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Effect of metal modification of HZSM-5 on catalyst stability in the shape-selective methylation of toluene

Yan Zhao [a], Hongyu Wu [a], Wei Tan [a], Mengmeng Zhang [a], Min Liu [a], Chunshan Song [a,b], Xiangsheng Wang [a], Xinwen Guo [a,*]

[a] State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, PR China
[b] EMS Energy Institute and Department of Energy & Mineral Engineering, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Shape-selective methylation of toluene (T) with methanol (M) was carried out in a continuous flow fixed-bed reactor over modified HZSM-5 catalysts. The effect of metal modification on the catalytic performance, especially the catalyst stability, was investigated. Various techniques including X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM), were used to characterize the catalysts. The results showed that P–Mg modified catalysts with 3 wt% SiO_2 exhibited excellent stability (more than 500 h), but lowered p-xylene selectivity (less than 90%). Upon further increasing the amount of SiO_2, the catalyst deactivated in a relatively short time on stream, although the para-selectivity was significantly increased up to 99.5%. The high p-xylene-selectivity catalyst modified further with Pt, Pd, Co, Ni metal demonstrated excellent stability, even after 100–400 h on stream, and the selectivity for p-xylene of more than 98.3% with toluene conversion of 20.0% was achieved. Hence, loading metals with good hydrogenation properties, such as Pt, Pd, Co and Ni, was an effective method to improve the catalyst stability.

1. Introduction

p-Xylene is an important raw material for the industrial production of terephthalic acid and dimethylterephthalate, which are essential intermediates in petrochemical production. Currently, p-xylene is produced predominantly by disproportionation of toluene and the p-xylene-oriented isomerization of mixed xylene isomers. In these processes, however, large quantities of benzene are also produced and the cost of product isolation and purification is relatively high. The alkylation of toluene with methanol, as a promising way of producing p-xylene, has therefore been studied extensively over the past few decades. A variety of zeolites have been used for catalyzing this reaction [1–5]. Acidic zeolite HZSM-5, because of its suitable pore size for p-xylene diffusion, attracted the most attention and a p-xylene selectivity approaching 100% could be achieved by modification of ZSM-5 with several inorganic agents, such as P, Mg, B and surface silylation [6–9] and by optimization of the process variables [10,11]. However, the stability of the catalyst was not satisfactory under high para-selectivity conditions. Therefore, it is still a challenging task to develop a catalyst with high activity and high para-selectivity with long-term stability.

To extend the catalyst lifespan, the deactivation of the HZSM-5 catalyst in the toluene alkylation with methanol has been studied [12–14]. According to previous work [12], methanol not only undergoes alkylation reaction, but also dehydrates to dimethylether and immediately forms ethylene through a secondary dehydration. This is problematic, as gaseous alkenes, such as ethylene, have shown a high tendency to become coke precursors on HZSM-5 zeolite catalysts [14]. More importantly, large molecules formed via polymerization of ethylene with itself and/or aromatics can easily block pores of the HZSM-5 catalysts and consequently result in deactivation. Minimizing the amount of alkenes (for instance by hydrogenating them to alkanes) may enhance the catalyst stability remarkably. Metals with good hydrogenation properties, such as Pt, Pd, Co and Ni, will most likely bring good results in this context.

Aboul-Gheit et al. [15] have previously studied the performance of Pt/HZSM-5 catalysts in the alkylation of toluene with methanol and found that increasing the Pt content in HZSM-5 could enhance the para-selectivity by narrowing the pores, but the overall selectivity to p-xylene was lower than 40%. Recently, an enhancement of the stability of silica-bound HZSM-5 by Rh modification has been reported and after 300 h reaction, the

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[*] Corresponding author at: State Key Lab of Fine Chemicals, Dalian University of Technology, P.O. Box 39, No 158 Zhongshan Road, Dalian 116012, PR China. Tel.: +86 411 39893990; fax: +86 411 83689065.
E-mail address: guoxw@dlut.edu.cn (X. Guo).

