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Effect of Pt on stability of nano-scale ZSM-5 catalyst for toluene alkylation with methanol into *p*-xylene

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ABSTRACT

Shape-selective methylation of toluene (T) with methanol (M) was carried out in continuous flow fixed-bed reactor over Pt-modified nano-scale HZSM-5 catalysts, and excellent stability was obtained. Even after 500 h on stream, toluene conversion of 22.0–23.0% was achieved simultaneously with the para-selectivity of >98%. The presence of Pt on the modified nano-scale HZSM-5 solves the apparent paradox of high para-selectivity and low stability. Catalysts were characterized by using X-ray diffraction (XRD), temperature programmed desorption of ammonia (NH_3-TPD), Pyridine IR (Py-IR), TG-SDTA, scanning electron microscope (SEM), etc. The results show that significant enhancement in stability over Pt-modified nano-scale HZSM-5 catalysts is mainly due to good hydrogenation properties of Pt particles.

1. Introduction

p-Xylene is essential intermediates in petrochemical production. It is mainly used for the production of terephthalican acid and dimethylterephthalate. Currently, *p*-xylene is produced predominantly by disproportionation of toluene and the *p*-xylene-oriented isomerization of mixed xylene isomers. These processes, however, are complex and costly. 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 [1–8]. Micron-scale HZSM-5, because its suitable pore size favors *p*-xylene diffusion out of the channels at a >10^3 times rate than that of *o*- and *m*-xylenes, attracted the most attention and a *p*-xylene selectivity approaching 100% could be achieved by modifying micro-scale HZSM-5 with several inorganic agents (such as P, Mg, B, Sb, etc.) and surface silylation or Silicalite/HZSM-5 composite catalysts [9–19], in addition, by optimizing process variables [20,21]. However, the stability of the modified micron-scale HZSM-5 catalyst was not satisfactory under high para-selectivity conditions. Catalyst deactivation, especially the loss of catalytic activity, is a problem of great and continuing concern in the research of catalyst for the processes. Therefore, it is still a challenging task to identify the reasons for catalyst deactivation and then develop a catalyst with long-term stability as well as high para-selectivity.

Numerous studies [22–24] aimed to explore the causes of catalyst deactivation have been carried out over the HZSM-5 catalyst in the toluene alkylation with methanol. According to these work, methanol not only undergoes alkylation reaction, but also dehydrates to dimethylether and immediately forms ethylene through a secondary dehydration. Moreover, ethylene has shown a high tendency to become coke precursors on HZSM-5 zeolite catalysts. Recently, an enhancement of the stability of silica-bound HZSM-5 by Rh modification has been reported and after 300 h reaction, the conversion of toluene almost stayed constant and the selectivity to *p*-xylene was around 90% [25]. Aboul-Gheit et al. [26] have previously studied Pt-modified HZSM-5. But relationship between Pt content and para-selectivity over Pt/HZSM-5 catalysts was studied in the alkylation of toluene with methanol. It was found that increasing the Pt content could enhance the para-selectivity by narrowing the pores. But the overall selectivity to *p*-xylene was lower than 40%.

It is true that there are many mechanisms of catalyst deactivation, nevertheless in this work, for the alkylation of toluene with methanol, large molecules formed via polymerization of ethylene with itself and/or aromatics is considered to block the pores of HZSM-5 catalysts and consequently lead to deactivation in a short time. It is particularly evident on the high para-selective catalyst. Based on the analysis above, Pt can be used to minimize the

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Table 1
Components and content of modified nano-scale HZSM-5 catalysts.

Catalysts	Components and content [wt]/%				
	I SiO_2	II P_2O_5	III MgO	IV SiO_2	V Pt
HZSM-5	0.0	0.0	0.0	0.0	0.0
Si/ZSM-5	3.0	0.0	0.0	0.0	0.0
(Si + P)/ZSM-5	3.0	5.0	0.0	0.0	0.0
(Si + P + Mg)/ZSM-5	3.0	5.0	3.0	0.0	0.0
(Si + P + Mg + Si)/ZSM-5	3.0	5.0	3.0	3.0	0.0
(Si + P + Mg + Si + 0.1Pt)/ZSM-5	3.0	5.0	3.0	3.0	0.1
(Si + P + Mg + Si + 0.3Pt)/ZSM-5	3.0	5.0	3.0	3.0	0.3
(Si + P + Mg + Si + 0.5Pt)/ZSM-5	3.0	5.0	3.0	3.0	0.5
(Si + P + Mg + Si + 1.0Pt)/ZSM-5	3.0	5.0	3.0	3.0	1.0
(Si + P + Mg + Si + 2.0Pt)/ZSM-5	3.0	5.0	3.0	3.0	2.0

