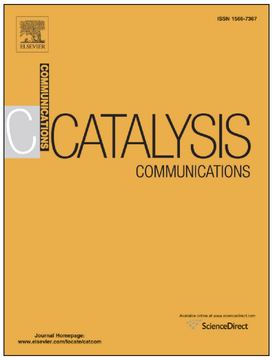

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PII: S1566-7367(17)30384-9
DOI: doi: 10.1016/j.catcom.2017.09.011
Reference: CATCOM 5193

To appear in: *Catalysis Communications*

Received date: 9 May 2017
Revised date: 11 September 2017
Accepted date: 11 September 2017

Please cite this article as: Tao He, Xinxin Liu, Yuanzheng Ge, Dezhi Han, Jianqing Li, Zhiqi Wang, Jinhu Wu , Gas phase hydrodeoxygenation of anisole and guaiacol to aromatics with a high selectivity over Ni-Mo/SiO2. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2017), doi: 10.1016/j.catcom.2017.09.011

Gas phase hydrodeoxygenation of anisole and guaiacol to aromatics with a high selectivity over Ni-Mo/SiO_2

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Abstract

A very active Ni-Mo bimetallic catalyst supported on SiO_2 was prepared for the hydrodeoxygenation (HDO) reaction of anisole and guaiacol under a H_2 partial pressure of 83 kPa. Generally, transition metal and their oxides were thought to have less HDO activity than others, such as sulfides, carbides, phosphides. However, this work achieved a novel deoxygenation result, where a high conversion (98.7%) at 673-693 ℃ and atmospheric pressure for the model compounds and high selectivity (more than 96%) to aromatic hydrocarbons (BTX) were obtained. Furthermore, the methyl transfer reaction is greatly promoted by abundant acid sites of the catalyst, leading to a low carbon-loss. The present work provides a promising way and new insight for an economic and efficient HDO process for the lignin-derived thermal degradation products.

1. Introduction

Lignin is an aromatic bio-polymer mainly connected by aryl ethers, it can be a renewable source for aromatic compounds production. However, during the lignin thermal degradation, most of the O atoms retain in the product molecules, leading to high oxygen content and poor chemical properties[1-2]. The removal of O via catalytic HDO reaction attracted much attention in the past decades[2-6].

Noble metals Pt, Pd, Ru show high activity and stability under 0.5-4 Mpa H_2 pressure，but undesired ring saturation to cyclanes usually coexists, leading to high H_2 consumption[7,8]. Traditional Ni, Mo, Co sulfides are extensively studied[9-11] under high H_2 pressure (2-8MPa). Transition metal phosphides Ni_2P, Co_2P and carbides W_2C, Mo_2C have been found to have better HDO activity and good selectivity to benzene in gas phase HDO reaction. Zhao et al.[12] found that the major products from HDO of guaiacol using N_2P were benzene and phenol, with a conversion of 80%, benzene selectivity of 60%. Lee et al.[13] firstly reported that Mo_2C could effectively catalyze vapor phase anisole HDO reaction, with benzene selectivity of 92~96% under H_2/anisole molar ratio of 110. Lu et al.[14] reported that ordered mesoporous W_2C catalyst had a higher than 96% benzene selectivity in vapor phase anisole HDO. Recently, Román-Leshkov et al.[15,16] found that MoO_3 can selectively cleave the C–O bond, MoO_3/ ZrO_2 was the optimal catalyst giving the cresol conversion of 78% and BTX (benzene, toluene, xylene) selectivity of 99%, but MoO_3/SiO_2 only gave a conversion of 13%. Although, the transition metal oxides deactivated in 5-7 h, the mild condition provides a promising way for an economic and efficient HDO process.

In this contribution, a bimetallic catalyst Ni/Mo oxides was prepared, SiO_2 with high surface area was used as the support to disperse the active metal and enhance the metal-support interaction. Anisole, phenol and guaiacol were used as the lignin-derived HDO model compounds. The fabricated Ni-Mo/SiO_2 catalyst exhibited high selectivity (>96%) to BTX and high conversion (99%) of model compounds under low H_2 partial pressure of 83 kPa. Commonly, transition metal and their oxides were thought to have less HDO activity than others, however, the bimetallic catalyst exhibited the highest BTX yield reported to date.