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conversion of toluene almost stayed constant and the selectivity to p-xylene was around 90% [16]. Here, we report that Si–P–Mg modified nano-scale HZSM-5 catalysts loaded with metals with good hydrogenation properties, such as Pt, Pd, Co and Ni, exhibit excellent stability as well as high activity and high para-selectivity.

2. Experimental

2.1. Preparation of catalysts

In this work, P–Mg modified nano-scale HZSM-5 (SiO_2/Al_2O_3 = 26, crystal size ~100 nm) catalyst was prepared by impregnating uniform nano-scale HZSM-5 with aqueous phosphoric acid and magnesium nitrate at room temperature for 24 h and then calcining at 540 °C for 4 h, respectively. In which, P_2O_5 content is 5% and MgO is 3%. Si–P–Mg modified nano-scale HZSM-5 catalyst was obtained by impregnating the P–Mg modified nano-scale HZSM-5 with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane at room temperature for 12 h, drying at 120 °C for 2 h and then calcining at 540 °C for 4 h. The P–Mg modified catalysts with 3 wt% SiO_2 and 6 wt% SiO_2 were named catalysts A-1 and A-2, respectively. A Pt/modified nano-scale HZSM-5 catalyst was prepared by impregnating catalyst A-2 with aqueous chloroplatinic acid at ambient temperature for 24 h, followed by drying at 120 °C for 2 h and calcining again at 350 °C for 4 h. The catalyst with 0.5 wt%Pt loading on catalyst A-2 was named catalyst A-3. Similarly, the catalyst with 1.0 wt% Pd loading on catalyst A-2 by impregnating A-2 with aqueous palladium nitrate at ambient temperature for 24 h, then drying at 120 °C for 2 h and calcining again at 500 °C for 4 h. The catalyst with 1.0 wt% Pd loading on catalyst A-2 was named catalyst A-4. A Co/modified nano-scale HZSM-5 catalyst was prepared by impregnating catalyst A-2 with aqueous cobalt nitrate at ambient temperature for 24 h, then drying at 120 °C for 2 h and calcining again at 540 °C for 4 h. The catalyst with 5.0 wt% Co loading on catalyst A-2 was named catalyst A-5. In the same way, a Ni/modified nano-scale HZSM-5 catalyst was prepared by impregnating catalyst A-2 with aqueous nickel nitrate at ambient temperature for 24 h, then drying at 120 °C for 2 h and calcining again at 540 °C for 4 h. The catalyst with 3.0 wt% Ni loading on catalyst A-2 was named catalyst A-6.

2.2. Characterization of catalysts

X-ray powder diffraction (XRD) was carried on a RIGAKU D/Max 2400 with Cu Kα-radiation (1.542 Å) 30 mA and 40 kV in the high voltage source, scanning angle (2θ) from 5 to 80; Scanning electron microscope (SEM) was taken on a Hitachi S-2700; and High resolution TEM was taken on a HF2000.

2.3. Reaction test

The alkylation of toluene (T) with methanol (M) was carried out in a continuous flow fixed-bed reactor. Before the reaction, the extruded catalyst (1.0 g) was activated and reduced in situ at 350–500 °C in hydrogen and steam flow for 2–10 h. Afterwards, a mixture of toluene and methanol (T/M molar ratio = 2:1) was fed into the reactor (weight hourly space velocity(WHSV) = 2 h^{-1}) at 460 °C while a co-feed H_2 and steam was introduced with molar ratios of $H_2/(T+M) = 8$ and $H_2O/(T+M) = 8$. The effluent from the reactor was collected in a cold trap and analyzed by gas chromatography using a PEG-20 M capillary column (50 m × 0.25 mm × 0.5 μm) and a flame ionization detector. p-Xylene selectivity was defined as follows:

