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Reducing coke formation in catalytic fast pyrolysis of bio-derived furan with surface modified HZSM-5 catalysts

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ABSTRACT

In order to reduce coke yield during biomass catalytic fast pyrolysis process, MgO and 2,4-dimethylquinoline (2,4-DMQ) were selected to deposit the external acid sites of HZSM-5. Both MgO and 2,4-DMQ deposition could cause a reduction in total acid sites (both weak acid sites and strong acid sites) and external acid sites of HZSM-5. The modified catalysts were used for catalytic conversion of bio-derived furan. For MgO/HZSM-5 catalyst, the effects of deposited amount and deposited time were studied. The carbon yields of aromatics, C_2-C_5 olefins, total chemicals, CO_2 and CO increased at first and then decreased slightly when deposited amount increased, while the carbon yield of coke decreased first and then increased gradually. Besides, with the deposited time increased, the carbon yields of petrochemicals, CO_2 and CO increased greatly, whereas that of coke decreased. For 2,4-DMQ/HZSM-5 catalyst, the effects of 2,4-DMQ treatment amount and treatment time were investigated. The experimental results illuminated that the increase in 2,4-DMQ treatment amount or treatment time could retard the generation of target products, CO_2 and CO but promote coke formation.

1. Introduction

HZSM-5 zeolite exhibits an excellent performance for catalytic fast pyrolysis (CFP) of lignocellulosic biomass.[1-3] However, the acid sites on the external surface of HZSM-5 can cause coke formation during CFP process,[4,5] thus resulting in the blockage of pore opening and the deactivation of HZSM-5 catalyst. 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.[6] Zhang *et al.* selectively inactivated the external acid sites of HZSM-5 catalyst by means of chemical liquid deposition of inert silica (SiO_2-CLD), and the characteristics of silanized HZSM-5 samples were tested by catalytic conversion of biomass pyrolysis-derived compounds.[7] Their results showed that the modified HZSM-5 could promote the production of olefins and aromatics and reduce the coke yield compared to parent HZSM-5. Bauer *et al.* also passivated the external acid sites of HZSM-5 catalyst by pre-coking treatment,[8,9] and the pre-coked HZSM-5 showed a better shape-selective effect for the formation of target products and led to a reduced formation of undesirable compounds. In this study, we propose HZSM-5-based catalysts with external surface deposition of magnesium oxide (MgO) and 2,4-dimethylquinoline (2,4-DMQ) to improve the catalytic effect during biomass CFP process, which has been seldomly studied. It is obviously beneficial for the promotion of bio-oil quality in biomass CFP process.

For MgO, magnesium acetate is used as the precursor, which will polymerize to large-molecule coordination compounds (see Fig. 1(a)) in aqueous solution.[10] The generated large-molecule coordination compounds can not enter the narrow inner channels, so their thermal decomposition will lead to the formation of MgO on the external surface of HZSM-5 catalyst (equation (1)). For 2,4-DMQ, as a bulky basic molecule, it can poison the acid sites irreversibly, and its molecule diameter is greater than the pore diameter of HZSM-5 catalyst.[11,12] Therefore, the external acid sites will be poisoned selectively when HZSM-5 catalyst is treated with 2,4-DMQ, whereas the internal acid sites will be kept intact. The molecular structure of 2,4-DMQ is shown in Fig. 1(b).

$$(C_4H_6O_4Mg)_n + 4nO_2 \rightarrow nMgO + 4nCO_2 + 3nH_2O \qquad (1)$$

In this work, the external acid sites of HZSM-5 catalyst were reduced or eliminated with the deposition of MgO and 2,4-DMQ. The obtained MgO or 2,4-DMQ modified HZSM-5 catalysts (referred to as MgO/HZSM-5 and 2,4-DMQ/HZSM-5, respectively) were used for the catalytic conversion of bio-derived furan, which was one of the most important intermediates in biomass CFP process.[13] For MgO/HZSM-5 catalyst, the effects of deposited amount and deposited time were studied and analysed. For 2,4-DMQ/HZSM-5 catalyst, the effects of 2,4-DMQ treatment amount and treatment time were investigated and discussed.

2. Experimental

2.1 Materials

Magnesium acetate (analytical reagent, AR) and 2,4-DMQ (AR) were bought from Sinopharm Chemical Reagent Co., Ltd. Furan (AR) was supplied by Aladdin Company. HZSM-5 zeolite catalyst (silicon-to-aluminum ratio: 50, particle diameter: 2-5 μm) was provided by the Catalyst Plant of Nankai University, with specific surface area (N_2 porosimetry and D-R equation) of 332 m^2/g and pore volume of 0.19 cm^3/g.

2.2 Preparation of MgO/HZSM-5 catalyst

First, magnesium acetate aqueous solution with a regulated concentration was prepared. Then, it was mixed with HZSM-5 catalyst in a beaker at room temperature using a magnetic stirrer, and a certain deposited time was maintained. Second, the prepared slurry was dried at 120 ^{o}C for 12 h. Finally, the dried sample was put into a muffle furance for calcination (550 ^{o}C, 6 h) to obtain the MgO/HZSM-5 catalyst we needed. The samples at different deposited amounts and deposited times were prepared.

2.3 Preparation of 2,4-DMQ/HZSM-5 catalyst

During our experiments, 2,4-DMQ was directly introduced into the heated reactor with desired flow rate and injection time (see Fig. 2). 2,4-DMQ would be vaporized and then poison the catalyst when passing through the reactor. In this paper, The 2,4-DMQ/HZSM-5 catalyst samples at different 2,4-DMQ treatment amounts and treatment times were studied.

2.4 Determination of acid sites on the external surface

The catalytic cracking of 1,3,5-tri-iso-propyl-benzene (1,3,5-TIPB, analytical grade chemical, Sigma-Aldrich Corporation) was carried out in a fixed bed to determine the extent of inactivation of the external acid sites of modified HZSM-5 catalysts.[14,15] 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).

