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Zeolite supported platinum catalysts for benzene hydrogenation and naphthene isomerization

Kun-Yeh Tsai^a, Ikai Wang^a, Tseng-Chang Tsai^{b,*}

^a Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan

^b Department of Applied Chemistry, National University of Kaohsiung, 700 Kaohsiung University Rd., Kaohsiung 811, Taiwan

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ABSTRACT

Benzene hydrogenation over zeolite supported platinum catalysts; particularly the effect of catalyst preparation procedures was studied. It was found that Pt/zeolite prepared with wet solution ion exchange procedure using cationic platinum precursors showed the best catalytic performances. The potential of Pt/beta in catalyzing benzene hydrogenation–naphthene isomerization cascaded reaction was demonstrated, showing the highest methyl-cyclopentane to cyclohexane product ratio comparable to the thermodynamic equilibrium value, the lowest cracking gas yield and a maximum octane barrel number. © 2010 Elsevier B.V. All rights reserved.

1. Introduction

The mandated gasoline regulation has been increasing stringent globally. For example, the maximum content of aromatics in gasoline is 35% and benzene specification is 1% (v/v) in the European Commission [1]. The oil industry needs to adjust its refinery structures to meet the increasing stringent regulation. For example, transferring heavy gasoline into transalkylation feed for xvlene production can reduce total aromatics content of gasoline and adjust refinery product slates [2]. On the other hand, hydrogenation of light end gasoline is widely practiced in refinery to reduce benzene content in gasoline. Benzene hydrogenation catalysts included noble metals such as Pt [3,4], Pd [5], base metals such as Ni [6,7], Ru [8,9], and bimetals such as PtNi [10], supported on alumina, silica or zeolites [11–13]. Among which the industrially proven catalysts are Pt/Al₂O₃ and Ni/Al₂O₃. Nevertheless, reduction of benzene content by hydrogenation suffers octane number (ON) loss associating with great economic loss during the transformation of benzene rated as 98 ON into cyclohexane (CH) rated as 83 ON. In addition, benzene hydrogenation involves large exotherm and cause large reactor temperature rise [14] which provokes excessive ring opening reactions and liquid product yield loss. In accordance with the trend, some new technologies were proposed, such as the use of cracked products C2–C4 paraffinic compounds as the feedstocks for steam crackers [15].

As shown in Fig. 1, by cascading benzene hydrogenation, isomerization of CH into methyl-cyclopentane (MCP) via ring contraction can boost the ON of CH from 83 to 95 for MCP. Thus, the octane loss associating with benzene hydrogenation can be partially recovered. Pt/zeolite catalysts are effective in catalyzing the isomerization reaction of naphthenic compounds [16-18]. Wang et al. proposed that over Pt/zeolite catalysts benzene hydrogenation takes place on metal sites and on acid sites. Brønsted acid sites favor the production of MCP and improve the overall hydrogenation activity [12]. According to Ohnishi et al. [19], metal catalysts can be classified into three catalysts for the conversion of naphthenic compounds. Group 1 catalysts, including silica supported Ir, Ru, Rh, Pt and Pd catalysts or some zeolite supported Pt catalysts [18], catalyze ring opening reactions for formation of acyclic compounds. Among which Ir/Al₂O₃ is the most active ring opening catalyst [20]. Group 2 catalysts, including Pt/beta, Pd/beta, etc., generate exclusively cyclopentane. Group 3 catalysts, including zeolite beta supported Ir, Rh, Ru catalysts, produce cyclopentane and acyclic compounds. Dual catalyst systems combining Pt and Ir catalyst, such as Pt/H-beta + Ir/Al₂O₃ [19], Pt/HY + Ir/SiO₂ [17], are synergistic catalyst systems for the enhancement of ring opening activity of naphthenic compounds.

The hydrogenation activities of supported metals depend on various parameters, such as type of support, metal particle size, etc. [21]. Metal supported materials can be prepared with physical methods, chemical methods and physicochemical methods [22]. Ion exchange and impregnation methods were widely practiced in preparing metal/zeolite material. Nevertheless, dedicate procedures are required for the preparation of optimum metal supported materials. Roldán et al. found that impregnation order of metal



^{*} Corresponding author. Tel.: +886 7 5919457; fax: +886 7 5919348. *E-mail address:* tctsai@nuk.edu.tw (T.-C. Tsai).