2. Experimental

2.1.Catalyst preparation

The catalyst with 15wt% NiO and 15wt% MoO_3 was prepared by a two-step incipient wetness impregnation method, as detailed in supplementary material.

2.2.Catalytic HDO tests

The catalytic HDO experiments were conducted in a fixed bed stainless steel reactor (internal diameter 8 mm, length 300 mm) surrounded by a temperature-controlled electrical oven. Anisole and guaiacol were fed with a syringe pump, while phenol was dissolved in benzene. The molar ratio of H_2 to liquid feed (mol/mol) was kept constant to the value of 5. The reactor outlet was connected to a condenser and two receiving bottles. Then the line was kept at 100 ℃ and connected to a gas chromatograph (GC) online.

Prior to HDO reaction, the catalyst was reduced with H_2 flow rate of 100 ml/min at 450 ℃ for 30 min. The liquid products were qualitatively analyzed by gas chromatography−mass spectrometry (GC-MS, Agilent 7890A-5975C**)**, and then quantitatively analyzed using an offline GC equipped with the same type capillary column and FID detector. The non-condensable gas was quantified by online GC.

The following relationships for the conversion, selectivity to aromatics and product yield were used:

$$\text{Conversion}\ (\%) = \frac{\text{moles of reactant consumed}}{\text{moles of reactant fed}} \times 100 \qquad (1)$$

$$\text{Selectivity to aromatic hydrocarbons}\ (\%) = \frac{\text{moles of aromatic hydrocarbons produced}}{\text{moles of total condensable organic product}} \times 100 \qquad (2)$$

$$\text{Yield}\ (\%) = \frac{\text{The weight of certain product}}{\text{The weight of liquid reactant fed}} \times 100 \qquad (3)$$

3. Results and discussion

3.1.Activity test and product distribution

Fig. 1 shows the anisole HDO catalytic results obtained over the investigated Ni-Mo/SiO_2 catalyst in the temperature range of 380-420 ℃ and after 60 min on time on stream (TOS). The anisole conversion and selectivity to aromatic hydrocarbons increase with reaction temperature. Above 390 ℃, the anisole conversion is more than 98.3%, and the hydrocarbons selectivity is higher than 97.5%. It can also be seen in Fig. 2 that the performance of the catalyst is stable with weight hourly space velocity (WHSV) in the range of 0.75 to 3 h^{-1}. In the subsequent HDO reaction, the experimental conditions were fixed at T=410℃, WHSV =1.5 h^{-1}, atmospheric pressure and H_2/liquid-feed molar ratio of 5.

Table 1: Conversion (%), product yield (%), selectivity to aromatic hydrocarbons (%) and condensable organics composition (mol%) for the anisol, guaiacol and phenol HDO reactions.

Feed	Anisole	Guaiacol	Phenol
Conversion (%)	99.35	99.79	99.30
Product yield (%)			
Gas(CH_4)	9.23	6.28	negligible
Condensable organics	72.91	62.96	79.23
water	14.7	26.34	16.35
Selectivity to aromatic hydrocarbons (%)	98.55	97.53	99.27
Condensable organics composition (mol%)			
Benzene	66.23	64.33	99.27
Toluene	24.46	27.43	
m-Xylene	0.09	0.36	
p-Xylene	4.83	2.74	
o-Xylene	1.43	1.77	
Anisole	0.42	0.83	
Phenol	0.40	0.86	0.73
Trimethylbenzene	0.94	0.39	
2-Methylanisole	0.10	0.05	
Ethyltoluene	0.33	0.40	
o-Cresol	0.21	0.18	
p-Cresol	0.08	0.13	
Guaiacol	0.00	0.3	
2,6-Dimethylphenol	0.07	0.00	
Tetramethylbenzene	0.24	0.11	
2,4-Dimethylphenol	0.18	0.11	

Reaction conditions: T=410 ℃, P=1 atm, WHSV=1.5 h^{-1}, H_2/anisole (mol/mol)=5, TOS=60 min.