2.5 Experimental setup

The schematic experimental setup is shown in Fig. 2. The catalytic conversion of furan with modified HZSM-5 catalysts was investigated in a laboratory-scale quartz tubular reactor (5) with an inner diameter of 15.5 mm, which was externally heated by an electric heater (6). 100 mg HZSM-5 catalyst was placed on a sieve plate in the reactor. During the experiments, nitrogen was applied as the carrier gas at a constant flow rate of 180 ml/min. When furan was introduced into the reactor by an injection pump (3), it would be vaporized and pass through the catalyst layer, resulting in its conversion and the formation of target products. For each experiment, the running time was 25 min, the reaction temperature was kept at 550 ^{o}C, and the total mass of influent furan was 50 mg. The bio-oil was collected in the condenser, and the noncondensable gas products were collected in a gas bag. Besides, injection pump (4) was used for 2,4-DMQ supply, and desired 2,4-DMQ treatment amount and treatment time could be set before each experiment.

2.6 Products Analysis and Data Processing

During the experiments, carbon yield and carbon selectivity were calculated and analysed, and they were defined as:

$$\text{Carbon yield} = \frac{\text{Moles of carbon in a certain kind of product}}{\text{Total moles of carbon in the converted feedstocks}} \times 100\% \qquad (2)$$

For 2,4-DMQ/HZSM-5 catalyst, the converted feedstocks included furan and

2,4-DMQ. After each experiment, 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 fully combusted (600 ^{o}C, 30 min) in a glass tube under the O_2 atmosphere (100 ml/min) so that the coke yield was obtained. The mass of generated CO_2 was achieved through sodium hydroxide absorption method, thus the carbon yield of coke could be determined. The bio-oil yield was achieved through weight difference of the condenser before and after every experiment. Besides, the noncondensable gas yield was calculated by difference.

The components of bio-oil were identified using GC/MS instrument (7890A/5975C, Agilent). The GC/MS injector temperature of 275 ^{o}C and interface temperature of 300 ^{o}C were held. The GC separation was carried out using a capillary column named HP-5MS (30 m × 0.25 mm × 0.25 μm). A split ratio of 1:80 was used. Typical operating conditions of MS were ionization energy 70 eV, and scan per second over range electron m/z=35-550 amu. The chromatographic peaks were discriminated and analyzed by means of the NIST MS library. 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. High-purity argon (99.999%) was used as the carrier gas. The temperatures of the injector and the detector were set at 120 ^{o}C. The temperatures of the 5A molecular sieve and PPQ column were kept at 80 and 150 ^{o}C, respectively.

3. Results and discussion

3.1 Acidity characteristics of HZSM-5 catalysts

A simple comparison of the acidity characteristics of parent and modified HZSM-5 catalysts is given in Table 1. Here, 2,4-DMQ was introduced into the heated reactor to passivate the outer surface of HZSM-5 without feeding furan. Then the obtained 2,4-DMQ/HZSM-5 catalyst was collected for acidity analysis. The acidity characteristics of HZSM-5 samples were analyzed by ammonia TPD. As can be seen, both MgO and 2,4-DMQ treatment led to a decrease in the total acid sites (both weak acid sites and strong acid sites) of HZSM-5 catalyst, because some external acid sites were passivated under this circumstance. It is anticipated that the modified HZSM-5 could inhibit coke formation and fine-tune catalytic performance.

In our present study, 1,3,5-TIPB was selected as probe molecule as its catalytic cracking conversion over HZSM-5 took place only on the external surface. Hibino *et al.* 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.[16] Namba *et al.* 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.[17] Table 1 also shows the conversion efficiencies of 1,3,5-TIPB over parent and modified HZSM-5 catalysts. As could be seen, conversions of 1,3,5-TIPB decreased significantly over MgO/HZSM-5 and 2,4-DMQ/HZSM-5 compared to parent

HZSM-5, indicating that MgO and 2,4-DMQ treatment could selectively inactivate the external surface.

3.2 Catalytic conversion of furan over MgO/HZSM-5

3.2.1 The effect of MgO deposited amount

The carbon yields of chemicals from the catalytic conversion of furan are shown in Fig. 3. The tested MgO/HZSM-5 catalysts were prepared at a deposited time of 6 h, and the deposited amounts were 0%, 1%, 2%, 4%, 6% and 8%, respectively.

It should be pointed that the catalytic conversion of bio-derived furan over HZSM-5 will lead to the production of hydraocarbons (mainly include aromatics and olefins), CO_2, CO and oxygenated organic compounds. HZSM-5 catalyst can favor the formation of aromatics and olefins due to its unique pore structures. Therefore, aromatics and olefins were selected as the target products in our study, and our paper focused on the carbon yields and selectivities of aromatics and olefins. From Fig. 3(a), we can see that the deposition of MgO promoted the carbon yields of aromatics, C_2-C_5 olefins and total chemicals (aromatics + C_2-C_5 olefins). Moreover, when the deposited amount of MgO increased from 0% to 8%, the carbon yields of aromatics, C_2-C_5 olefins and total chemicals tended to increase at first and then decrease slightly, while the maximun values were achieved at the deposited amount of 4%. The carbon yields of CO_2 and CO showed the same tendency (see Fig. 3(b)), whereas that of coke decreased first and then increased gradually. The deposition of MgO passivated the outer surface of HZSM-5 catalyst, and as a result, the external acid sites decreased largely, thus restraining the formation of coke and promoting the subsequent shape-selective reactions. Besides, it is reported that MgO could crack some heavy compounds into smaller oxygenated organic compounds,[18] and these oxygenates would suffer deoxygenation reactions inside the internal structure, which was also conducive to the production of aromatics, olefins, CO_2 and CO. Therefore, their carbon yields increased and the carbon yield of coke decreased. However, redundant MgO deposited amount would give rise to the pore mouth blockage and prevent relative reactions. Consequently, the further increase of MgO deposited amount led to a decrease in petrochemical yield and increase in coke yield. The selectivities of C_2-C_5 olefins and aromatics are shown in Fig. 3(c) and (d). Aromatics included benzene, toluene, ethylbenzene, xylene, indene and naphthalene. Obviously, the deposition of MgO increased the selectivities of propylene, butylene and xylene, and decreased the selectivities of ethylene and C_5 olefin. Besides, when the MgO deposited amount increased from 0 to 8%, the selectivity of benzene decreased at first and then increased, whereas that of toluene increased at first and then decreased. The selectivities of ethylbenzene, indene and naphthalene alomost kept constant.