$$\text{p-xylene selectivity } (\%) = \frac{\text{p-xylene}}{\text{p-xylene} + \text{m-xylene} + \text{o-xylene}} \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The powder XRD patterns of catalysts A-1, A-2 and A-3 are shown in Fig. 1. It can be seen that the structure and the relative crystallinity of ZSM-5 were unchanged after TEOS modification. The silica deposition occured on the external or intra-crystalline surface of zeolite, and the modification did not influence its framework structure. In the XRD spectrum of A-3 catalyst, an obvious diffraction maximum (Pt 200) was found at $2\theta = 45°$, which indicates Pt particles were cluster.

Fig. 2 shows the morphology of nano-scale HZSM-5 sample. It can be seen that the crystal size of nano-scale HZSM-5 was about 100 nm and the morphology were the aggregate of small cuboids.

Fig. 3 shows the features of Pt particles on surface of Pt/modified HZSM-5 catalyst, which was characterized by using high-resolution TEM. It can be seen that Pt particles are clusters (2–10 nm) and highly dispersed on surface externally of zeolite crystals from the representative selected area electron diffraction pattern of the 0.5% Pt/modified HZSM-5 catalyst (A-3).

3.2. Shape-selective methylation of toluene over catalysts modified by TEOS

Toluene alkylation with methanol as a typical shape-selective reaction was used to evaluate the catalytic performance of the modified nano-scale HZSM-5 catalysts. It is well known that p-xylene selectivity of 24% over HZSM-5 was close to its equilibrium value (p-xylene 24%, m-xylene 51%, o-xylene 25%) in three xylene isomers. As shown in Fig. 4, the catalyst modified by 3% SiO_2 (A-1 catalyst) exhibited high stability (more than 500 h). However, it showed only 84–90% p-xylene in the xylene products. It may be attributed to that the remaining acidic sites on external surface promote a rapid isomerization of p-xylene formed inside pores.

With increasing SiO_2 content, catalyst A-2 enhanced the para-selectivity significantly up to 99.5%, after 80 h on stream, the toluene conversion decreased to 20.0% (see Fig. 5), which was attributed to the deposition of TEOS on the surface of the catalysts. Moreover, the molecular size of TEOS is much larger than the pore opening of ZSM-5. Therefore, SiO_2 from TEOS was only deposited on the acidic sites of the external surface, which effectively prevented the product p-xylene from isomerization and consequently, improved the selectivity. At the same time, however, the pore opening was slightly reduced due to deposition of TEOS near

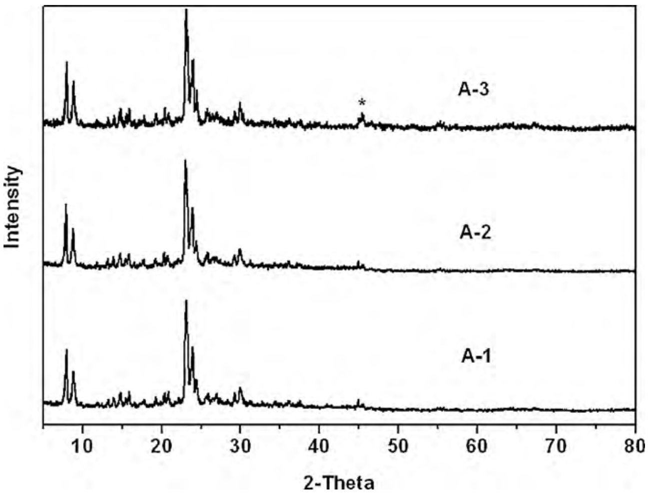

Fig. 1. Powder XRD patterns of A-1, A-2, and A-3.