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Fig. 1. Benzene hydrogenation-naphthene isomerization network.

precursors affected significantly the nature of metal particles of bi-functional PtPd/beta materials and their catalytic activity in the hydroisomerization of alkanes [23]. Recently, Bisio et al. found that platinum dispersion of Pt/beta decreased with increasing basicity of zeolite beta with progressive formation of PtOx particles [24]. On the other hand, while Pt(NH₃)₄(NO₃)₂ precursor dissociates into platinum cations, H₂PtCl₆ and H₂Pt(OH)₆ dissociates into platinum anions. Choice of platinum precursors to manipulate the type of platinum ions and pH value for ion exchange would change significantly the property of Pt/zeolite material.

The objective of this work was to find a suitable zeolite supported metal catalyst for benzene hydrogenation reaction for the enhancement of octane number. In particular, the catalytic potential of Pt/beta and the effect of preparation protocols on its catalytic performance in benzene hydrogenation were examined.

2. Experimental

Mordenite (Süd-Chemie), ZSM-5 (Mobil) and zeolite beta (PQ) were used in this study. Platinum was incorporated into zeolite with either dry impregnation procedure or wet solution procedure. The sources and physical properties of the catalyst samples used in this study are described in Table 1. Four zeolite beta supported platinum samples were prepared from different platinum precursors and preparation protocols. For example, the B25-WPtNH⁺ and B25-DPtNH⁺ were prepared from Pt(NH₃)₄(NO₃)₂ precursor by using wet solution procedure and dry impregnation procedure, respectively. On the other hand, using dry impregnation procedure, the B25-DPtOH⁻ was prepared from H₂Pt(OH)₆ precursor and B25-DPtCl⁻ was prepared from H₂Pt(Cl)₆ precursor. With wet solution procedure, the H-form zeolite sample either in powder form or extrudate in 12-20 mesh was first suspended in an aqueous solution of a platinum compound, i.e., Pt(NH₃)₄Cl₂, (1:20 by weight) at the amount equivalent for desirable Pt content, and the solution was kept at 333 K for 6 h. Whereas for the dry impregnation method, an appropriate amount solution in accordance with incipient wetness method [22] prepared at the desirable equivalent Pt

Table 1		
Description	of experimental	catalyst samples.

content from 1% platinum stock solution, i.e., platinum compound hexachloroplatinic acid (H₂PtCl₆), was added drop-wise to the zeo-lite sample.

Subsequently, each zeolite supported platinum sample was calcined in air stream at 623 K, then cooled down to 573 K in nitrogen stream, followed by reduction treatment under flowing hydrogen at the same temperature for 2 h. Finally, the reduced sample was cooled under hydrogen environment to a desirable reaction temperature for further catalytic test.

Hydrogenation activity of each Pt supported catalyst was tested in a continuous-flow fixed-bed micro-reactor. A mixture of catalyst sample (450 mg), quartz chips (ca. 10–20 mesh), and sand (ca. 10–20 mesh) was packed into the reactor followed by injection of benzene (chemical grade) using a syringe pump under the conditions: temperature of 483–523 K, pressure of 2068 kPa, WHSV of $2-6 h^{-1}$ g/g-catalyst, and hydrogen-to-hydrocarbon (H2/HC) molar ratio of 4–8. The reactor effluent was collected at a specified interval and its composition was analyzed by a gas chromatograph (Varian CP-3380) equipped with a 30 m long, low polar capillary column Equity-1 and a flame ionization detector. A standard gas has been sampled and analyzed following with the above procedure to check the reproducibility of the sampling procedure.

3. Results and discussion

Referring to Table 2, the catalytic performances of four zeolite beta supported platinum samples prepared from different platinum precursors are compared. All the Pt/beta samples except for B25-DPtOH⁻ showed about 100% benzene conversion at 503 K. With increasing reaction temperature, all zeolite beta samples showed increasing MCP/CH ratio, product yield of product gases smaller than C_4 (C_4^- gas), and decreasing liquid product larger than C_5 (C_5^+ liquid yield). The B25-WPtNH⁺ showed much higher MCP/CH ratio and liquid yield than other Pt/beta samples prepared with dry impregnation method.