3.2.2 The effect of MgO deposited time

The carbon yields of chemicals from the catalytic conversion of furan are shown in Fig. 4. The tested MgO/HZSM-5 catalysts were prepared at a deposited amount of 4%, and the deposited times were 1, 2, 4, 6, 8 and 10 h, respectively.

Obviously, the MgO deposited time has a great impact on the product dirtribution of furan catalytic conversion over MgO/HZSM-5 catalyst. When the deposited time increased from 1 to 10 h, the carbon yields of aromatics, C_2-C_5 olefins, total chemicals, CO_2 and CO increased greatly. Meanwhile, the carbon yield of coke decreased over the range of deposited time studied. The main reason is that more deposited time would make the deposition more uniform,[7] so more external acid sites of HZSM-5 catalyst would be covered by MgO on this condition. From Fig. 4(c) and (d), we can see that the selectivities of ethylene and benzene decreased, while the selectivities of propylene, butylene and toluene increased with increasing deposited time. Besides, the selectivities of C_5 olefin, ethylbenzene, xylene, indene and naphthalene fluctuated.

3.3 Catalytic conversion of furan over 2,4-DMQ/HZSM-5 catalyst

2,4-DMQ could eliminate the external acid sites of HZSM-5 catalyst selectively. However, on the other hand, it may also act as the coke precursor and provide the growing space for coke growth on the outer surface of HZSM-5 catalyst. It was not clear whether the 2,4-DMQ deposition was positive or negative, and it had been studied in this paper.

3.3.1 The effect of 2,4-DMQ treatment amount

The carbon yields of chemicals from the catalytic conversion of furan are shown in Fig. 5. During these experiments, the tested HZSM-5 catalysts were treated with 2,4-DMQ and the mass ratios of 2,4-DMQ to HZSM-5 catalyst were 0, 3, 6, 9 and 12×10^{-4} mol·h^{-1}·g^{-1}, respectively. Besides, the treatment time was kept at 10 min.

From Fig. 5(a) and (b), we can see that the carbon yields of aromatics, C_2-C_5 olefins, total chemicals, CO_2 and CO decreased with the increase in the 2,4-DMQ treatment amount, while the carbon yield of coke increased significantly. It was found that 2,4-DMQ seemed to accelerate rather than retard coke formation. 2,4-DMQ could poison the external acid sites of HZSM-5 catalyst selectively. However, when it was adsorbed on the external acid sites, the benzene ring in its structure could easily suffer the electrophilic substitution reactions with other chemicals and function as aromatic coke precursor,[19-23] thus resulting in the production of polycyclic aromatic hydrocarbon and promotion of coke formation progress. Consequently, the carbon yields of target products decreased but the coke yield increased. As shown in Fig. 5(c) and (d), the selectivities of ethylene and benzene increased, while that of butylene and C_5 olefin decreased with increasing mass ratio of 2,4-DMQ to HZSM-5 catalyst. It seemed that 2,4-DMQ treatment could promote the production of low-carbon content compounds.

3.3.2 The effect of the 2,4-DMQ treatment time

The carbon yields of chemicals from the catalytic conversion of furan are shown in Fig. 6. During these experiments, the tested HZSM-5 catalysts were treated with 2,4-DMQ and the treatment times were 0, 10 and 20 min. Besides, the mass ratio of 2,4-DMQ to HZSM-5 catalyst was kept at 3×10^{-4} mol·h^{-1}·g^{-1}.

From Fig. 6(a) and (b), we can see that the carbon yields of aromatics, C_2-C_5 olefins, total chemicals, CO_2 and CO decreased over the range of 2,4-DMQ treatment time studied, while that of coke increased significantly from 36.5% to 41.5%. The effect of the 2,4-DMQ treatment time could be explained as follows. Obviously, more 2,4-DMQ would be adsorbed on the external acid sites of HZSM-5 catalyst as a result of longer treatment time. Therefore, these coke precursors would inevitably accelerate the production of coke and retard the generation of other chemicals. As shown in Fig. 6(c) and (d), the treatment time of 10 min produced the highest selectivities of ethylene and benzene and the lowest selectivities of C_5 olefin, ethylbenzene and indene. Besides, the selectivities of propylene, toluene, xylene and naphthalene increased, whereas that of butylene decreased with increasing 2,4-DMQ treatment time.

Although both MgO and 2,4-DMQ can passivate or eliminate the external acid sites of HZSM-5 catalyst, their experimental results are totally different. Maybe organics which have benzene rings in their molecular structures should not be selected as the modifiers, and we will do more researches to evaluate the influence of different modifiers in the future.

4. Conclusion

Both MgO and 2,4-DMQ treatment could reduce the total acid sites (both weak acid sites and strong acid sites) and external acid sites of HZSM-5. In this work, MgO and 2,4-DMQ modified HZSM-5 catalysts were used for furan catalytic conversion. For MgO/HZSM-5 catalyst, the carbon yields of aromatics, C_2-C_5 olefins, total chemicals, CO_2 and CO increased first and then decreased with a increase in deposited amount, whereas that of coke decreased first and then increased. Besides, when deposited time increased, the carbon yields of petrochemicals, CO_2 and CO increased, while that of coke decreased. For 2,4-DMQ/HZSM-5 catalyst, more 2,4-DMQ treatment amount or longer treatment time could reduce the the carbon yields of target products, CO_2 and CO but promote the coke formation.