Detailed results of the anisole and guaiacol catalytic HDO reactions are listed in Table 1. As shown, the conversion is as high as 99.35% and 99.72% for anisole and guaiacol respectively. Seventeen types of organic condensable compounds were detected and quantified, including benzene, toluene, xylene, trimethylbenzene, ethyltoluene, 2-methylanisole, anisole, phenol, 2-methylanisole, o-cresol, p-cresol, guaiacol, 2,6-dimethylphenol, tetramethylbenzene, 2,4-dimethylphenol. For anisole HDO reaction, the selectivity to aromatic hydrocarbons reaches 98.55%, and it achieves 97.53% for guaiacol. The comparison of the present work with literature is also shown in Table 2. It is noted that the BTX selectivity is relatively high. This is an encouraging result considering that BTX are high atom-economy and high value-added products. These results demonstrate that the bimetallic Ni-Mo/SiO_2 catalyst has very good HDO activity and BTX selectivity, and it further proves Román-Leshkov's opinion on MoO_x HDO activity[16].

In the present work, Ni loading and reaction temperature dramatically enhance both the HDO conversion and aromatic hydrocarbons selectivity. It is believed that nickel promotes the splitting of molecular hydrogen to active atomic hydrogen species, where the split-over hydrogen can then attack and cleave the C_{aro}-O bond[19]. It is also noteworthy that the over-hydrogenation products of cyclohexane and cyclohexene were not observed in all tests due to the low H_2 pressure of 83 kPa and selective adsorption on the catalyst surface. In the non-condensable gas, methane is the main product with a yield of 9.23% for anisole and 6.28% for guaiacol, where trace amounts of C_2-C_5 alkanes are negligible. Thus, the decomposition of aromatic ring to C_2-C_3 alkanes hardly occurred.

Table 2: Comparison of HDO results over several catalysts reported in the literature.

Catalyst	Molecule	T/P (℃/atm)	Conversion (%)	BTX Selectivity (%)	Stability
Fe/SiO_2 [5]	Guaiacol	400/1	~100	38.0	Activity lose ~30%, within 150 min
MoO_3 [16]	Anisole	320/1	78.7	81.7	Activity lose ~30%, within 60 min, at 400 ℃

Pd-Fe/C [17]	Guaiacol	450/1	~100	83.2	Activity lose <10%, within 120 min
MoO_3/ZrO_2 [18]	Anisole	320/1	~63.5	~49.5	Activity lose ~10%, within 120 min
This work	Anisole	410/1	99.3	97.1	Activity lose ~10%, within 120 min

3.2.Proposed reaction mechanism

Water was detected as the dominant oxygen-containing compound in the condensable products with a yield of 14.7% for anisole and 26.34% for guaiacol, whereas carbon dioxide and methanol were not found. This indicates that the initial step is neither the phenolic C_{aro}-O bond scission nor the decarbonation reaction. In addition, apart from benzene, the total concentration of toluene and xylene is found to be higher than 30% for both anisole and guaiacol conversion. The latter suggests for a methyl transfer reaction. Phenol may be an intermediate product of anisole HDO conversion, because the etheric bond CH_3-OPh energy (268±7 kJ/mol) is much lower than that of aryl ether bond C_{aro}-OCH_3 (417±5 kJ/mol). Anisole HDO mechanism is depicted in Fig. 3. The homolytic cleavage of weakest etheric bond CH_3-OPh occurs firstly, forming methyl radical CH_3• and phenoxy radical. The phenoxy radical is more active and has very short lifetime[2], and is further transformed into benzene and water via hydrogenolysis reaction at elevated temperatures. Simultaneously, trans-alkylation reaction occurs, partial methyl radicals adhere to the aromatic ring forming toluene, xylene and other alkylbenzenes. In order to further prove the anisole HDO mechanism, phenol HDO experiments were conducted at the same experimental conditions, and the obtained results are also presented in Table 1. As expected, there was only negligible amounts of methane detected in the gas products, mainly from impurities. The condensable organic products were mainly composed of benzene (99.27%) and no other trans-alkylation product was detected. The phenol HDO results provide an important counterevidence for the ether bond homolytic cleavage and methyl transfer mechanism.

It is estimated that about 36-40% of the methyl groups were transferred to the benzene ring during anisole and guaiacol HDO process, and this ratio is relatively high compared with previous works[16,18]. Alkylated aromatics are more valuable and imply a lower carbon loss. NH_3-TPD spectras are shown in Fig. S1, where abundant acid sites in the present catalyst seem to play an important role in methyl transfer reaction[15,19,20].