The octane barrel (OB) number of reaction product was estimated from reactor effluent compositions using Eq. (1):

$$OB number = C_5^+ \times ON_{C_5^+} \times \frac{\rho_{Ben}}{\rho_{C_5^+}} + MCP\% \times ON_{MCP} \times \frac{\rho_{Ben}}{\rho_{MCP}} + Ben\% \times ON_{Ben} + CH\% \times ON_{CH} \times \frac{\rho_{Ben}}{\rho_{CH}}$$
(1)

where $C_5^+\%$ and Ben% were the C_5^+ paraffin and benzene product liquid yield, respectively; ρ and ON represented their densities and blending ON of the corresponding molecules, respectively. According to Eq. (1), the OB number of the hydrogenation product increases with increasing C_5^+ liquid yield and MCP product yield, thus MCP/CH ratio. Having the much higher MCP product yield and MCP/CH ratio, B25-WPtNH⁺ showed the highest OB number, followed by B25-DPtCl⁻, B25-DPtNH⁺, and B25-DPtOH⁻ as the

ID	Si/Al ratio	Description
M23-DPtNH ⁺	23	Parent sample: mordenite powder form; $Pt(NH_3)_4(NO_3)_2$ precursor; dry impregnation procedure
M16E-WPtNH ⁺	16	Parent sample: industrial mordenite catalyst in 1/3 in. extrudate form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; wet solution procedure
M90E-WPtNH ⁺	90	Parent sample: 1/16 in. mordenite extrudate form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; wet solution procedure
M90E-DPtNH ⁺	90	Parent sample: 1/16 in. mordenite extrudate form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; dry impregnation procedure
M200E-DPtNH ⁺	200	Parent sample: 1/16 in. mordenite extrudate form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; dry impregnation procedure
Z12E-DPtNH ⁺	12	Parent sample: ZSM-5 extrudate form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; dry impregnation procedure
Z70E-DPtNH ⁺	70	Parent sample: $1/16$ in. ZSM-5 extrudate form; $Pt(NH_3)_4(NO_3)_2$ precursor; dry impregnation procedure
B25-WPtNH ⁺	25	Parent sample: zeolite beta in powder form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; wet solution procedure
B25-DPtNH ⁺	25	Parent sample: zeolite beta in powder form; Pt(NH ₃) ₄ (NO ₃) ₂ precursor; dry impregnation procedure
B25-DPtCl ⁻	25	Parent sample: zeolite beta in powder form; H ₂ PtCl ₆ precursor; dry impregnation procedure
B25-WPtOH ⁻	25	Parent sample: zeolite beta in powder form, $H_2Pt(OH)_6$ precursor; wet solution procedure

Table 2

Catalytic performances of Pt/beta catalysts in benzene hydrogenation (pressure: 2068 kPa, WHSV: 2 h⁻¹ g/g-catalyst, H2/HC (molar ratio: 6).

	ID									
	B25-DPtNH ⁺		B25-WPtNH ⁺		B25-DPtCl-		B25-DPtOH ⁻			
Rx. T (K)	503	523	483	503	523	503	523	503	513	523
Conv. (%)	100.0	100.0	100.0	100.0	100.0	99.8	99.5	86.3	88.1	99.7
C ₅ ⁺ liq. (%)	93.6	87.6	99.5	99.1	95.9	97.5	90.8	97.0	93.3	76.4
MCP/CH	0.8	2.9	0.3	2.3	3.6	0.3	2.1	0.4	0.6	2.0
OB number	93.6	92.0	96.1	102.7	101.5	93.8	94.5	94.8	92.6	79.6
Product yield (%)										
$C_1 + C_2$	0.82	1.81	0.02	0.06	0.26	0.01	0.03	0.03	0.04	0.08
$C_3 + C_4$	5.61	10.63	0.48	0.89	3.85	2.54	9.2	3	6.67	23.51
C ₅ ⁺ parraffin	3.07	6.84	0.49	2.35	8.74	2.13	7.3	1.44	2.92	8.21
MCP	40.18	60.17	25.17	67.16	68.25	19.93	56.62	23.56	30.12	45.26
Benzene	0.02	0.02	0.03	0.03	0.03	0.24	0.46	13.72	11.9	0.31
CH	50.3	20.52	73.8	29.5	19.01	75.14	26.4	58.25	48.36	22.64