amount of alkenes through hydrogenating them to alkanes and consequently enhanced the catalyst stability. Hence, we report the synthesis of 0.1–2.0% Pt-modified nano-scale HZSM-5 catalyst and investigate their catalytic performance and stability in the toluene alkylation with methanol.

2. Experimental

2.1. Preparation of catalysts

In this work, nano-scale HZSM-5 (SiO_2/Al_2O_3 = 26, crystal size: ~100 nm) was synthesized by hydrothermal method. Preparation process of modified catalysts is as follows (Table 1): Firstly, 3% SiO_2/ZSM-5 was prepared by impregnating nano-scale HZSM-5 with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane at room temperature for 24 h, drying (120 °C × 12 h) and then calcining (540 °C × 4 h); Secondly, (3% SiO_2 + 5% P_2O_5)/ZSM-5 was prepared by impregnating 3% SiO_2/ZSM-5 with aqueous phosphoric acid at room temperature for 24 h, drying (120 °C × 12 h) and then calcining (540 °C × 4 h); Thirdly, (3% SiO_2 + 5% P_2O_5 + 3% MgO)/ZSM-5 was prepared by impregnating (3% SiO_2 + 5% P_2O_5)/ZSM-5 with aqueous magnesium nitrate at room temperature for 24 h, drying (120 °C × 12 h) and then calcining (540 °C × 4 h); Fourthly, (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/ZSM-5 was prepared by impregnating (3% SiO_2 + 5% P_2O_5 + 3% MgO)/ZSM-5 with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane at room temperature for 1 h, drying (100 °C × 2 h) and then calcining (540 °C × 4 h); Finally, 0.1–2.0 wt% Pt-modified nano-scale HZSM-5 catalysts were prepared by impregnating (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale HZSM-5 with designed amount of chloroplatinic acid dissolved in deionized water at 40 °C for 12 h, followed by drying at 120 °C for 12 h and calcining again at 360 °C for 2 h and 500 °C for 4 h. In the preparation of the catalysts, the contents of modifiers (6% SiO_2, 5% P_2O_5 and 3% MgO), impregnation conditions and the order are optimized results through a large number of experiments.

2.2. Characterization of catalysts

The samples were studied by X-ray powder diffraction (XRD) using a RIGAKU D/Max 2400 with Cu Kα-radiation (1.542 Å) at 30 mA and 40 kV in the high voltage source, scanning angle (2θ) from 5° to 80°; NH_3-TPD were recorded on Micromerities 2910; Py-IR was tested on EQUINOX55; TG was analyzed by using METTLER TOLEDD, TGA/SDTA 851; Scanning electron microscope (SEM) was taken on JEOL JSM-6700F field emission scanning electron microscope.

2.3. Reaction test

The alkylation of toluene (T) with methanol (M) was carried out in a continuous flow fixed-bed reactor. Standard reduction of the calcined catalysts was conducted in the fixed-bed flow reactor under different conditions at 1 atm using a temperature ramp from ambient to 500 °C at 4 °C/min and holding at 500 °C for 1 h in a H_2 flow having a space velocity of 3000 h^{-1}. Then H_2 and water vapour (50 vol%) were introduced and holding at 500 °C for 1 h. Before water vapour was added, high space velocity of the H_2 flow insured that the partial pressure of water vapour in the catalyst bed produced by platinum oxide reduction would be essentially zero. Afterwards, a mixture of toluene and methanol (T/M molar ratio = 2:1) was fed into the reactor (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 (Agilent Technologies GC6890) with an INNOWAX capillary column (60 m × 0.25 mm × 0.5 μm) and a flame ionization detector. Selectivity of *p*-xylene and conversion of toluene were defined as follows:

