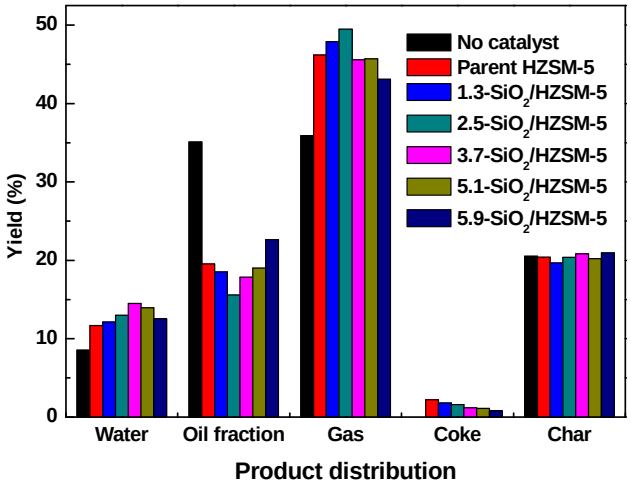
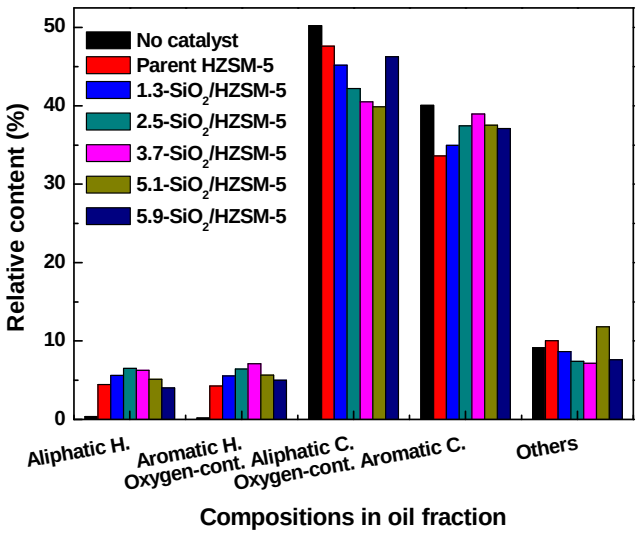
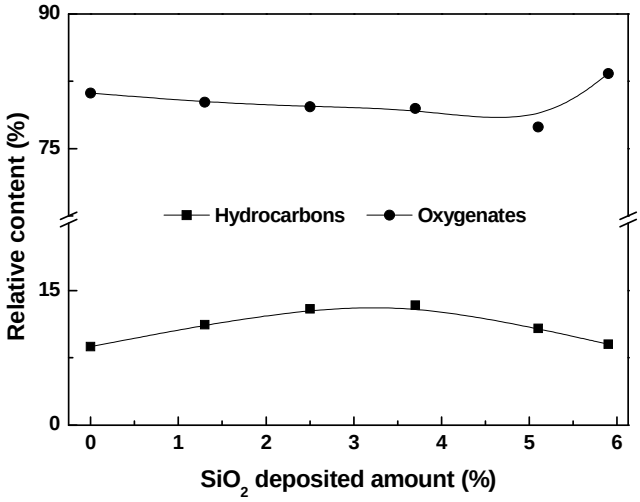


Fig. 3. Product distribution.

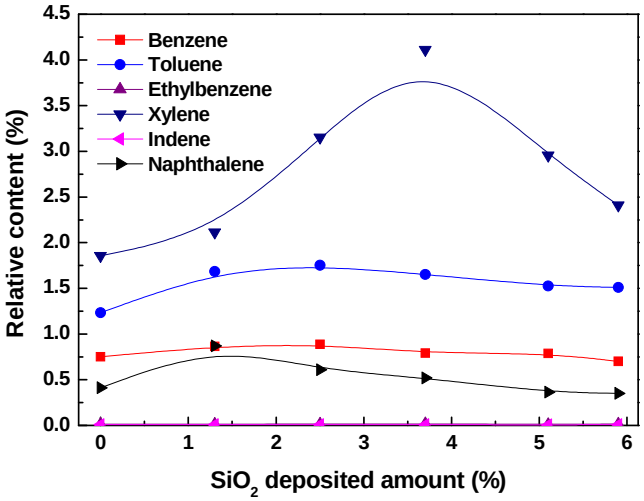


(a)

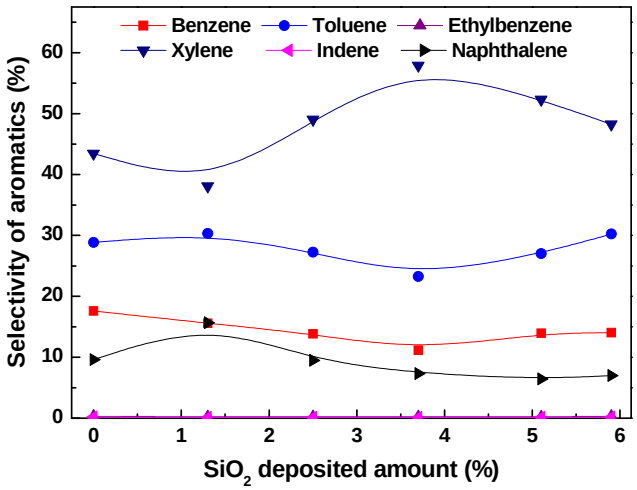


(b)

Fig. 4. Compositions in oil fraction: (a) Relative contents of different groups; (b) Relative contents of hydrocarbons and oxygenates.



(a)



(b)

Fig. 5. Production of aromatic hydrocarbons: (a) Relative contents; (b) Selectivities.

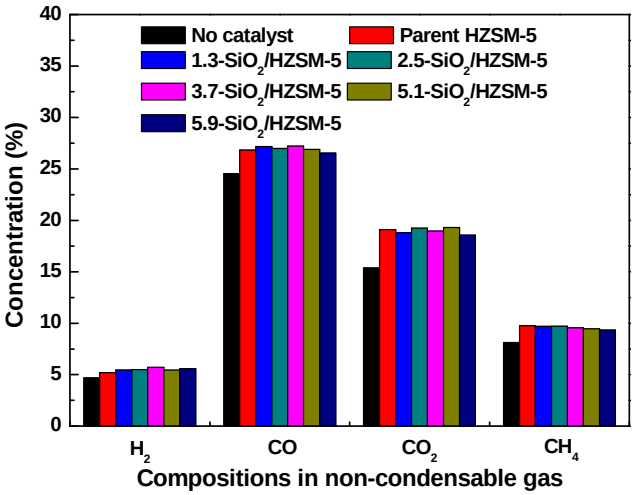


Fig. 6. Compositions in non-condensable gas.