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Metal zeolites for transalkylation of toluene and heavy aromatics

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Abstract

The fabrication and modification of metal zeolite catalysts for the conversion of heavy aromatics were investigated. The catalytic performances for various metal-free 12-MR zeolites were evaluated in terms of conversion, product yields, benzene purity and reaction network analyses using transalkylation of toluene and 1,3,5-trimethylbenzene as the test reaction. The effects of metal content, feed impurity, and steaming treatment on the catalytic performances of Pt/mordenite zeolites prepared by different metal incorporation methods were also examined. A sulfuration technique for fine tuning the catalytic activity of the metal catalyst while sustaining desirable stability and performance was developed and its application for transalkylation of heavy aromatics was illustrated by Pt/ZSM-12 catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Transalkylation; Platinum zeolite; ZSM-12; Sulfuration; Hydrogenation; Catalyst stability

1. Introduction

Transalkylation and disproportionation are the two prominent processes for the inter-conversion of aromatics by alkyl group transferring reactions, especially for the production of dialkylbenzenes. While the former invokes conversion of toluene and heavy aromatics (particularly C_9 alkylbenzenes) to xylenes, the latter process yields benzene and xylenes when toluene was used as feed. Moreover, the mixed xylene yields provoked by conventional transalkylation and disproportionation processes are strictly controlled by thermodynamic equilibrium isomer distribution. In this context, since the thermodynamic equilibrium xylene yield is known to increase with increasing feed methyl-to-ring (M/R) ratio, transalkylation reaction is more favorable than toluene disproportionation especially in terms of the demand of xylenes over benzene and the availability of excessive heavy aromatics [1].

Recent developments of cost effective transalkylation process tend to aim at the utilization of heavy aromatics. In view of the more stringent limitations on the content of aromatics in reformulated gasoline, increasing the amount of heavy aromatics during transalkylation, thus increases the feed M/R ratio and, in turn, promotes the thermodynamic equilibrium xylene yields and also cut down the feed cost. Among others, the TransPlus™ commercialized in 1997 [2], represents the first developed processes which took full advantages from legislative, thermodynamic, and economic aspects.

Zeolites that possess 12-MR pore aperture, such as beta [3,4], mordenite [5], USY [6], and ZSM-12 [7], are the potential solid acid catalysts for

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inter-conversion of alkylbenzenes. Nevertheless, the major drawback of using heavy aromatics as feed arises from the difficulty in dealing with complicated feed compositions that normally contain catalyst poisoning components, which in turn tend to deactivate the catalyst (due to coking) and hence reduce its cycle length. Magnoux et al. [8] revealed that the coke formed during toluene disproportionation over H-USY are mostly polyaromatic in nature, whose structures depend on the reaction temperature; the higher the temperature the more condense rings the carbonaceous residues. A probable solution to resolve the aging problem during heavy aromatics processing is to incorporate metals into the zeolite catalyst to hydrogenate polyaromatics coke precursors. Different zeolites incorporated with various metals (Cu, Ni, Pt, etc.) have been studied for transalkylation reactions [4,5,9–11]. Unfortunately, the issue of product purity, jeopardized by the formation of saturates as the consequence of hydrogenation reactions, was seldom discussed in the literature.

Thus, the development and fabrication of metal zeolites for transalkylation process that resulted in minimum yield of saturates while maintaining good catalytic stability remains a challenging task. In this work, we investigate from the perspective of technology development the methodology of fabricating platinum zeolites for transalkylation of toluene and heavy aromatics. The catalytic performance of the catalysts were evaluated in terms of their product yields, stability, benzene purity and the controllability of exothermic heat during the start-up procedure.

2. Experimental

Platinum of 0.06–5 wt.% was incorporated into zeolites beta, USY, ZSM-12, and mordenite with SiO_2/Al_2O_3 of 12.5, 14.0, 120.0, 22.9, respectively, either by ion-exchange (IE) or impregnation (IMP) methods using H_2PtCl_2 or $Pt(NH_3)_4Cl_2$, respectively. The Pt-loaded zeolites were then subjected to treatments by first calcined in flowing 1% O_2/N_2 gas at 573 K for 3 h then reduced under flowing H_2 at 673 K for 2 h. For steaming treatment, the sample was calcined in flowing air at 753 K for 3 h and then hydrothermal treated in the flowing gas comprising 70% steam and 30% air at for 4–20 h. For sulfuration treatment, the reduced metal zeolite sample was presulfided with 1000 ppm H_2S/H_2 gas at 673 K and 12 kg/cm^2 until breakthrough was observed. Transalkylation of toluene and 1,3,5-trimethylbenzene (1,3,5-TMB) were conducted in a continuous flow, fixed-bed microreactor under the conditions: $T = 673$ K; WHSV $= 2$–$6.3\,h^{-1}$; pressure $= 21.4\,kg/cm^2$, $H_2/HC = 3$ mol/mol. As for the sulfur co-feeding experiment, at the specified process condition, polysulfide agent TNPS (di-*t*-nonyl polysulfide) at 1000 ppm sulfur concentration was fed together with the transalkylation feed. Reaction products were analyzed with gas chromatography using methylsilicone high resolution HP-1 capillary column in accordance with the ASTM D5134 DHA (detailed hydrocarbon analysis) from which the conversion and product benzene purity were determined.