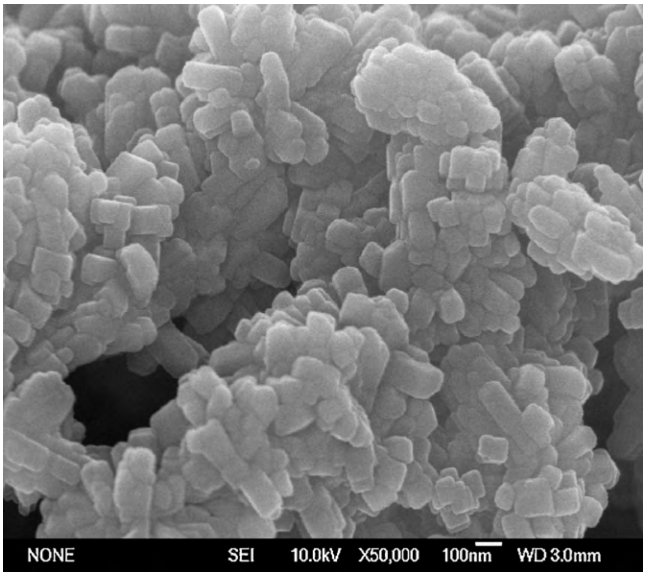

Fig. 2. High-resolution SEM (S-2700) image of nano-scale HZSM-5.

pore mouth. This severely restrained the diffusion and desorption of other aromatic hydrocarbon by-products formed in the pores and led to coke deposition and catalyst deactivation in a relatively short time on stream.

3.3. *Effect of Pt modification on the shape selective methylation of toluene*

For the present investigation on Pt modified nano-scale ZSM-5, the preparation method for Pt particles highly dispersed on surface externally of zeolite crystals was different from traditional methods. Pores of crystals were not be blocked, therefore, conversion of toluene and para-selectivity were unaffected, as can be seen from Fig. 6 and Table 1. In addition, calcination at lower temperature (not more than 500 °C) was reasonable, since Pt metal particle size (which is influenced by calcination) may influence its hydrogenation activity for the unsaturated species (such as ethylene and propene). TEM image in Fig. 3 revealed that most particles on the support had the size of about 2–10 nm.

As shown in Fig. 6, the catalyst modified with Pt demonstrated excellent stability, after 400 h on stream (see Fig. 4); the selectivity for p-xylene more than 98.3% with toluene conversion of 20.0% was obtained. More importantly, the stability of the catalyst A-3 modified by Pt was enhanced remarkably.

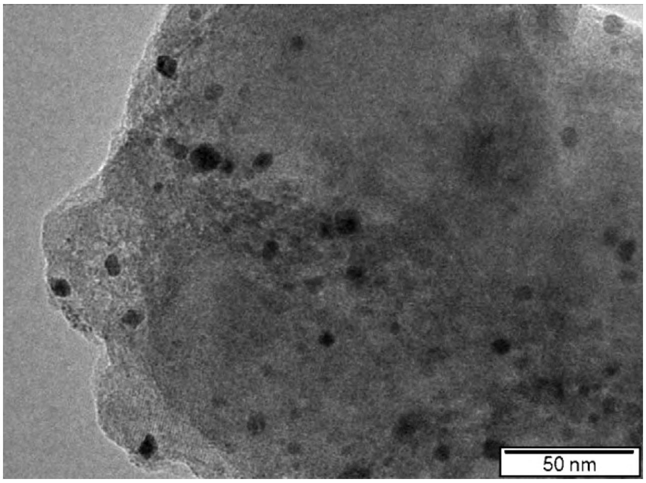

Fig. 3. High-resolution TEM (HF2000) image of catalyst (A-3).