Acknowledgement

The work was supported by the National Basic Research Program of China (973 Program) (No. 2013CB228106), the National Natural Science Fund Program of China (No. 51276040), the Scientific Research Foundation of Graduate School of Southeast University (No.YBJJ1430), the Fundamental Research Funds for the Central Universities and the scientific innovation research program of college graduate in Jiangsu province (No. KYLX_0183), China Scholarship Council (CSC), as well as Minnesota Environment and Natural Resources Trust Fund, North Central Regional Sun Grant Center at South Dakota State University through a grant provided by the US Department of Agriculture (2013-38502-21424) and a grant provided by the US Department of Transportation, Office of the Secretary (DTOS59-07-G-00054).

Notes and references

1 Z. Du, B. Hu, X. Ma, Y. Cheng, Y. Liu, X. Lin, Y. Wan, H. Lei, P. Chen and R. Ruan, *Bioresour. Technol.*, 2013, **130**, 777-782.

2 B. Zhang, Z. Zhong, K. Ding, Y. Cao and Z. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 9979-9984.

3 B. Kunwar and T. Mlsna, *Proceedings of the 245th ACS National Meeting and & Exposition*, 2013, **58**, 90-92.

4 B. Zhang, Z. Zhong, K. Ding and Z. Song, *Fuel*, 2015, **139**, 622-628.

5 T. R. Carlson, Y. Cheng, J. Jae and G. W. Huber, *Energ. Environ. Sci.*, 2011, **4**, 145-161.

6 P. Matias, J. M. Lopes, S. Laforge, P. Magnoux, M. Guisnet and F. R. Ribeibo, *Appl. Catal. A*, 2008, **351**, 174-183.

7 H. Zhang, M. Luo, R. Xiao, S. Shao, B. Jin and G. Xiao, *Bioresour. Technol.*, 2014, **155**, 57-62.

8 F. Bauer, W. Chen, Q. Zhao, A. Freyer and S. Liu, *Micropor. Mesopor. Mat.*, 2001, **47**, 67-77.

9 F. Bauer, W. Chen, E. Bilz, A. Freyer, V. Sauerland and S. Liu, *J. Catal.*, 2007, **251**, 258-270.

10 J. Wang, B. Zhao and Y. Xie, *Acta Phys. Chim. Sin.*, 2001, **17**, 966-971.

11 S. Laforge, D. Martin and M. Guisnet, *Appl. Catal. A*, 2004, **268**, 33-41.

12 H. Wei, K. Liu, S. Xie, W. Xin, X. Li, S. Liu and L. Xu, *J. Catal.*, 2013, **307**, 103-110.

13 Y. Cheng and G. W. Huber, *ACS Catal.*, 2011, **1**, 611-628.

14 J. Kim, A. Ishida, M. Okajima and M. Niwa, *J. Catal.*, 1996, **161**, 387-392.

15 J. Zhang, W. Qian, C. Kong and F. Wei, *ACS Catal.*, 2015, **5**, 2982-2988.

16 T. Hibino, M. Niwa and Y. Murakami, *Zeolites*, 1993, **13**, 518-523.

17 S. Namba, A. Inaka and T. Yashima, *Zeolites*, 1986, **6**, 107-110.

18 R. Li, Z. Zhong, B. Jin and A. Zheng, *Bioresour. Technol.*, 2012, **119**, 324-330.

19 C. Fu and A. M. Schaffer, *Ind. Eng. Chem. Prod. Res. Dev.*, 1985, **21**, 68-75.

20 A. Corma, V. Fornes, J. B. Monton and A. V. Orchilles, *Ind. Eng. Chem. Res.*, 1987, **26**, 882-886.

21 T. Ho, A. R. Katritzky and S. J. Cato, *Ind. Eng. Chem. Res.*, 1992, **31**, 1589-1597.

22 H. S. Cerqueira, G. Gaeiro, L. Costa and F. R. Ribeiro, *J. Mol. Catal. A*, 2008, **292**, 1-13.

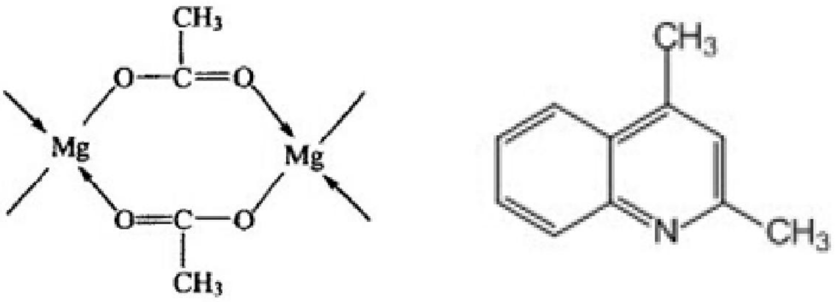
23 B. Zhang, Z. Zhong and Z. Fu, *J. Cent. South Univ.*, 2015, **22**, 82−87.

Table 1 Acidity characteristics of parent and modified HZSM-5

Catalyst	Acidity characteristics (NH_3-TPD)			Catalytic conversion efficiency of 1,3,5-TIPB (%)
	Total acid sites (mmoles NH_3/g)	Weak acid sites (<300^{o}C, mmoles NH_3/g)	Strong acid sites (>300^{o}C, mmoles NH_3/g)	
Parent HZSM-5	1.435	0.578	0.857	14.9
MgO/HZSM-5[a]	0.869	0.417	0.452	9.2
2,4-DMQ/HZSM-5[b]	1.194	0.507	0.687	6.3

[a] Deposited condition of MgO/HZSM-5: deposited amount of 4% and deposited time of 6 h.

[b] Deposited condition of 2,4-DMQ/HZSM-5: mass ratio of 2,4-DMQ to HZSM-5 catalyst of 3×10^{-4} mol·h^{-1}·g^{-1} and treatment time of 10 min.



(a) (b)

Fig. 1. Molecular structures of modifiers. (a) Large-molecule coordination compounds generated from magnesium acetate. (b) 2,4-DMQ.