Table 3

Catalytic performances of Pt/mordenite samples in benzene hydrogenation (pressure: 2068 kPa, WHSV: 2 h⁻¹ g/g-catalyst, H2/HC molar ratio: 6).

	ID						
	M23-DPtNH ⁺	i-DPtNH ⁺ M16E-WPtNH ⁺ M90E-DF ider ^a 1/16 in. extrudate ^a 1/16 in. e impregnation ^b Wet solution ^b Dry impr		M90E-DPtNH ⁺		M200E-DPtNH ⁺	
	Powder ^a			1/16 in. extra	udate ^a	1/16 in. extrudate ^a	
	Dry impregnation ^b			Dry impregn	/ impregnation ^b		Dry impregnation ^b
Rx. T (K)	523	503	523	503	523	503	523
Conv. (%)	100	99.8	99.8	98.4	99.6	91.3	98.2
C ₅ ⁺ liq. (%)	93.1	96.9	90	84	83.5	95.5	74.5
MCP/CH	3.9	0.6	3.8	0.3	1.6	0.1	1.3
OB number	96.7	95.4	95.2	81.3	86	90.9	69.9
Product yield (%)							
$C_1 + C_2$	0.3	0.11	0	0	0.47	0.13	19.05
$C_3 + C_4$	6.6	3.04	10.05	16.01	16.05	4.39	6.49
C5 ⁺ parraffin	9.25	1.47	8.62	4.78	5.41	1.45	1.45
MCP	66.73	34.85	64.12	15.88	47.47	10.17	36.69
Benzene	0	0.2	0.19	1.61	0.37	8.75	1.82
СН	17.11	60.35	17.02	61.63	30.3	75.11	28.9

^a Shape.

^b Method.

poorest one. The B25-WPtNH⁺ and B25-DPtNH⁺ were prepared from $Pt(NH_3)_4(NO_3)_2$ precursor using wet solution method and dry impregnation method, respectively. On the other hand, using dry impregnation method, the B25-DPtOH⁻ was prepared from $H_2Pt(OH)_6$ precursor and B25-DPtCl⁻ was prepared from $H_2Pt(CI)_6$ precursor.

The catalytic performances of mordenite supported platinum samples prepared from $Pt(NH_3)_4NO_3$ with dry impregnation method are presented in Table 3. Having the higher benzene conversion, liquid yield of C_5^+ and MCH, and MCP/CH ratio, thus M23-DPtNH⁺ and M16E-WPtNH⁺ sample showed the highest OB number. While M23-DPtNH⁺ was prepared from powder sample with dry impregnation method, M16E-WPtNH⁺ sample was prepared from extrudate sample using wet solution method. On the other hand, M90E-DPtNH⁺ and M200E-DPtNH⁺, which were prepared from extrudate samples using dry impregnation, gave poor catalytic performances with much lower MCP/CH ratio and OB number by 10–20.

The catalytic performances of Pt/ZSM-5 samples are presented in Table 4. Z13E-DPtNH⁺ and Z90E-DPtNH⁺ were prepared from ZSM-5 extrudate using dry impregnation method. Both Z13E-DPtNH⁺ and Z90E-DPtNH⁺ showed high benzene conversion. Their MCP/CH ratio and also OB number were relatively lower than the Pt/mordenite and Pt/beta samples.