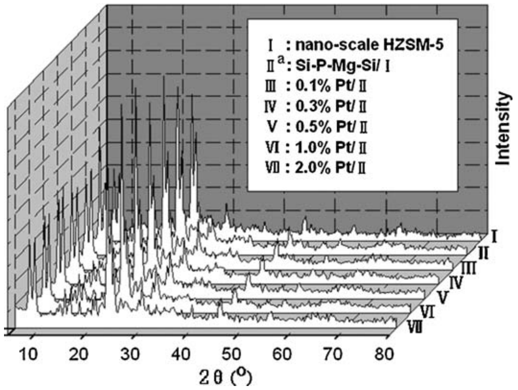

Fig. 1. Powder XRD patterns of catalysts.

$$\text{Selectivity of } p\text{-xylene} = \frac{p\text{-xylene}}{p\text{-xylene} + m\text{-xylene} + o\text{-xylene}} \times 100\%$$

$$\text{Conversion of toluene} = \frac{\text{toluene in feed} - \text{toluene in product}}{\text{toluene in feed}} \times 100\%$$

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 is XRD spectra of samples, in the spectra, nano-scale HZSM-5 was analysed in order to compare the effect of Pt modification on the nano-scale ZSM-5 structure, while ZSM-5 samples loaded 0.1–2.0% Pt were analysed in order to compare the effect of Pt loading on ZSM-5 structure. It can be seen that SiO_2 (deposited on the external or intra-crystalline surface of zeolite), P_2O_5 and MgO modification does not influence its framework structure and the relative crystallinity of nano-scale ZSM-5 were unchanged after 0.1–2.0% Pt modification. In addition to, the XRD spectra of samples show that there are no obvious differences between Pt-modified catalysts and nano-scale HZSM-5, which indicates Pt particles are highly dispersed on the external surface of nano-scale ZSM-5 zeolite crystals.

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

3.2. Shape-selective methylation of toluene over nano-scale HZSM-5 modified by SiO_2, P_2O_5 and MgO

Toluene alkylation with methanol as a typical shape-selective reaction was used to evaluate the catalytic performance of the mod-

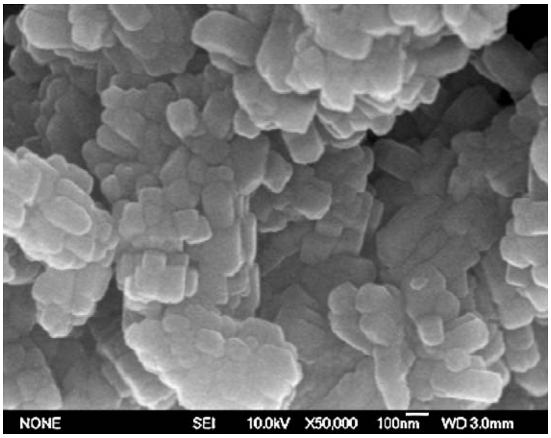

Fig. 2. High-resolution SEM image of nano-scale HZSM-5.

ified nano-scale HZSM-5 catalysts. Fig. 3 compares the performance of nano-scale HZSM-5 ($SiO_2/Al_2O_3 = 26$, ~100 nm) and micron-scale HZSM-5 ($SiO_2/Al_2O_3 = 26$, ~2 μm) in toluene alkylation with methanol. It can be seen that nano-scale HZSM-5 (modified with SiO_2, P_2O_5 and MgO) is better than micron-scale HZSM-5 (same modification) in activity, selectivity and stability, especially in stability. It is most probably due to the much smaller crystals and thus to higher number of framework defects with respect to nano-scale one. Indeed, longer channels in micron-scale HZSM-5 favor the formation of large quantities of carbon filaments which plug catalyst pores and voids, further leading to rapid deactivation of the catalyst, while over nano-scale HZSM-5 catalyst, the deactivation is postponed.

As shown in Fig. 4, p-xylene selectivity of 28% over nano-scale HZSM-5 is close to its equilibrium value (*p*-xylene 24%, *m*-xylene 51%, *o*-xylene 25%) in three xylene isomers. It may be attributed to the remaining acidic sites on external surface which promote a rapid isomerization of *p*-xylene formed inside pores. (3% SiO_2 + 5% P_2O_5 + 3% MgO)/nano-scale HZSM-5 catalyst exhibits high para-selectivity (85%), which is attributed to the deposition of modifiers (SiO_2 + P_2O_5 + MgO) on the acidic sites of the external surface and to the slight reducing in the size of pore mouth. Both catalysts have little change in toluene conversion. The catalyst (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale HZSM-5 exhibits higher *p*-xylene selectivity (near 100%), however the conversion of toluene decreases from 23.3% to about 15% during 50 h reaction on stream (Fig. 5). Its deactivation rate is about 0.16%/h. In the light of high *p*-xylene selectivity, both the yields of xylene and *p*-xylene are very close. Moreover, in the reaction of toluene alkylation with methanol, side reactions (such as toluene disproportionation, dealkylation and multi-alkylation and so on) were not extremely obvious. So the conversion of toluene was very close to the yield of *p*-xylene.