3. Results and discussion

Heavy aromatics fraction normally consist of 75–90% aromatics of carbon number 9 (A_9), such as trimethylbenzenes (TMB), methylethylbenzenes (MEB), and other minor components, such as indan, indene, etc., and 10–25% of heavier aromatics $A_{10}{}^{+}$ [2]. 1,3,5-TMB was used as the feed source for heavy aromatics throughout this study. The catalytic performances for transalkylation of toluene and TMB over various H-form 12-MR zeolites are summarized in Table 1. In general, a higher conversion was observed for TMB than toluene, except in the case of mordenite, which can be ascribed due to the lower diffusivity of TMB imposed by the pore structure of mordenite. In comparison, ZSM-12 zeolite, which reveals the greatest product yields of benzene and xylene ($A_6 + A_8$) and the lowest xylene-to-benzene molar ratio (X/B), appears to be the most active catalyst. In contrast, USY appears to be the least active one. Moreover, in terms of product yield and selectivity, while the overall catalytic performance of beta and mordenite zeolites are compatible, the former is more favorable for TMB conversion whereas the latter is more favorable for toluene conversion. That the M/R ratio of the products for mordenite remained unchanged as comparing to the original reaction feed ($M/R = 1.56$) indicates the occurrence of nearly perfect methyl group transfer among the aromatic rings. The stability

Table 1
Catalytic performances of various H-form 12-MR zeolites during transalkylation of toluene and 1,3,5-TMB[a]

	Mordenite	Beta	ZSM-12	USY
Conversion (%)[b]				
Toluene	39.1	34.6	39.3	16.2
TMB	37.8	48.2	48.0	38.1
Yield (%)[b]				
Benzene	4.7	4.7	7.0	1.1
Xylene	31.1	31.5	33.5	19.8
MEB	0.6	0.5	0.2	0.2
A_{10}	2.7	2.7	1.9	2.7
Selectivity[b]				
$A_6 + A_8$ (%)	35.8	36.2	40.5	20.9
X/B (mol/mol)	4.87	4.94	3.50	12.84
M/R ratio	1.56	1.49	1.50	1.49
Stability[c]				
X_6/X_0 (toluene)	0.03	0.16	0.20	0.25
X_6/X_0 (TMB)	0	0.14	0.18	0.15

[a] Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol.

[b] Toluene/TMB: 66.7/33.3 w/w.

[c] Toluene/TMB feed (66.7/33.3 w/w) doped with 2% indan + 1% indene.

of various catalysts, evaluated by the conversion of toluene at time-on-stream (TOS) of 6 vs. extrapolated conversion at TOS of zero, X_6/X_0 (toluene), follow the trend: USY > ZSM-12 > beta ≫ mordenite in despite of the severe deactivation were observed for all samples.

Conventional strategic approaches toward heavy aromatics processing normally involve removal of olefinic compounds by clay treating and/or restricting the feed impurity by the boiling point cut of heavy aromatics, for example, by rejecting cuts of carbon number greater than 10 (A_{10}) at indan boiling point (451 K). To avoid possible olefin breakthrough during clay treating and to accelerate the aging test, impurity-doped feeds were used to test the stability of the catalyst in this study. More specifically, the contamination effects of $A_{10}{}^+$ to A_9 was simulated by indan and indene probe molecules, whereas the effects of olefin impurities arising from clay upset operation were followed by indene and *n*-decene, respectively.