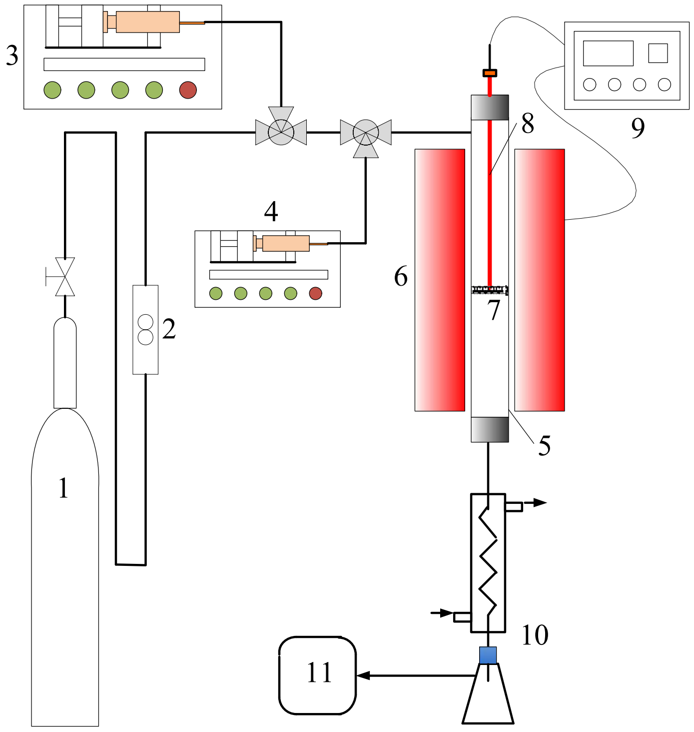
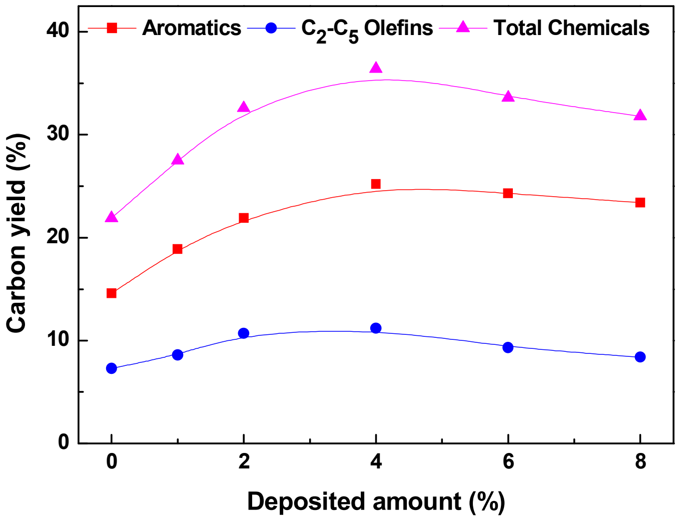
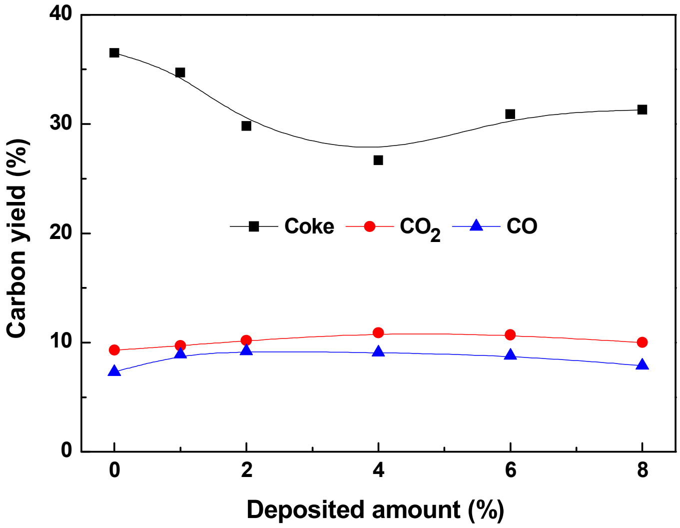


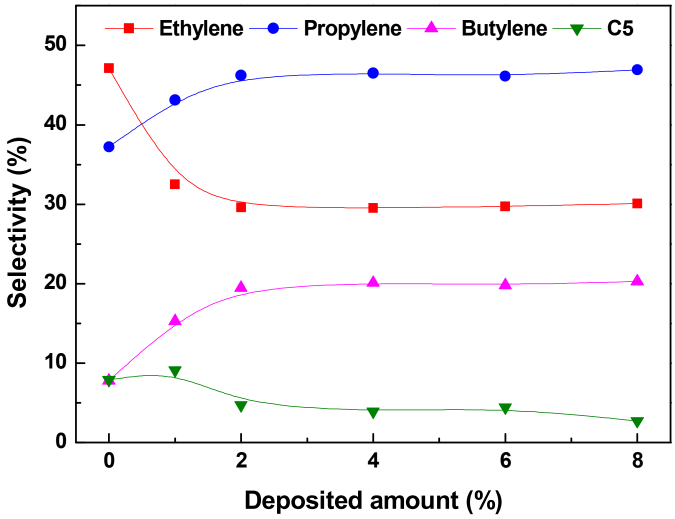
Fig. 2. Schematic diagram of the experimental setup. 1. N_2 gas cylinder. 2. Flowmeter. 3. Injection pump (furan). 4. Injection pump (2,4-DMQ). 5. Quartz tubular reactor. 6. Electric heater. 7. HZSM-5 catalyst. 8. Thermocouple. 9. Temperature controller. 10. Condenser. 11. Gas bag.