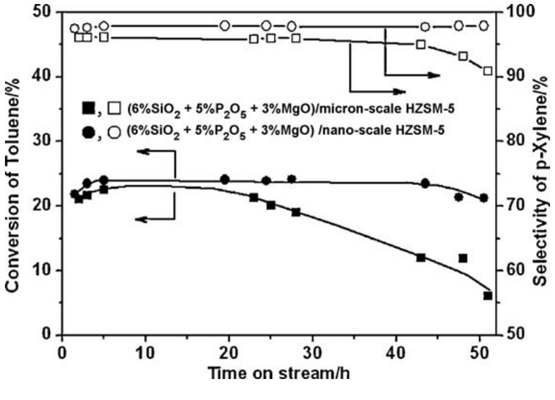

Fig. 3. Comparison of nano-scale HZSM-5 and micron-scale HZSM-5 in performance.

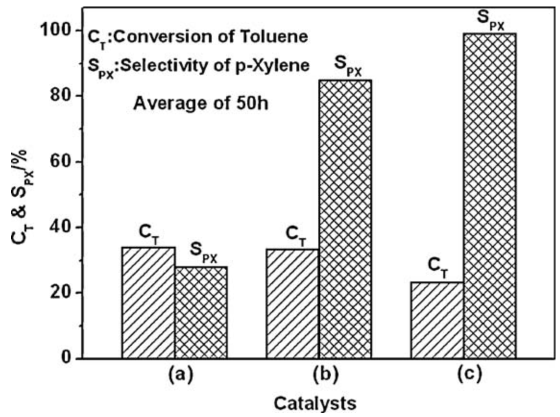

Fig. 4. Conversion of toluene and selectivity of *p*-xylene over nano-scale HZSM-5 (a), 3% SiO_2 + 5% P_2O_5 + 3% MgO/nano-scale HZSM-5 (b) and 3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2/nano-scale HZSM-5 (c).

Above all, modification of SiO_2, P_2O_5 and MgO, to a certain extent, effectively prevents the *p*-xylene from isomerization and consequently, improves *p*-xylene selectivity, however severely restrains the diffusion and desorption of other aromatic hydrocarbon by-products formed in the pores and leads to coke deposition and catalyst deactivation in a relatively short time on stream. Thus, the deactivation issue is a key factor for the commercialization of the alkylation catalyst.

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

The strategy of improving the catalyst stability becomes the most challenging task of developing the route of toluene methylation into *p*-xylene. Identical preparation methods were used for 0.1–2.0% Pt-modified nano-scale HZSM-5 catalysts. In order to prevent the pores of catalysts from being blocked, calcination at lower temperature (not more than 500 °C) was reasonable. Because Pt metal particle size (which is influenced by calcination) may influence its hydrogenation activity for the unsaturated species (such as ethylene, propene, etc.). H_2-TPR (Fig. 6) shows that little oxidation state of the Pt on catalysts modified with 0.1–1.0% Pt and a reduction peak at about 72 °C on 2.0% Pt. Then it is enough to pre-reduce in situ at 500 °C in hydrogen and steam flow for 2 h. As

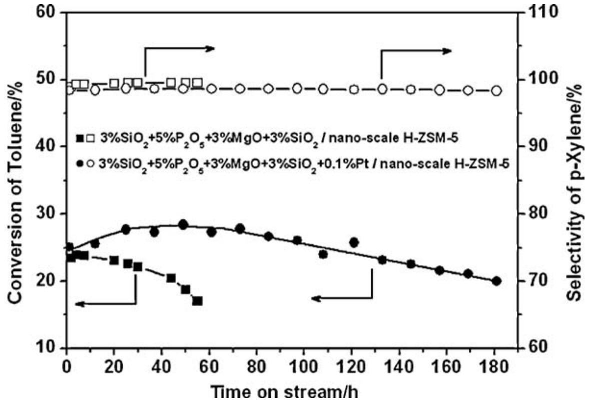

Fig. 5. Conversion of toluene and selectivity of *p*-xylene over catalysts: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale HZSM-5 (a) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.1% Pt)/nano-scale HZSM-5 (b).