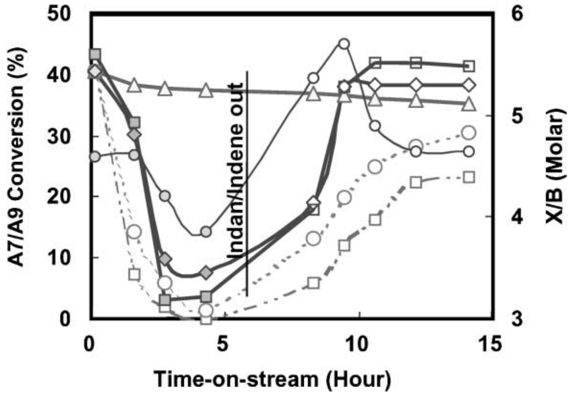

Fig. 1. Deactivation of H-mordenite during transalkylation of toluene (A_7) and 1,3,5-TMB (A_9) (66.7/33.3 w/w) evaluated as A_7/A_9 conversion and X/B ratio vs. TOS, in the presence of various impurity-doped feeds. Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2, H_2/HC, 3.0 mol/mol. Legends: (◇) A_7 (0.5% indan); (■) A_9 (0.5% indan); (●) X/B (0.5% indan); (○) A_7 (3% indan); (□) A_7 (2% indan + 1% indene); (▲) A_7 (decene 1%).

The variations in the stability of H-mordenite, as monitored by the changes in toluene and TMB conversions and X/B ratio vs. TOS, in the presence of various impurity-doped feeds are displayed in Fig. 1. When the feed is doped with 0.5% indan, the conversion curves for toluene and TMB nearly coincide and decrease rapidly with TOS. As shown in Fig. 1, upon removal of impurity from the feed, the activity of the catalyst gradually recovered to its full capacity within a period of 3–4 h. For comparison, in the separated cases of 3% indan and 2% indan puls 1% indene doped feeds, only ca. 85 and 60% of the initial activities were, respectively, recovered after impurity cut-off. The results indicate that poisoning of active sites caused by strong adsorption of impurities is responsible for the observed catalyst deactivation. The effects of co-feeding/removal of suitable amount of indan impurity on deactivation/reactivation of the H-mordenite catalyst appear to be reversible. However, this effect is less favorable when indene or excessive amounts of indan impurities were incorporated in the feed. The deactivation of H-mordenite in the presence of indene impurity may be associated with the formation of indene oligomers at the active sites located in the intracrystalline voids or on the extracrystalline surfaces. Presumably, deactivation can be also caused by blocking/narrowing of pores in H-mordenite when excessive amounts of impurities were introduced. Interestingly, co-feeding of 1% *n*-decene impurity seems to

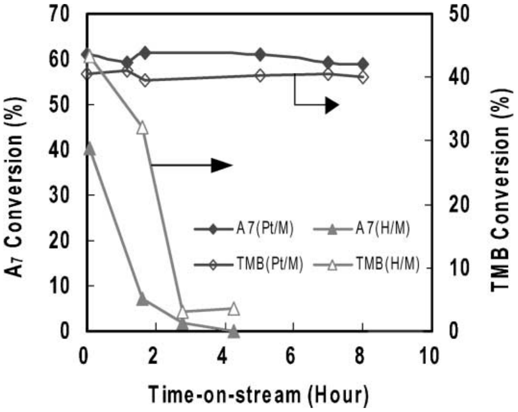

Fig. 2. Catalytic performances of parent H-mordenite and Pt(IE, 5%)/mordenite catalysts during transalkylation reaction. Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol. Feed: toluene (64.8%) + 1, 3, 5-TMB (32.3%) + indan (1.9%) + indene (1%).

Table 2
Catalytic performances of various Pt/mordenite catalysts prepared by different methods[a,b]

	Pt loading (%)[c]			
	0	0.06 (IE)	5.0 (IE)	0.06 (IMP)
Conversion (%)				
Toluene	39.3	37.2	56.9	36.8
TMB	38.0	38.5	38.6	36.9
Yield (%)				
C_5^- gas	0.37	1.06	2.16	1.48
$A_6 + A_8$	35.58	34.56	39.33	31.13
MEB	0.60	0.31	1.42	0.70
A_{10}	2.66	2.04	4.93	2.18
N_6	0	0.03	0.85	0.36
N_7	0	0.07	1.33	0.96
N_8	0	0.00	0.21	0.11
Selectivity				
Benzene purity (%)	99.9	99.4	83.9	92.5
X/B (mol/mol)	4.87	5.18	6.22	5.37
RL (mol%)	0	2.13	8.67	4.39
N_6/A_6	0	0.01	0.20	0.09
N_7/A_7	0	0	0.05	0.02
N_8/A_8	0	0	0.01	0.00
Stability				
X_6/X_0	0.03	0.23	0.96	0.44

[a] Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol.

[b] Toluene/TMB feed (66.7/33.3 w/w) doped with 2% indan + 1% indene.