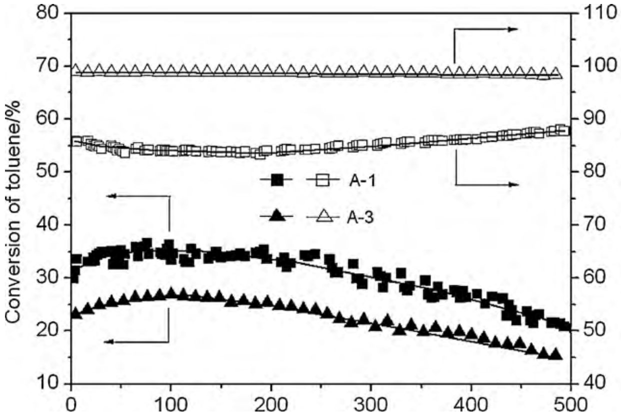

Fig. 4. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-1 (■,□) and A-3 (▲,△).

The average results of liquid and gaseous products are listed in Tables 1 and 2. From Table 2, it seemed that enhancement of stability for the catalyst A-3 modified by Pt may be ascribed to the hydrogenation of alkenes (generated from methanol decomposition) to alkanes on them and to the effective suppression of the formation of multi-substituted alkylbenzenes, thereby retarding the catalyst deactivation. The hydrogenation explanation is also supported by the analysis of the gaseous products (see Table 2), in which the alkene/alkane molar ratio was infinity over catalyst A-1 and A-2, however less than 0.5 over catalyst A-3. Otherwise, the Pt-loaded catalyst generated less alkenes (precursors of coking). It is clear that Pt clusters loaded on the surface of nano-scale HZSM-5 promote H_2 dissociation and decrease the activation energy associated with the whole process. In the presence of Pt, the hydrogenation of alkenes can proceed rapidly at the reaction temperature (460 °C). In addition, pores of HZSM-5 crystals were not blocked, therefore, conversion of toluene was unaffected.

3.4. *Effect of Pd, Co, Ni modification*

Pd, Co, and Ni modified catalysts (A-4, A-5 and A-6) were also investigated and the results were shown in Figs. 7–9, respectively.

The catalyst with 1.0 wt% Pd loading on catalyst A-2 was investigated and good stability was observed (Fig. 7). Within 100 h on stream, both the conversion of toluene (~23%) and the

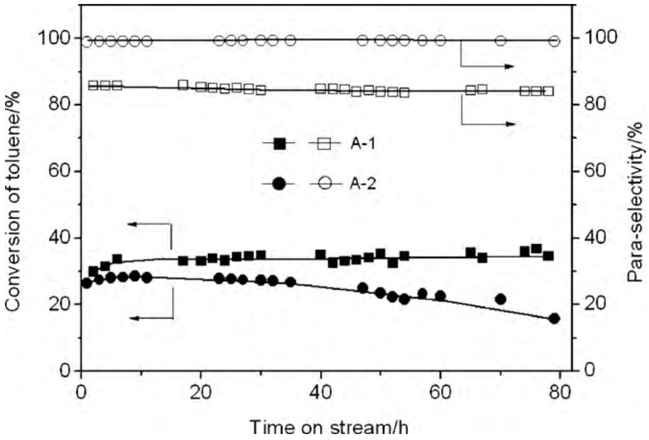

Fig. 5. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-1 (■,□) and A-2 (●,○).