From practical viewpoint, high MCP/CH ratio and low cracking gas yield were most desirable for high OB number. Gas yields at various reaction conditions were plotted in against MCP/CH ratios in Fig. 2. In general, at a same level of gas yield, the MCP/CH ratios of Pt/zeolite samples ranked as Pt/beta > Pt/mordenite > Pt/ZSM-5. Particularly B25-WPtNH⁺ sample showed the highest MCP/CH ratio at very low cracking gas yield. Referred to Tables 2–4, OB number ranked as Pt/beta > Pt/mordenite \approx Pt/ZSM-5. The highest OB number of zeolite beta is associated with the highest MCP/CH ratio and low cracking gas yield. On the other hand, Pt/zeolite samples

Table 4

Catalytic performances of Pt/ZSM-5 samples in benzene hydrogenation (pressure: 2068 kPa, WHSV: 2 h^{-1} g/g-catalyst, H2/HC (molar ratio: 6).

	ID				
	Z13E-DPtNH ⁺		Z90E-DPtNI	H⁺	
	Extrudate ^a		Extrudate ^a		
Rx. T (K)	503	523	503	523	
Conv. (%)	99.3	99.0	88.9	95.4	
C ₅ ⁺ liq. (%)	100.0	99.9	95.6	88.8	
MCP/CH	0	0.01	0.7	0.7	
OB number	92.7	92.8	94.7	88.3	
Product yield (%)					
$C_1 + C_2$	0	0.01	0.71	1.32	
$C_3 + C_4$	0.01	0.05	3.69	9.88	
C5 ⁺ parraffin	0.24	0.57	1.06	2.14	
MCP	0.38	1.13	33.18	34.02	
Benzene	0.68	0.97	11.13	4.65	
СН	98.7	97.27	50.23	48	

^a Shape.



Fig. 2. Plot of C_4^- gas yield versus MCP/CH ratio over various zeolite supported platinum catalysts (temperature: 483–523 K, pressure: 2068 kPa, WHSV: $2 h^{-1}$ g/g-catalyst, H2/HC molar ratio: 6).

prepared with wet solution method from the $Pt(NH_3)_4(NO_3)_2$ precursor generally showed higher MCP/CH ratio and lower C_4^- gas yield and vice versa for that prepared with H_2PtCl_6 precursor by dry impregnation method.

The low MCP/CH ratio over Pt/ZSM-5 for low MCP selectivity should be attributed to the shape selectivity of ZSM-5. Calemma et al. reported that the pore size and topology of medium-pore zeolites (ZSM-5 and ZSM-23) have a strong shape selective effect on the activity and selectivity of dimethylcyclopentane for ring contraction and ring opening of C₈ naphthenic compounds [16]. Wang et al. proposed that proximity of metal sites and on acid sites of Pt/zeolite catalysts is essential [12]. According to McVicker et al. CP has higher ring opening reactivity than CH [20]. Therefore, formation of MCP from CH isomerization is favorable over Brønsted acid sites which properly balanced with the metal function of Pt sites. Tsai et al. [13] reported that zeolite supported with platinum by ion exchange method has higher MCP/CH ratio and lower cracking gas vield. Samoila et al. reported that the location of Pt and Rh affects strongly ring opening activity [25]. Limited by the product shape selectivity, ring contraction of CH into MCP product is suppressed by the 10-membered oxygen ring pores of ZMS-5, therefore, much higher CH product yield and low C₄⁻ gas yield was observed.

On the other hand, improper balance of metal-acid function would induce more ring opening/cracking reaction and high C_4^- gas yield. The hydrogenation and ring contraction/opening activities of platinum depend on type of support, Pt location and particle size [21]. By means of ¹²⁹Xe NMR technique, Ryoo et al. [26] concluded that for zeolite Y supported Pt catalyst, the ion-exchanged Pt particles are mostly located inside the internal pores whereas the impregnated Pt tends to locate on the external surfaces of zeolite Y. Moreover, in an earlier EXAFS study, Khodakov et al. [27] concluded that the platinum tend to form small clusters inside the pore of mazzite for a Pt/mazzite catalyst prepared by ion-exchange method.