[c] The Pt/mordenite samples were either prepared by IE or IMP methods.

have little effect on the overall activity of H-mordenite. Furthermore, while the observed X/B ratio decreased accordingly with catalyst activity in the presence of 0.5% indan impurity (see Fig. 1), a notable relative increase in xylene selectivity was found upon removal of indan. The introduction and subsequent removal of small amount of indan impurity thus modify xylene selectivity.

Upon incorporating Pt onto mordenite zeolite, marked increase in both stability and activity of the catalyst were observed, as can be seen by comparing the results obtained from the 5% Pt/mordenite samples prepared by IE method with the unmodified H-mordenite in Fig. 2. However, the observed increase in toluene conversion for Pt-incorporated mordenite are also accompanied by the formation of saturates, among which some naphthenes are co-boilers of aromatics and hence also resulted in deterioration of the purity of aromatic products (see Table 2). The strategies invoked by the design and fabrication of metal zeolite catalysts, therefore, deserve further justification, as discussed below.

First of all, it is noted that commercially nitration grade benzene product is normally specified with minimum purity of 99.85%. Therefore, further separation of naphthenes from aromatics would boost the operation cost since it can only be achieved via extraction rather than conventional distillation process. Second, excessive exothermal heat will also result from hydrogenation reactions associated with the incorporated metal, which is reflected by the ring loss (RL) that can be defined either in mol% or wt.% as

$$\text{Ring loss (mol\%)} = \frac{(\sum A_n\,(\text{wt.\%})/\text{MW}_{A_n})_{\text{Feed}} - (\sum A_n\,(\text{wt.\%})/\text{MW}_{A_n})_{\text{Product}}}{(\sum A_n\,(\text{wt.\%})/\text{MW}_{A_n})_{\text{Feed}}} \times 100 \qquad (1)$$

$$\text{Ring loss (wt.\%)} = (\sum A_n\,(\text{wt.\%}))_{\text{Feed}} - (\sum A_n\,(\text{wt.\%}))_{\text{Product}} \qquad (2)$$

Furthermore, undesirable cracking reactions and excessive heat may arise due to built-up of naphthenes carbon 7 in the recycle toluene stream. Not to mention the stringent specification on naphthenes of carbon 8 in mixed xylene feed of the adsorptive separation unit, for example, as in the Parex process. Therefore, prime design of metal zeolite catalysts aim at not only the substantial improvement of catalyst stability but also the fulfillment of product specifications especially with minimized saturate formation.

Benzene purity of the benzene distillation towers can be simulated using thermodynamics equilibrium of states. Among the commercially available softwares, PROII is widely applied for the design of distillation towers. In this context, PROII was used to derive the benzene purity formula (Eq. (3)) for estimation from compositions of the reactor effluents:

$$\text{Benzene purity} = 100 \times \frac{Y_{A_6}}{Y_{A_6} + 0.1 \times Y_{C_6P} + 0.7 \times Y_{MCP} + Y_{CH} + Y_{C_7N}} \tag{3}$$

It is found that while the catalytic stability (X_6/X_0) increases with increasing Pt loading during transalkylation reaction over Pt/mordenite catalysts prepared by IE method, deterioration of benzene purity was observed. As shown in Table 2, the X_6/X_0 values increased from 0.03 for parent H-mordenite to 0.23 for Pt(IE, 0.5%)/mordenite and 0.96 for Pt(IE, 5%)/mordenite, while their corresponding benzene purity decreases from 99.9 to 99.4 and 83.9%, respectively. This is ascribed due to the formation of naphthenes. Sapre and Gates [12] have revealed that the rates of hydrogenation for naphthalenes and its aryl substituents are faster than benzene by at least 20-fold. However, it is noted that for the transalkylation system study here, the toluene feed as well as the benzene and xylene products are also likely to be hydrogenated. In this context, the fabrication of an ideal metal catalyst with optimized hydrogenation activities for polyaromatics coke precursors while also with minimized hydrogenation of benzene product, is seemingly a challenging task. Nevertheless, as can be seen by the observed naphthene-to-aromatics ratios (i.e., N_6/A_6, N_7/A_7 and N_8/A_8) listed in Table 2, only trace N_6 was found for the Pt(IE, 0.5%)/mordenite catalyst, whereas for Pt(IE, 5%)/mordenite, N_6, N_7 and N_8 were simultaneously observed. It is known that the hydrogenation rate of alkylbenzenes decreases with increasing number of methyl group substituted aromatics rings [13]. Moreover, as reviewed by Stanislaus and Cooper [14], the relative ratio of hydrogenation rate for benzene:toluene:xylene (B:T:X) is dependent on the types of catalyst used; for example the B:T:X ratio is 1:0.3:0.08 for Pt/SiO_2 [13] and 1:0.63:0.65 for Pt/Al_2O_3 [15]. The Pt(IE, 5%)/mordenite prepared in this study, possessing a relative ratio N_6/A_6:N_7/A_7:N_8/A_8 of 1:0.25:0.05, therefore has hydrogenation performance analogous to the Pt/SiO_2 catalyst. Moreover, upon increasing Pt content of the Pt/mordenite, the conversion of toluene was notably increased while the conversion of 1,3,5-TMB remained practically unchanged (Table 2). The overall A_6+A_8 yield increased from 35.58% for H-mordenite to 39.33% for Pt(IE, 5%)/mordenite. Meanwhile, additional hydrocracking and consequently more formation of C_5^- light gas were observed. As a result, the X/B ratio also increased accordingly.