3.3.Catalyst deactivation analysis and regeneration stability

It is observed in Fig. S2 that the HDO conversion and BTX selectivity maintained at a steady level at the first 70-90 min of reaction and then decreased, meanwhile the phenol selectivity increased, and some heavy products (yellow color) appeared. These observations present evidence for catalyst deactivation. The heavy products of anisole HDO in the deactivation stage (120 min on TOS) were analysed by GC-MS as shown in Fig. S3. The increase in the aromatic ring number can be easily deduced from Fig. S3, thus, it is rather predictable that products with even higher ring numbers would condense on the catalyst surface. As revealed by the results shown in Fig. S1, carbon deposition would likely cover part of the active acid sites, thus potentially leading to the deactivation of catalyst.

X-ray diffraction (XRD) analysis of the fresh and spent catalysts was performed in order to study the Ni and Mo chemical states (crystal phases) during the reaction. As shown in Fig. S4, for the fresh catalyst, Ni and MoO_2 phases are present, whereas a NiO phase emerges for the spent catalyst. Also, X-ray photoelectron spectroscopy (XPS) studies were conducted in order to probe the evolution of the oxidation states of surface Mo species with reaction (Fig. S5). Mo^{4+} and Mo^{5+} species were found to co-exist on the catalyst surface, the proportion of Mo^{4+} is about 23~30%, and the reaction obviously did not change the nature of Mo surface species. It was reported [15] that Mo^{5+} and Mo^{3+} play an important role in the HDO reaction due to the presence of oxygen vacancies in the MoO_x crystal phase.

The spent catalyst was regenerated by combustion in air flow (80 ml/min) at T=550 ℃. Fourteen regeneration cycles were performed using anisole as the feedstock material, and the obtained results are shown in Fig. 4. It is observed that the anisole conversion and hydrocarbons selectivity are increased slightly after the first regeneration cycle, and then reach a plateau. The regeneration catalyst exhibits practically stable performance for short TOS.

4. Conclusions

In summary, the present SiO_2-supported Ni-Mo bimetallic catalyst shows high conversion and selectivity to C_{aro}-O bond cleavage in the gas phase HDO reactions of anisole, phenol and guaiacol, giving BTX selectivity more than 96%. The low H_2 consumption and carbon loss results are encouraging and novel. It is estimated that about 36-40% of the methyl radicals are transferred to the benzene ring during anisole and guaiacol HDO processes due to abundant suitable surface acid sites. Major precursors of coke such as biphenyl, anthracene and phenanthrene were detected after catalyst deactivation. The spent catalyst can be regenerated by combustion in air at 550 °C, and it kept stable performance after fourteen regeneration cycles with short TOS. We have further proved that the use of higher H_2 pressure would prolong catalyst's lifetime.

Acknowledgements

Financial support from the National Natural Science Foundation of China through contract (Grant no. 11375249) is greatly acknowledged.

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Figure captions:

Fig. 1. Effect of reaction temperature on anisole conversion. Reaction conditions: P=1 atm, WHSV=1.5 h^{-1}, H_2/anisole(mol/mol)=5, TOS=60 min.

Fig. 2. Effect of WHSV(h^{-1}) on anisole conversion. Reaction conditions: P=1 atm, T=410 ℃, H_2/anisole(mol/mol)=5, TOS=60 min.

Fig. 3. Proposed reaction pathway for anisole HDO.

Fig.4. Catalyst regeneration performance for anisole HDO conversion. Reaction conditions: T=410 ℃, P=1 atm, WHSV=1.5 h^{-1}, H_2/anisole (mol/mol)=5, TOS=60 min.

Fig. 1.