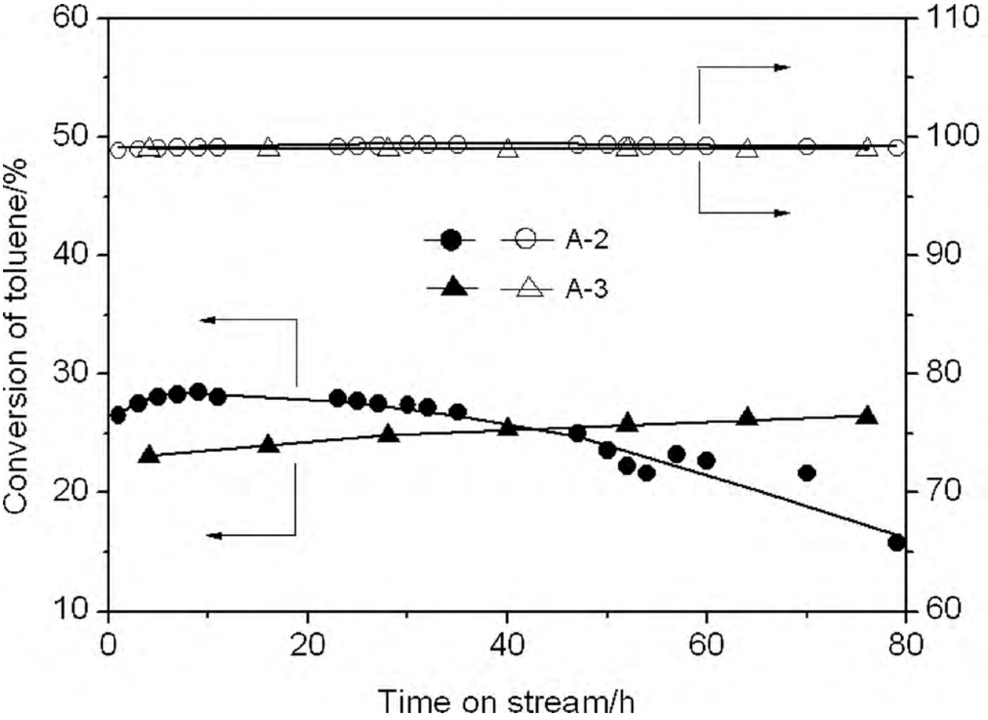

Fig. 6. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-2 (●,○) and A-3 (▲,△).

Table 1
Liquid product distribution of toluene methylation with methanol over A-1, A-2 and A-3.

Components	Content (mol%)		
	A-l	A-2	A-3
C_6^-	0.00	0.00	0.00
Benzene	0.02	0.01	0.00
Toluene	68.10	72.19	71.30
Ethyl benzene	0.05	0.02	0.02
Para-xylene	25.08	27.27	27.92
Meta-xylene	3.38	0.20	0.37
Ortho-xylene	1.04	0.04	0.07
Ethyl toluene	0.29	0.16	0.15
Trimethylbenzene	1.77	0.11	0.17
$C9^+$	0.27	0.00	0.00
Total	100	100	100

Table 2
Gas product distribution of toluene methylation with methanol over A-1, A-2 and A-3.

Components	Content (wt%)		
	A-1	A-2	A-3
Methane	0.76	0.41	0.84
Ethylene	9.04	3.79	0.25
Ethane	0.00	0.00	4.90
Propylene	1.53	0.50	1.05
Propane	0.00	0.00	0.00
C4	0.49	0.62	1.41
C5	0.01	0.12	0.01
Benzene	0.69	0.28	0.59
Toluene	84.73	91.93	88.31
Xylene	2.05	1.83	2.07
Other	0.70	0.52	0.57
Total	100	100	100

para-selectivity (~98.2%) were almost unchanged, which could be attributed to good hydrogenation property of Pd.

The catalyst with 5.0 wt% Co loading on catalyst A-2 was investigated and good stability was observed (Fig. 8). Within 100 h on stream, para-selectivity (~98.5%) was kept constant, although the conversion of toluene varied from 21% to 25%. It seemed that Co has also good hydrogenation property to C=C of alkenes.

The catalyst with 3.0 wt% Ni loading on catalyst A-2 was investigated and good stability was also observed (Fig. 9). Within 100 h, the conversion of toluene and the para-selectivity were almost unchanged, although the conversion of toluene varied from 21% to 24% and the para-selectivity was lower (~97%) than other ones (more than 98%).