Comparisons of the catalytic performances between Pt/mordenite catalysts prepared by the IE and IMP methods should also be made. With the same Pt loading of 0.06%, the Pt(IMP, 0.06%)/mordenite apparently has better catalytic stability than the Pt(IE, 0.5%)/mordenite but with much lower benzene purity and $A_6 + A_8$ product yield. Together with the higher N_6/A_6 and N_7/A_7 ratio observed for the Pt(IMP, 0.06%)/mordenite sample, it may thus be concluded that Pt/mordenite catalyst prepared by IMP method tends to promote more hydrogenation activity than that prepared by IE method. Unlike Pt incorporation by IE method which is facilitated by the exchange of cationic Pt complexes with protons locate predominantly in the intracrystalline pores, the IMP method invoked anionic Pt complexes and hence the Pt should locate mostly on the extracrystalline surfaces of the zeolite. Consequently, as the secondary reaction of transalkylation, hydrogenation of the benzene product should occur mostly on external surfaces of the Pt(IMP, 0.06%)/mordenite catalyst.

To manipulate the hydrogenation activities associated with the incorporated Pt, various sample treatment conditions have been examined, for example, by varying the steaming temperature and/or duration time or sulfiding treatment. The effects of steam treatment on the catalytic performances of Pt(IE, 5%)/mordenite are shown in Figs. 3 and 4. It is noted that, even under such severe steam treatment (at 753 K), high X_6/X_0 values were observed for extended period of 20 h (Fig. 3),

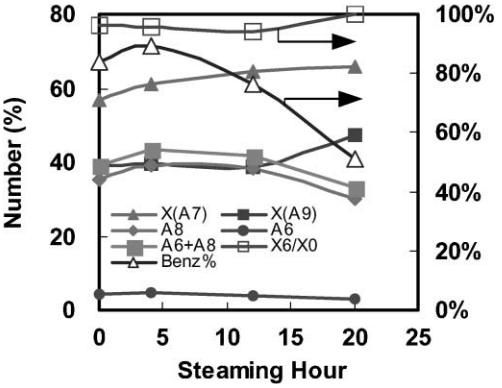

Fig. 3. Variations of major product yields with duration of steam treatment (at 753 K) for Pt(IE, 5%)/mordenite during transalkylation reaction. Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol. Feed: toluene (64.8%) + 1, 3, 5-TMB (32.3%) + indan (1.9%) + indene (1%).

indicating that the sample possesses a high catalytic stability. Upon increasing steaming time, the conversion of toluene increased while conversion of 1,3,5-TMB remained practically unchanged except for the deep steam treated (20 h) sample. Overall, optimal benzene purity and $A_6 + A_8$ yield were achieved when sample steam treated for 4 h, prolonged streaming tends to deteriorate its performance.

Furthermore, detailed analysis of reaction network for the Pt(IE, 5%)/mordenite sample can be inferred from the results shown in Fig. 4. Overall, the observed naphthalenes to aromatics ratios (N_6/A_6, N_7/A_7 and N_8/A_8) and RL all reveal upward concave dependence having their respective minimum at the steaming time of about 4 h and thus the greatest benzene purity. Since the benzene yield was found to decrease with steaming time (see Fig. 3), the X/B ratio that reflects the effects of steam treatment on reaction selectivity must be calibrated. This is achieved by including the N_6 yield as the part of the 'effective' benzene yield, and can be expressed as

$$\frac{X}{B} = \frac{\text{xylene (wt.\%)}/106}{\text{benzene yield (wt.\%)}/78} \tag{4}$$

$$\frac{X}{B}\,(\text{cal}) = \frac{(\text{xylene (wt.\%)}/106) + (Y_{N_8}/112)}{(\text{benzene yield (wt.\%)}/78) + (N_6\ (\text{wt.\%})/84)} \tag{5}$$