Aromatics
C2-C5 Olefins
Total Chemicals
Carbon yield (%)
Deposited amount (%)
0
10
20
30
40
0
2
4
6
8

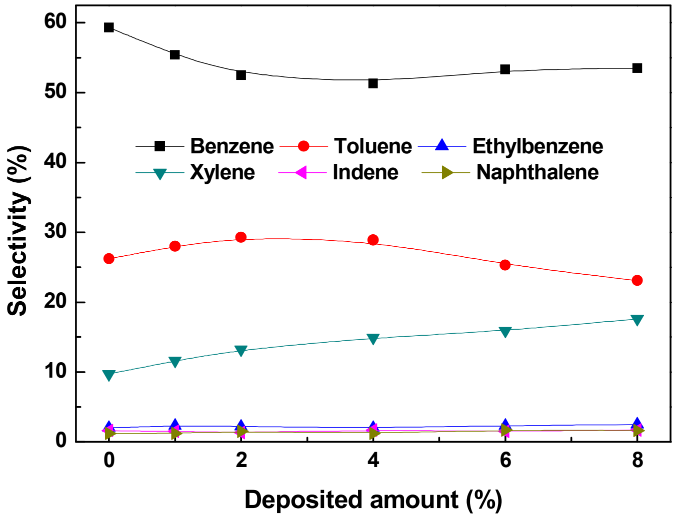
(a)


Coke
CO2
CO
Carbon yield (%)
Deposited amount (%)
0
10
20
30
40
0
2
4
6
8

(b)

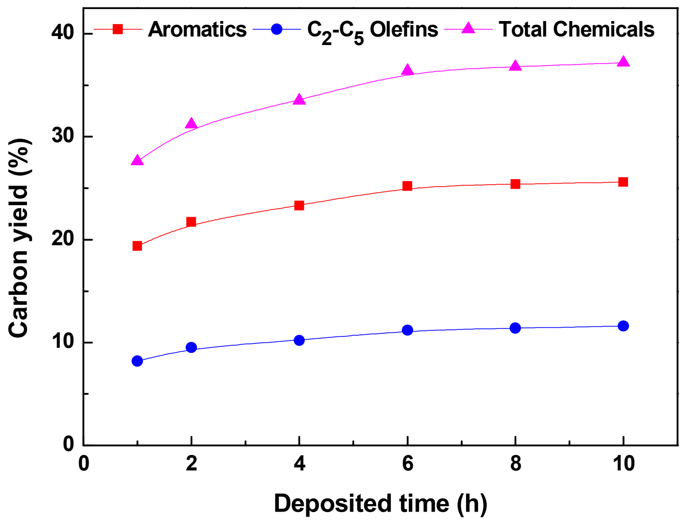


(c)

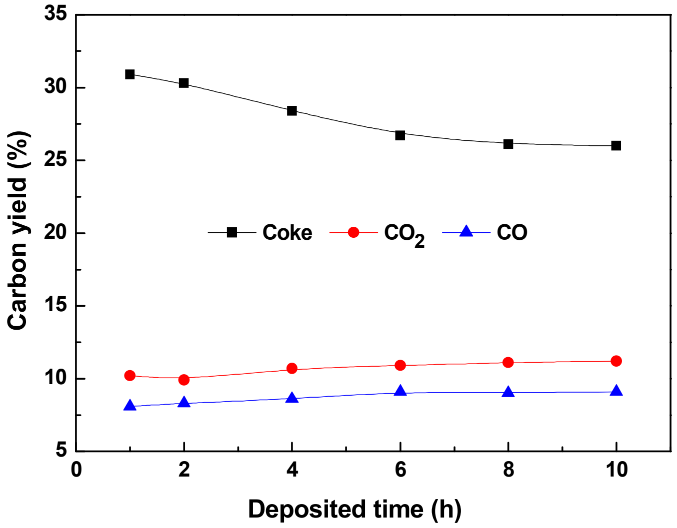


(d)

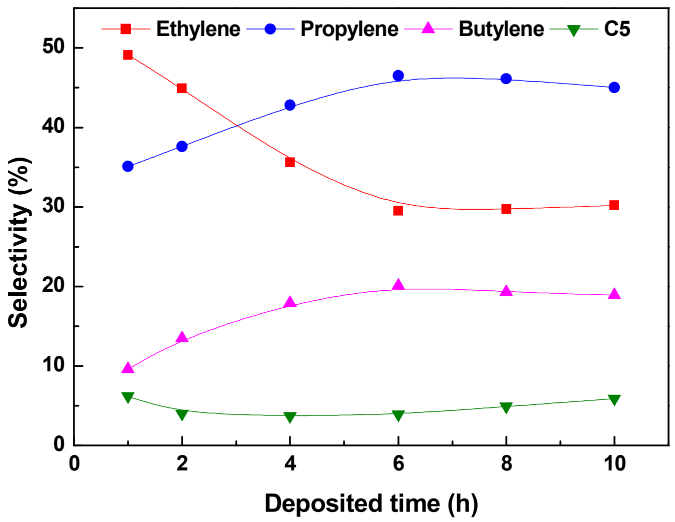
Fig. 3. Carbon yields of chemicals from the catalytic conversion of furan over MgO/HZSM-5 catalysts with different MgO deposited amounts. (a) Carbon yields of aromatics, olefins and total chemicals. (b) Carbon yields of coke, CO_2 and CO. (c) Selectivities of C_2-C_5 olefins; (d) Selectivities of aromatics.


Aromatics
C2-C5 Olefins
Total Chemicals
Carbon yield (%)
Deposited time (h)
0
10
20
30
40
0
2
4
6
8
10

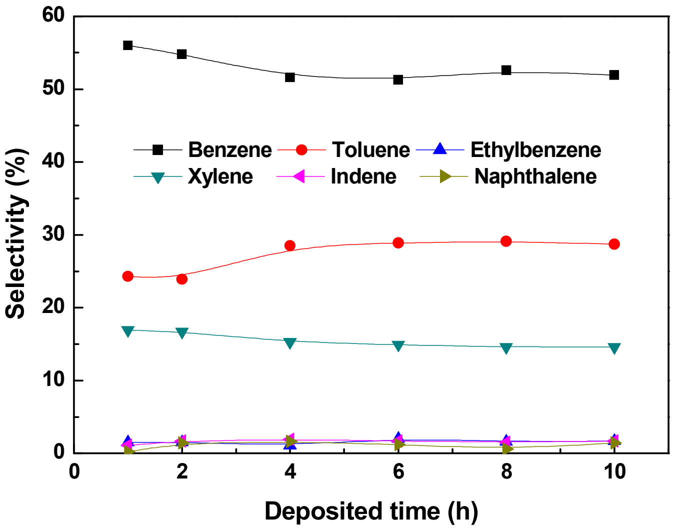
(a)