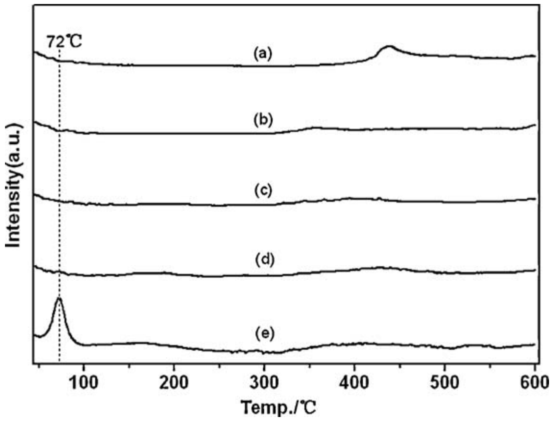

Fig. 6. H_2-TPR of catalysts as follows: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.1% Pt)/nano-scale HZSM-5 (a), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5 (b), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.5% Pt)/nano-scale HZSM-5 (c), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5 (d) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 2.0% Pt)/nano-scale HZSM-5 (e).

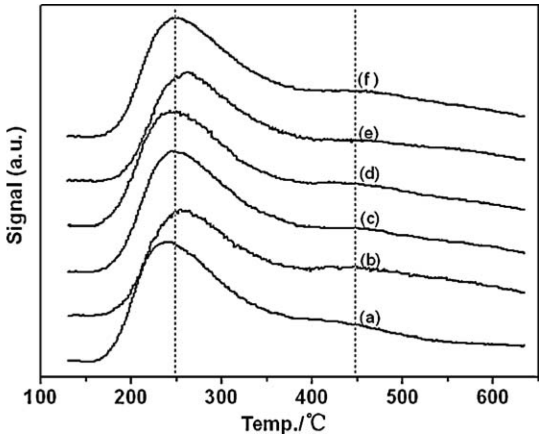

Fig. 8. NH_3-TPD of catalysts as follows: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale H-SM-5 (a), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.1% Pt)/nano-scale HZSM-5 (b), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5 (c), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.5% Pt)/nano-scale HZSM-5 (d), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5 (e) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 2.0% Pt)/nano-scale HZSM-5 (f).

shown in Fig. 5, the catalyst modified with 0.1% Pt demonstrated distinct improvement in activity. Conversion of toluene increases during the first 30 h and reaches maximum of 28%. That is to say, the induction period of the catalyst is about 30 h. In the next 150 h, the conversion of toluene slightly decreases to 20%, and the deactivation rate is 0.054%/h.

Long-running investigation was carried out over catalysts 0.3% Pt-modified nano-scale HZSM-5 and 1.0% Pt-modified nano-scale HZSM-5 (Fig. 7). It can be seen that the stability of both catalysts are higher than that of the 0.1% Pt-modified nano-scale HZSM-5. Both induction periods are about 30 h. The conversion of toluene over catalyst loaded 0.3% Pt maintains 23% and *p*-xylene selectivity is 98% during 500 h reaction on stream. Further increases the Pt amount to 1.0%, the conversion of toluene maintains 22% and *p*-xylene selectivity is 97% during 500 h reaction on stream.