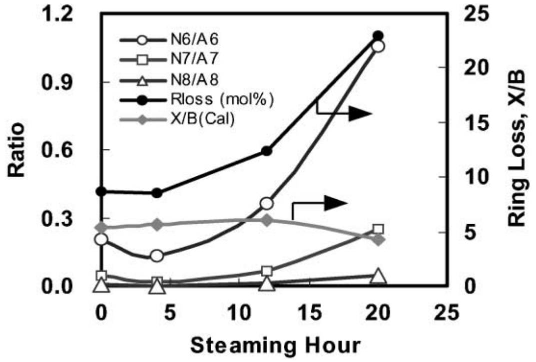

Fig. 4. Reaction network analyses for transalkylation over Pt(IE, 5%)/mordenite under steam treatment (753 K). Reaction conditions: temperature, 673 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol. Feed: toluene (64.8%) + 1, 3, 5-TMB (32.3%) + indan (1.9%) + indene (1%).

As shown in Fig. 4, the resultant calibrated X/B (cal) ratios remain in the range of 5.3–6.0 mol/mol for moderate steaming times (≤12 h), however, further elongation of steaming time tends to reduce xylene selectivity. For example, for a steaming time of 20 h, the X/B (cal) decreased to ca. 4.3 mol/mol.

For comparison, the effects of steam treatment on the catalytic performances of Pt(IMP, 0.06%)/mordenite are shown in Figs. 5 and 6. In contrast to the Pt(IE, 5%)/mordenite sample, the conversion of toluene and TMB for the IMP sample tend to decrease after steam treatment. With increasing steaming time, sharp decreases in N_6/A_6, N_7/A_7, N_8/A_8 and RL, thus improved benzene purity, were observed (Fig. 6). While notable increase in benzene yield and catalytic stability (X_6/X_0) were found for the IMP sample upon steaming treatment, elongation of treatment time showed negligible effects (Fig. 5). The calibrated X/B (cal)

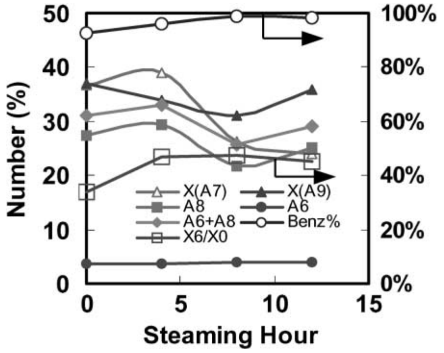

Fig. 5. Similar to Fig. 3, but for Pt(IMP, 0.06%)/mordenite sample.

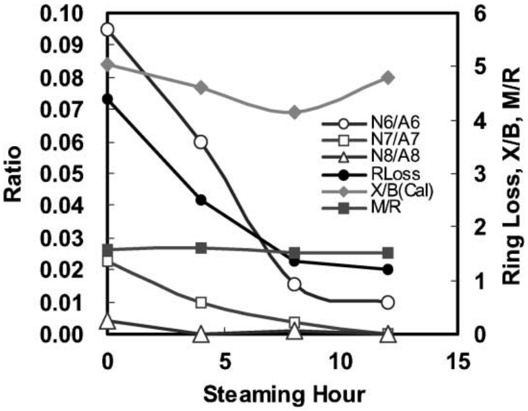

Fig. 6. Similar to Fig. 4, but for Pt(IMP, 0.06%)/mordenite sample.

ratios were found to decrease gradually with steaming time at first then increase at prolonged steaming treatment, revealing a minimum X/B (cal) ratio with a maximum $A_6 + A_8$ yield at ca. 8 h.

The discrepancies in catalytic performances found for the two different samples, namely Pt/mordenite zeolites prepared by IE and IMP methods, under varied steaming times can be attributed to the differences in the particle sizes and locations of the Pt, which would in turn affect the activity of the metal and the overall acidity of the catalyst [16]. For sample prepared by the IE method, the Pt initially located inside the zeolite pores apparently migrates to the external surface during steaming treatment, and thus promoting more actively secondary hydrogenation reaction of aromatics. The relative distribution of internal vs. external Pt sites therefore depends on the extent of steaming treatment. Kustov and Sachtler [17] showed that the presence of water during reduction treatment of metal zeolites may provoke transformation of Lewis acid sites to Bronsted acidity and may also change the dispersion and electronic structure of the metal. The authors also concluded that the aforementioned effects are more pronounced for Pt/mordenite than Pt/HY. Indeed, upon elongation of steam treatment, more Pt would migrate to the external surfaces of Pt(IE, 5%)/mordenite, thus the more naphthenes observed. Presumably, the formation of naphthenes should begin from N_6 and then N_7, thus more severe steam treatment is needed to force more Pt migration toward the external surfaces to catalyze N_8 formation. In this context, the observed gradual increase in toluene conversion with increasing severity of steam treatment therefore could be ascribed mostly due to hydrogenation activity associated with Pt on the external surfaces rather than transalkylation, which take place predominantly within the zeolite pores.