Coke
CO2
CO
Carbon yield (%)
Deposited time (h)
5
10
15
20
25
30
35
0
2
4
6
8
10

(b)

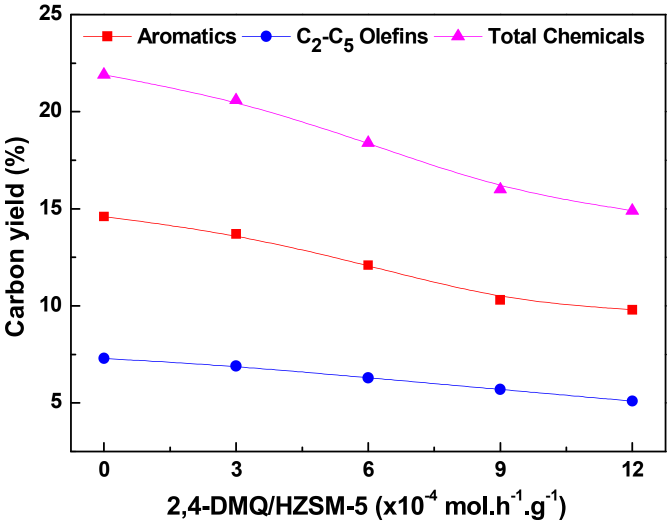


(c)

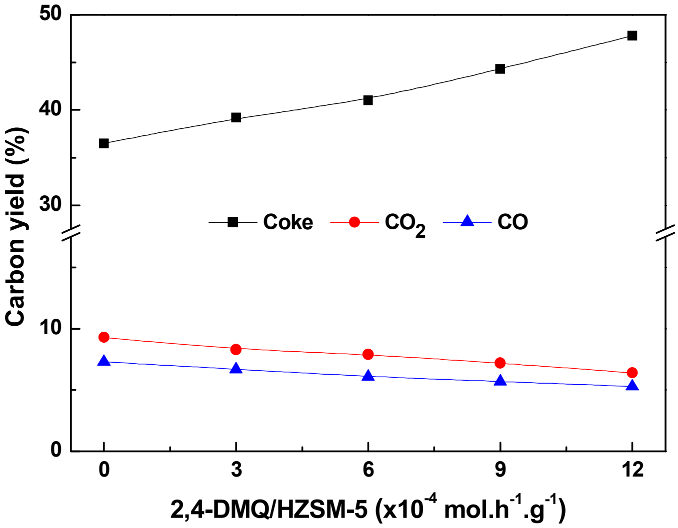


(d)

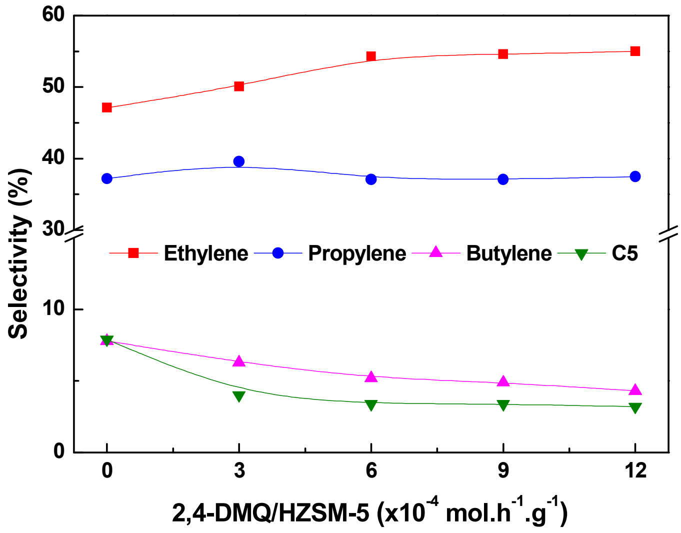
Fig. 4. Carbon yields of chemicals from the catalytic conversion of furan over MgO/HZSM-5 catalyst with different MgO deposited times. (a) Carbon yields of aromatics, olefins and total chemicals. (b) Carbon yields of coke, CO_2 and CO. (c) Selectivities of C_2-C_5 olefins; (d) Selectivities of aromatics.


Aromatics
C2-C5 Olefins
Total Chemicals
Carbon yield (%)
25
20
15
10
5
0
3
6
9
12
2,4-DMQ/HZSM-5 (x10-4 mol.h-1.g-1)

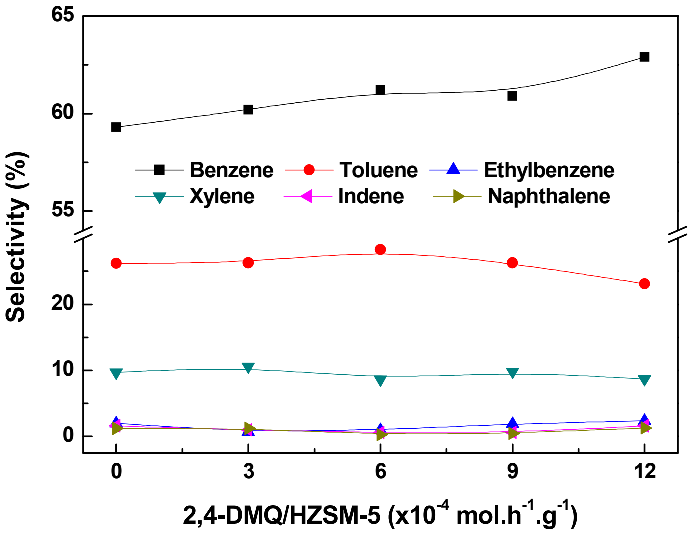
(a)


Coke
CO2
CO
Carbon yield (%)
50
40
30
10
0
0
3
6
9
12
2,4-DMQ/HZSM-5 (x10-4 mol.h-1.g-1)