The reasons for the improvement in stability on catalysts modified with Pt were investigated. The NH_3-TPD curves of the catalysts (Fig. 8) show that acid strength and concentration (at 450 °C) increases on all of the catalysts after Pt loading. Accordingly, the para-selectivity decreases slightly, the possible reason is that the isomerization of *p*-xylene occurs on acid sites. Generally, the rate and extent of coke formation increase with increasing acid strength and concentration. But the enhancement on stability over catalysts modified with Pt is very obvious. Moreover, the Py-IR (Fig. 9) shows the change on Brönsted acid sites and Lewis acid sites (expressed by B/L). The ratio of B/L on the catalyst modified with 0.1 wt% Pt is higher at 150 °C and 450 °C than the catalyst precursor (nano-scale HZSM-5, just modified with SiO_2, P_2O_5 and MgO). As shown in Fig. 5, the increase of B/L seems to favor the enhancement of catalyst activity. It is noteworthy that the stability of nano-scale HZSM-5 catalysts modified with Pt is better than others (Fig. 7). Above all, it seems that no direct relationship between the catalyst acid properties and enhancement in stability of catalysts modified with Pt. At least, the changes on acid sites (strength and concentration) are not the most important factors affecting the stability of catalysts modified Pt. Table 2 is the composition of gas products, it can be seen that the big difference is the content of ethylene and ethane. With regard to the catalyst modified with 6.0% SiO_2, 5.0% P_2O_5 and 3.0% MgO, the amount of ethylene in gas product is 35.92%, and ethane is only 0.29%. However, the content of ethylene decreases to 15.82% in the gas product over catalyst loaded 0.1% Pt and the content of ethane increases to 17.79%. It should be noted that the content of ethylene drastically reduces to 1.57% and the content of ethane increases dramatically to 28.73% on catalyst loaded 0.3% Pt. On the catalyst loaded 0.5% Pt and 1.0% Pt, the amount of ethylene reduces to 0.33% and 0.3% respectively. Even

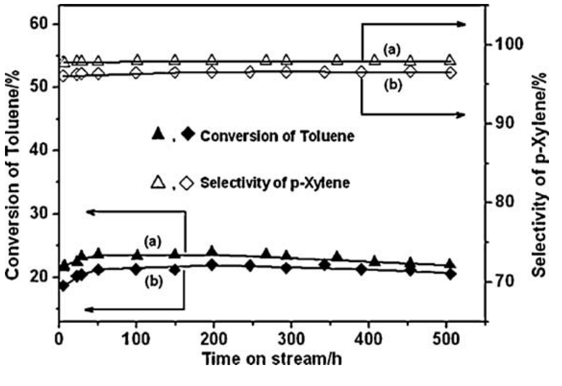

Fig. 7. 500 h long-run on catalysts: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5 (a) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5 (b).

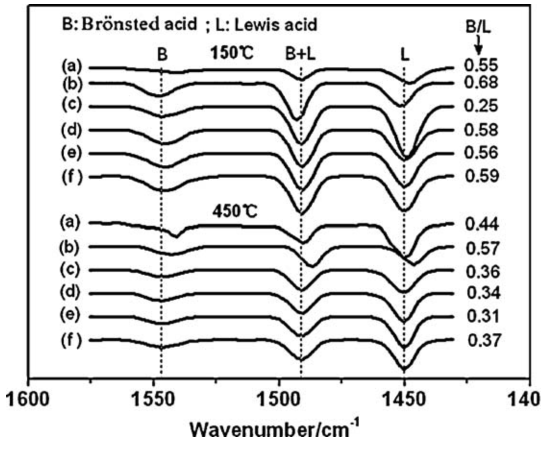

Fig. 9. Py-IR of catalysts as follows: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale H-SM-5 (a), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.1% Pt)/nano-scale HZSM-5 (b), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5 (c), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.5% Pt)/nano-scale HZSM-5 (d), (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5 (e) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 2.0% Pt)/nano-scale HZSM-5 (f).

Table 2
Gas products of toluene alkylation with methanol over catalysts modified with SiO_2, P_2O_5, MgO and Pt.

Components	Catalysts and content [wt]/%					
	(a)	(b)	(c)	(d)	(e)	(f)
Methane	1.91	2.16	4.05	3.21	3.61	12.58
Ethylene	35.92	15.82	1.57	0.33	0.30	0.11
Ethane	0.29	17.79	28.73	28.19	21.33	29.62
Propylene	9.31	9.29	9.04	7.86	6.58	7.49
Propane	0.00	0.00	0.00	0.00	0.00	0.00
C4	1.78	1.86	1.39	1.33	0.99	2.65
C5	0.37	0.41	0.34	0.25	0.28	0.14
Benzene	0.41	0.34	0.95	0.34	0.84	0.75
Toluene	47.98	49.59	49.94	56.51	62.96	45.06
Xylene	2.03	2.74	3.99	1.98	3.11	1.60
Other	0.00	0.00	0.00	0.00	0.00	0.00
Total	100	100	100	100	100	100

(a): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2)/nano-scale HZSM-5; (b): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.1% Pt)/nano-scale HZSM-5; (c): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5; (d): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.5% Pt)/nano-scale HZSM-5; (e): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5; (f): (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 2.0% Pt)/nano-scale HZSM-5.