On the other hand, extensive steam treatment of sample prepared by IMP may provoke agglomeration of the Pt particles on the external surface, resulting in a lower dispersion consequently the formation of larger Pt particles. Penchev et al. [18] revealed that the hydrogenation activity of benzene for Ni/A and Ni/X tend to decrease with increasing metal particle size. Therefore, the observed increase in benzene purity and reduction of RL with increasing severity of steaming for the Pt(IMP, 0.06%)/mordenite could be ascribed due to lowering of Pt dispersion on the external surface, which in turn reducing the hydrogenation activity. By the same token, hydrogenation of toluene is also reduced and thus the observed decrease in toluene conversion.

The effects of sulfuration on catalytic performances of Pt/ZSM-12 were also investigated. Catalysts containing 0.5 wt.% Pt were prepared by the IMP method and are denoted as Pt(IMP, 0.19%)/ZSM-12. Each sample was subjected to steam treatment at 753 K for 4 h prior to the transalkylation test take place. As can be seen from the results depicted in Table 3, sulfuration treatment significantly improves the catalytic performances of the sample. More specifically, notable increase in benzene purity and yields of premium products, such as benzene and xylene, were evident. Moreover, lowering of X/B product ratio, RL, C_5^- gas yield, and toluene conversion were also observed. Sulfur, which tends to form a strong bond with Pt, is known as an effective poison for platinum catalysts. In this context, the aforementioned catalytic performance features for Pt(IMP, 0.19%)/ZSM-12 after sulfuration treatment can be attributed due to formation of Pt–S, which effectively reduce the hydrogenation activity of the catalyst. Pt/USY is known to have strong resistance for sulfur poisoning compare to Pt on other catalytic supports. This was ascribed mainly due to the electronic charge transfer (from the support to Pt) effect [19,20], which depends strongly on the SiO_2/Al_2O_3 ratio of the support [21]. Sulfuration treatment is known to have positive impacts during start-up procedure. In practical operation of commercial unit, the temperature rise is normally

Table 3
Catalytic performances of Pt(IMP, 0.19%)/ZSM-12 with and without sulfuration treatment[a,b]

	Sulfuration treatment	
	No	Yes
Conversion (%)		
Toluene	52.5	45.0
TMB	42.0	41.4
Yield (%)		
C_5^- gas	2.4	1.6
Benzene	4.1	8.1
Xylene	31.2	33.2
N_6	1.1	0.02
N_7	2.8	0.0
N_8	0.5	0.0
Total C_{10}^+	3.9	4.2
Selectivity		
$A_6 + A_8$ (%)	35.3	41.3
Benzene purity (%)	79.7	93.5
RL (mol%)	10.9	1.9
X/B (mol/mol)	5.6	3.0

[a] Reaction conditions: temperature, 688 K; WHSV, 5.5 h^{-1}; pressure, 21.4 kg/cm^2; H_2/HC, 3.0 mol/mol.

[b] Toluene/TMB feed (66.7/33.3 w/w) doped with 2% indan + 1% indene.

correlated with the RL number, as the result, excessive hydrogenation of aromatics can lift the reactor temperature up to ca. 150 K when RL exceeds 5.

In this work, a continuous sulfur co-feeding technique was developed to improve benzene purity of metal/zeolite during transalkylation reaction. The results obtained from a Pt/ZSM-12 catalyst are shown in Fig. 7 as an illustration of the technique. Steamed Pt(IMP, 0.19%)/ZSM-12 catalyst, was first pre-sulfided with H_2S before start-up of transalkylation feed. A benzene product purity exceeding 99.85% was obtained at initial TOS. As a reference test, an experiment was conducted by regular transalkylation feed without co-feeding H_2S. In this case, a notable decrease in benzene purity was observed eventually level off at 5 day-on-stream reaching a value of ca. 97%, which is below the commercial product specification of 99.85%. Meanwhile, an opposite trend was found for toluene conversion; it gradually increases from the initial conversion of ca. 48.7% to an average plateau value of ca. 50.5% at day-on-stream ≥ 6. As for the sulfur co-feeding experiment, polysulfide agent TNPS (di-*t*-nonyl polysulfide) was fed together with the transalkylation feed, the observed benzene purity maintained well beyond the 99.85% specification value. This is accompanied by marginal decrease in toluene conversion. Then, sulfur co-feed was switched off for the first time at 12 day-on-stream, while only marginal decrease in toluene conversion was found, the benzene purity dropped to 99% indicating that the adsorption of sulfur on platinum is reversible. Ribeiro et al. [11] showed that although sulfuration treatment improves the activity and product selectivity during toluene disproportionation over Ni/mordenite, the adsorption of sulfur on nickel is very strong and cannot be desorbed even at elevated temperature. Here, the observed decrease in benzene purity after stopping the sulfur co-feed is attributed to desorption of sulfur at very low desorption rate, such as 1–4 days. Polysulfide co-feed was resumed at 14 day-on-stream, the benzene purity immediately returned to values well beyond product specification again. Polysulfide injection was stopped again at day-on-stream of 23, from then on, benzene purity maintained well above specification.