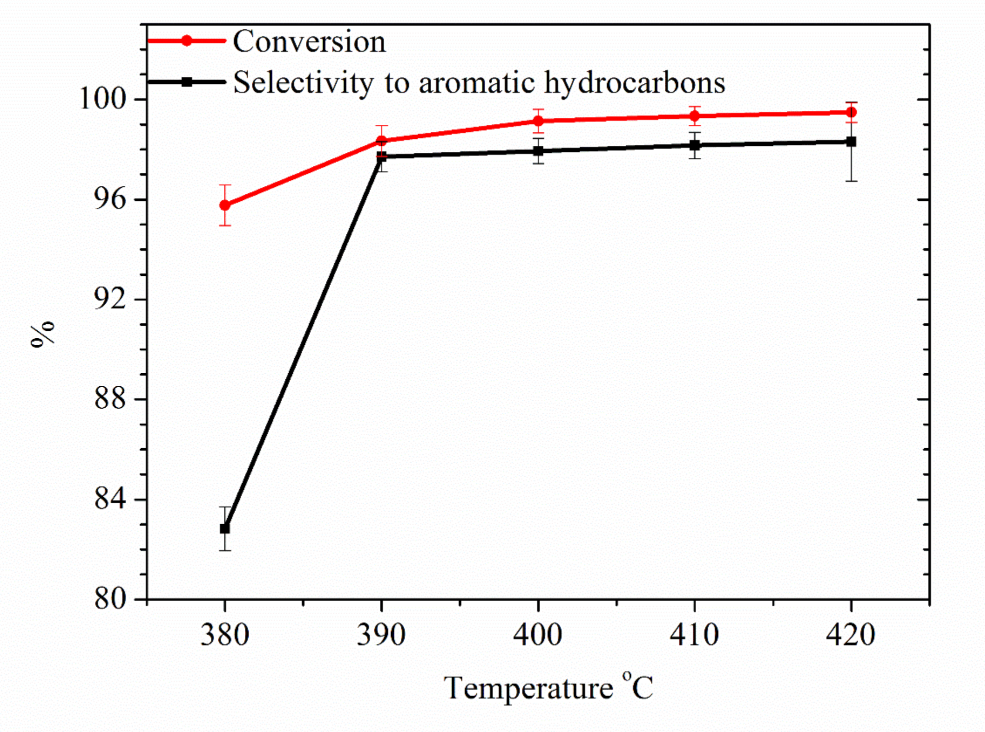

Conversion
Selectivity to aromatic hydrocarbons
100
96
92
88
84
80
%
380
390
400
410
420
Temperature °C

Fig. 2.

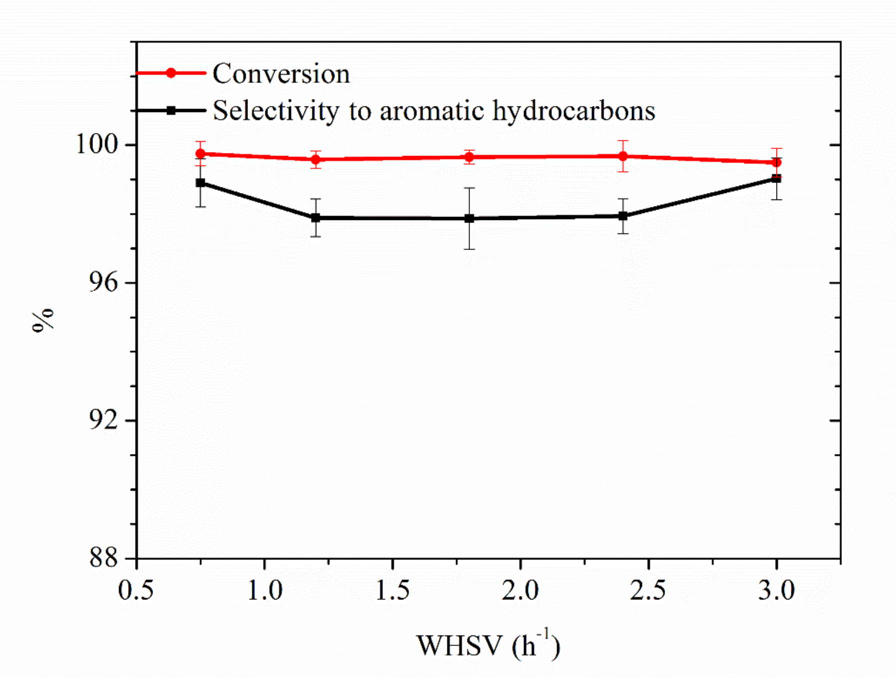

Conversion
Selectivity to aromatic hydrocarbons
%
100
96
92
88
0.5
1.0
1.5
2.0
2.5
3.0
WHSV (h^{-1})

Fig. 3.