(b)

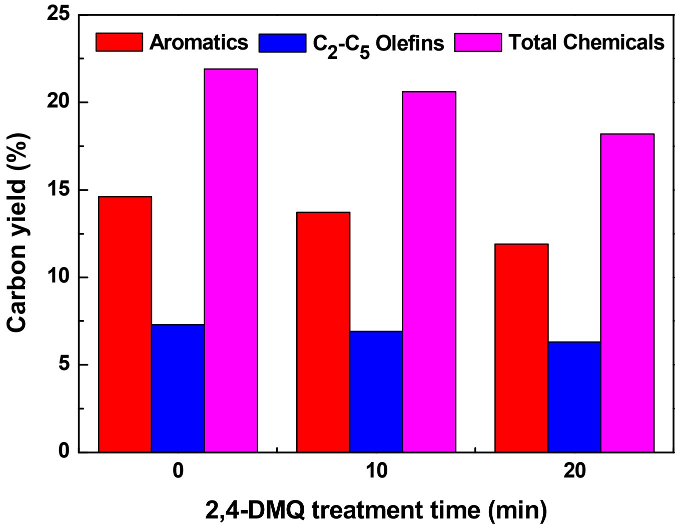


(c)

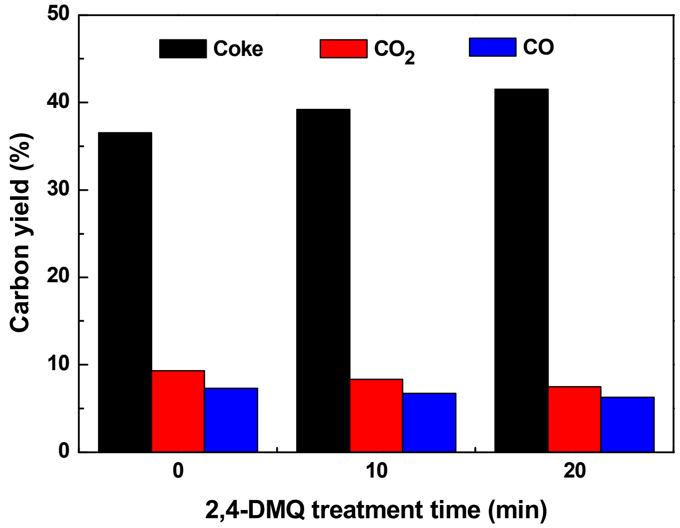


(d)

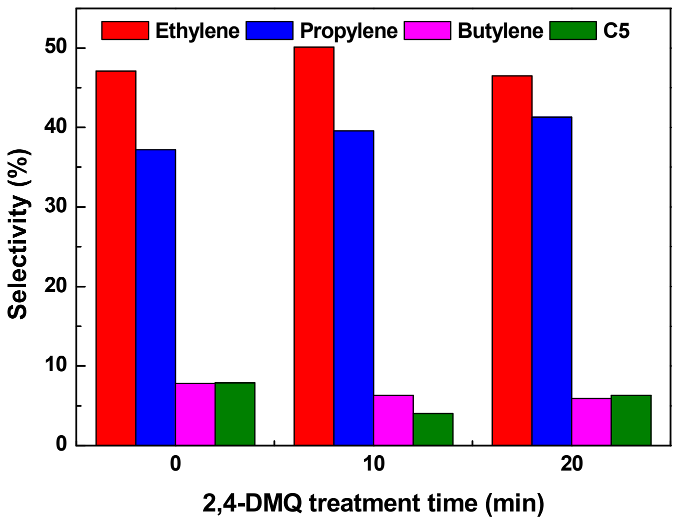
Fig. 5. Carbon yields of chemicals from the catalytic conversion of furan over 2,4-DMQ/HZSM-5 catalyst with different 2,4-DMQ treatment amounts. (a) Carbon yields of aromatics, olefins and total chemicals. (b) Carbon yields of coke, CO_2 and CO. (c) Selectivities of C_2-C_5 olefins; (d) Selectivities of aromatics.


Aromatics
C_2-C_5 Olefins
Total Chemicals
Carbon yield (%)
0
5
10
15
20
25
0
10
20
2,4-DMQ treatment time (min)

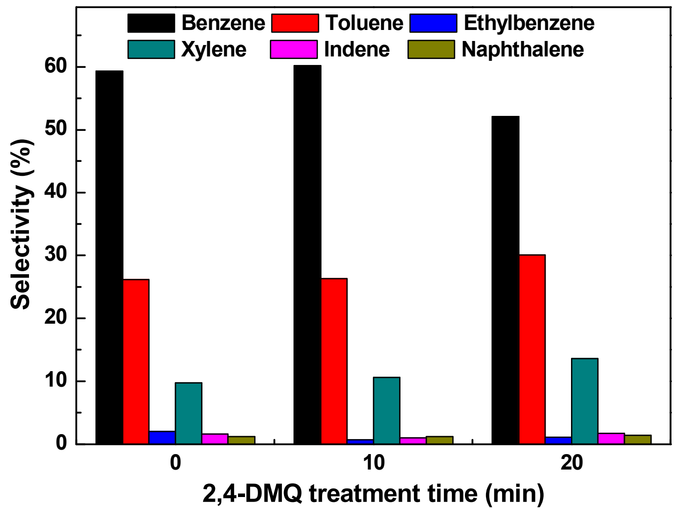
(a)


Coke
CO_2
CO
Carbon yield (%)
0
10
20
30
40
50
0
10
20
2,4-DMQ treatment time (min)

(b)



(c)



(d)

Fig. 6. Carbon yields of chemicals from the catalytic conversion of furan over 2,4-DMQ/HZSM-5 catalyst with different 2,4-DMQ treatment times. (a) Carbon yields of aromatics, olefins and total chemicals. (b) Carbon yields of coke, CO_2 and CO. (c) Selectivities of C_2-C_5 olefins; (d) Selectivities of aromatics.