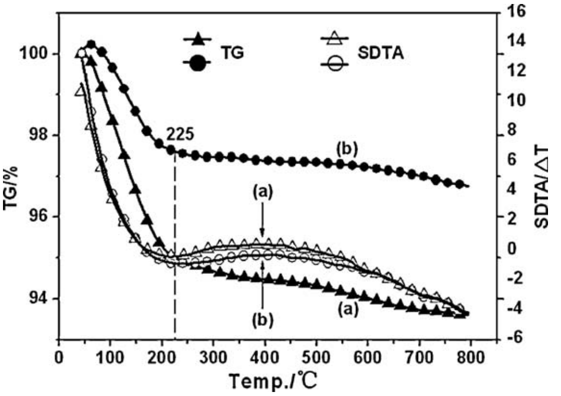

Fig. 10. TG-SDTA of 500 h reaction on stream over catalysts: (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 0.3% Pt)/nano-scale HZSM-5 (a) and (3% SiO_2 + 5% P_2O_5 + 3% MgO + 3% SiO_2 + 1.0% Pt)/nano-scale HZSM-5 (b).

the amount of ethylene decreased only to 0.11% over the catalyst loaded 2.0% Pt.

Based on the above results, the great enhancement of the stability over the catalysts modified with Pt are mainly attributed to the hydrogenation of ethylene occurring on Pt clusters. As we know, when reaction runs on acid catalyst, ethylene is formed through methanol dehydration to dimethylether and immediately a secondary dehydration, and large molecules are further formed via polymerization of ethylene with itself and/or aromatics which can easily block the pores of ZSM-5 catalysts and consequently result in the deactivation over nano-scale HZSM-5 modified with SiO_2, P_2O_5 and MgO in a short time. Methane, ethane and C4 produced over catalyst loaded 0.1% Pt is due to the hydrogenation cracking of the coke species on Pt clusters dispersed on the external surface of ZSM-5 catalyst. At the same time, part of the ethylene is hydrogenated to ethane; Similar to the previous, methane, ethane, C4 and C5 also appear in gas products over all catalysts loaded 0.3–2.0% Pt. Compared to catalyst loaded 0.1% Pt, catalysts loaded >0.1% Pt received a substantial increase in the stability. Obviously, loading more Pt (>0.1%) is helpful to reduce the ethylene content. Thus increasing the amount of Pt loading, the stability of the catalyst will be further improved. One reason for that is the amount of ethylene decreases from 15.82% to 0.11% (Table 2), which will significantly reduce the carbon deposition rate. In addition, the result from TG-SDTA (Fig. 10) of the catalysts loaded 0.3% Pt and 1.0% Pt after 500 h reaction on stream further proves the inference above. The amount of carbon deposition which is easy to remove (removed at ≤225 °C) is 5% on the catalyst loaded 0.3% Pt and 2.5% on the catalyst loaded 1.0% Pt; more importantly, the amount of carbon deposition (removed within 225–800 °C) is 1.5% on the former and only 0.5% on the latter. Thereby the catalyst loaded 1.0% Pt may be more stable. However, considering the performance (activity, para-selectivity and stability) and catalyst cost, 0.3% Pt loading is enough to extend the life-span of catalyst to 500 h or more.

4. Conclusion

Shape-selective methylation of toluene with methanol was studied over Pt-modified nano-scale HZSM-5 in this work. Nano-scale HZSM-5 was chosen as catalyst precursor for its advantages in activity and stability. The modification with Pt inhibited the formation of coke from alkenes and significantly improved the stability with constant para-selectivity (~98%). The Pt-modified nano-scale HZSM-5 catalysts show excellent stability as well as para-selectivity. Extending on life-span of catalyst is ascribed to the hydrogenation of alkenes to alkanes on Pt clusters and to the effective suppression of the formation of carbon deposition, thereby retarding the catalyst deactivation. 0.3% Pt loading is enough for the catalyst (modified with SiO_2, P_2O_5 and MgO) to extend the life-span more than 500 h.

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