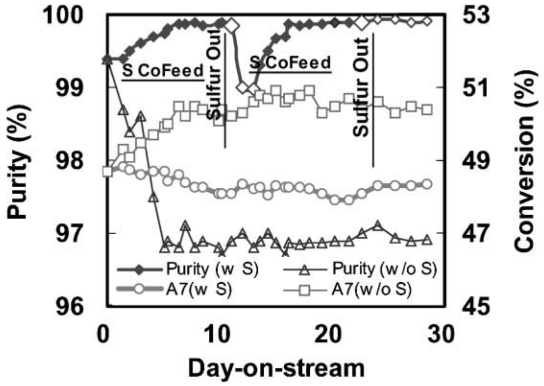

Fig. 7. Variations of benzene purity and toluene conversion vs. day-on-stream for Pt(IMP, 0.19%)/ZSM-12 zeolite during transalkylation reaction (temperature: 688 K; WHSV: 5.5 h^{-1}; $P = 21.4\ kg/cm^2$; H_2/HC: 3.0 mol/mol) with and without sulfuration treatment. Feed: toluene (64.8%) + 1, 3, 5-TMB (32.3%) + indan (1.9%) + indene (1%).

4. Conclusion

The methodologies for the fabrication of zeolitic catalysts and their applications in transalkylation of heavy aromatics were studied from the perspectives of technology development. The catalytic performances of various H-form 12-MR zeolites, such as mordenite, beta, ZSM-12 and USY, were examined. Their catalytic activity, in terms of product yields of benzene and xylene and reversibly X/B ratio, follow the trend: ZSM-12 $>$ beta $>$ mordenite $\gg$ USY. Those zeolites posses a higher conversion for 1,3,5-TMB than toluene, except in the case of mordenite. As for their stability, they obey the order: USY $>$ ZSM-12 $>$ beta $\gg$ mordenite.

To mimic the presence of contaminants in heavy aromatics feed during transalkylation, impurity-doped feed was used during the reaction test for H-mordenite. It was found that strong adsorption of impurity is responsible for the deactivation of the catalyst. However, unlike indene, the adsorption of indan impurity appeared to be reversible. In the case of *n*-decene, impurity doping has negligible effect on the activity of the catalyst. To resolve the problem of catalyst aging during heavy aromatics processing, metal incorporated catalyst was commonly used, however, as the consequence of hydrogenation reactions, the formation of saturates may also jeopardize the purity of benzene product. Thus, the methodology for fabricating metal zeolite catalyst with desirable stability while maintaining minimum yield of saturates during transalkylation process was also developed. Pt/mordenite zeolites prepared by different metal incorporation methods were investigated by varying the metal content and steaming treatment conditions.

It was found that the hydrogenation activities of transalkylation metal catalysts are closely related to the physical properties (location and particle size) of the metal and acidity of the catalyst. A more active hydrogenation activity and thus lower purity of benzene product was observed for Pt/mordenite prepared by IMP method than by IE procedures. Steam treatment of the Pt(IE)/mordenite provokes Pt migration from the zeolite pore to the external surface of the catalyst. Whereas for the Pt(IMP)/mordenite, Pt on external surface tends to agglomerate into large particle upon steaming. As a result, purity of benzene product is deteriorated over steam treated Pt(IE)/mordenite, in contrast, benzene purity is improved over steam treated Pt(IMP)/mordenite.

A sulfuration technique was also developed to fine tun the catalytic activity of the metal catalyst during transalkylation while sustaining desirable stability and performance. Consequently, as illustrated for a Pt(IMP)/ZSM-12 catalyst, the resultant benzene purity was observed to maintain at a level well beyond the commercial specification at only slight expense of toluene conversion.

We have demonstrated that the catalytic performance of metal zeolites during transalkylation of heavy aromatics can be improved by the combined procedures of metal incorporation, steaming and continuous sulfuration treatments.

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