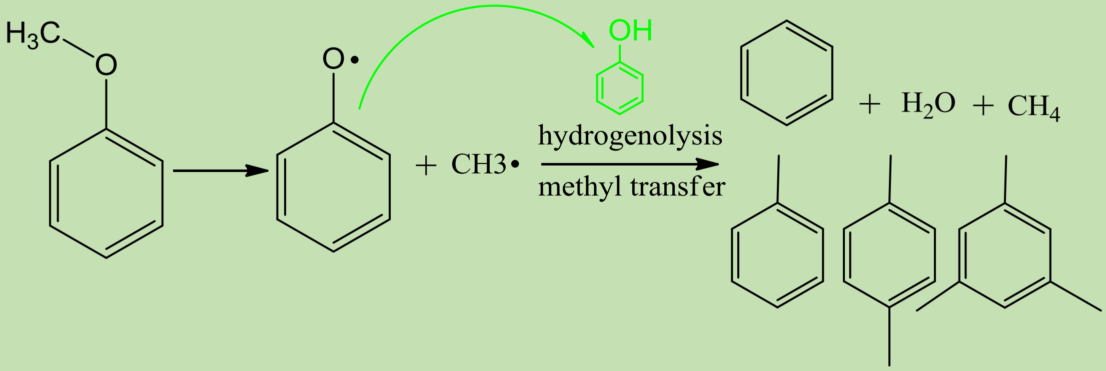
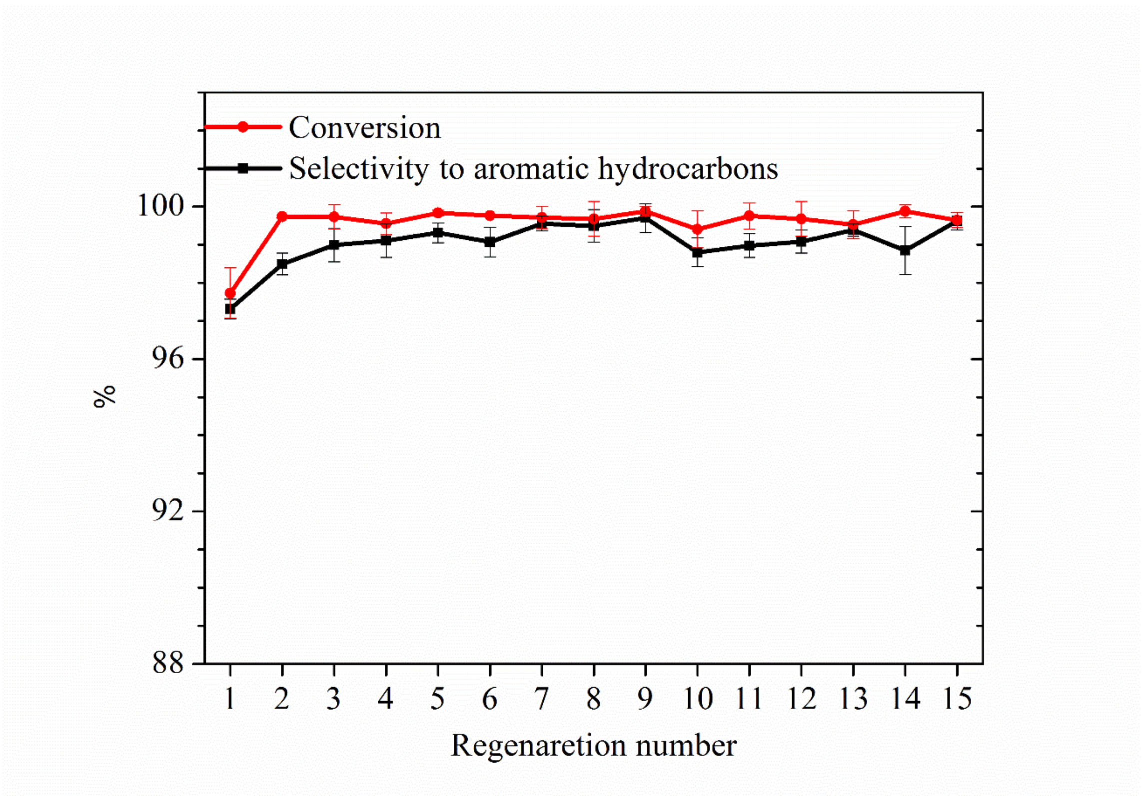


Fig. 4.


Conversion
Selectivity to aromatic hydrocarbons
100
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Highlight

- Ni-Mo/SiO_2 shows >96% selectivity to BTX in anisole gas phase HDO reaction.
- Methyl transfer reaction is promoted by abundant acid sites of the catalyst.
- No obvious active phase change in the catalyst after the reaction.
- Low H_2 consumption and carbon loss, easy regeneration are the traits of the process.