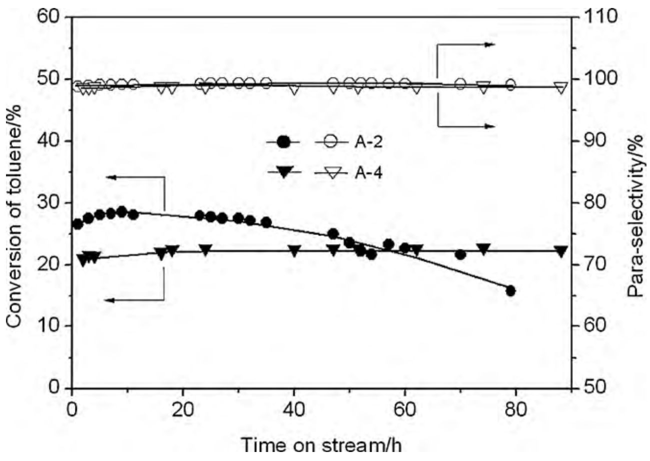

Fig. 7. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-2 (●,○) and A-4 (▼,▽).

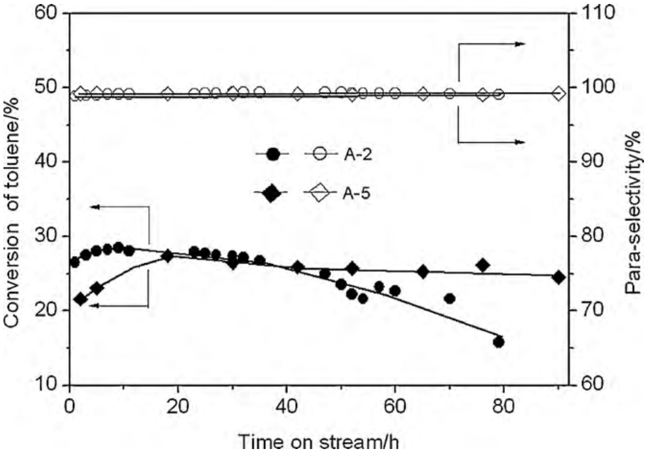

Fig. 8. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-2 (●,○) and A-5 (◆,◇).

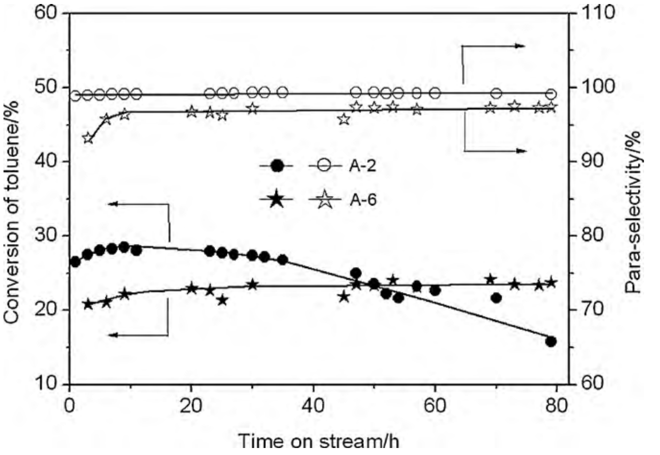

Fig. 9. Toluene conversion and selectivity for p-xylene during the toluene alkylation with methanol on catalyst A-2 (●,○) and A-6 (★,☆).

In general, loading Co and Ni was also a good alternative path to improve the catalyst stability, because it is of critical importance to lower cost for a large-scale and comparatively low-cost production of catalysts.

4. Conclusion

In conclusion, the shape-selective alkylation of toluene with methanol was investigated over modified nano-scale HZSM-5 zeolite catalysts. The modification with Pt, Pd, Co and Ni metal inhibited the formation of coke from alkenes and significantly improved the stability at the condition of high para-selectivity. The novel Pt, Pd, Co and Ni/modified nano-scale HZSM-5 catalysts show unprecedentedly excellent stability as well as high activity and para-selectivity at optimized conditions, which is of critical importance to a large-scale and comparatively low-cost production of p-xylene.

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