As the electronic force of zeolitic framework comes to play, the framework alumina anion would attract cations and repel anions, thus alumina is determinant to the location of platinum. While $Pt(NH_3)_4(NO_3)_2$ precursor dissociates into platinum cations (Eq. (2)), H_2PtCl_6 and $H_2Pt(OH)_6$ also dissociates into platinum anions (Eqs. (3) and (4)).

$$Pt(NH_3)_4(NO_3)_2 \to Pt(NH_3)_4^{2+} + 2NO_3^{-}$$
(2)

$$H_2 PtCl_6 \rightarrow 2H^+ + PtCl_6^{2-} \tag{3}$$

$$H_2Pt(OH)_6 \rightarrow 2H^+ + Pt(OH)_6^{2-}$$
 (4)

Platinum anions such as $PtCl_6^{2-}$ and $Pt(OH)_6^{2-}$ are repelled by alumina anions and kept away from zeolite pores, thus platinum tends to stay on the external surface of zeolites. On the other hand, the platinum cation $Pt(NH_3)_4^{2+}$ is attracted by alumina anions and exchanged with the cations of zeolite, i.e., H^+ in the present study, enter into zeolite channels. Ion exchange of cationic platinum precursors in wet solution procedure can be facilitated by the hydration of cations. Depending on the porosity of support, the mobility of cationic precursor in using dry impregnation procedure should be much slower than that in solution phase. The location could be heterogeneously distributed inside zeolite pores and on the external surface of zeolite crystals. Therefore, platinum location can be manipulated with the choice of platinum precursors and preparation procedures.

As shown above, ion exchange with the cationic precursor $Pt(NH_3)_4$ by wet solution procedure always gave the best performance, for example, B25-WPtNH⁺ for zeolite beta and M16E-WPtNH⁺ for mordenite. Their good catalytic properties can be attributed to the proper balance of acid function and metal function. Ion exchange of cationic platinum precursors by wet solution method can introduce platinum into zeolite pores at the corresponding position of framework alumina anions. Therefore, proximity between acid sites and metal sites in Pt/zeolite can be generated for the dual functional catalysis of benzene hydrogenation and ring contraction of CH. On the other hand, because of repulsive force with alumina anions, for example, platinum in B25-DPtOH- prepared by dry impregnation using anionic precursor H₂Pt(OH)₆ was located on the external surface of zeolite beta. External platinum has much higher hydrogenation activity and ring opening activity than the internal platinum [13]. The much higher C_4^- gas and lower MCP/CH ratio over B25-DPtOH⁻ (Table 2) could be attributed to the effect of types of precursor in terms of platinum location.

Preparing from extrudate samples by using cationic precursor Pt(NH₃)₄ with dry impregnation method, the M90E-DPtNH⁺ and M200E-DPtNH⁺ samples showed worse catalytic performances than M16E-WPtNH⁺ prepared with wet solution method (Table 3). As discussed above, the difference in catalytic performance of Pt/mordenite samples between wet solution and dry impregnation procedure could be attributed to the heterogenous distribution of platinum. Notice that the catalytic performance of M23-DPtNH⁺ prepared by dry impregnation using powder sample was comparable to M16E-WPtNH⁺, indicating that diffusion of platinum precursors varies significantly with the property of the support.

Benzene hydrogenation is controlled by thermodynamics. The equilibrium conversion of benzene hydrogenation at different reaction pressure as a function of reaction temperature is shown in Fig. 3. Clearly, hydrogenation reaction is favorable for high reaction



Fig. 3. Thermodynamic equilibrium conversion at various reaction pressures as a function of reaction temperature.

Table 5

Effect of H_2/HC molar ratio on the catalytic performances of B25-WPtNH⁺ sample in benzene hydrogenation (temperature: 523 K, pressure: 2068 kPa, WHSV: 2 h⁻¹ g/g-catalyst).

	H ₂ /HC					
	4 (Rx. T = 523 K)	6 (Rx. T=523 K)	8 (Rx. <i>T</i> = 523 K)			
Conv. (%)	99.2	100.0	99.9			
C ₅ ⁺ liq. (%)	99.5	96.0	99.0			
MCP/CH	1.6	3.6	1.0			
OB number	102.0	101.5	99.5			
Product yield (%)						
$C_1 + C_2$	0.02	0.98	0.2			
$C_3 + C_4$	0.45	3	0.78			
C5 ⁺ parraffin	2.83	8.74	1.24			
MCP	58.92	68.25	48.14			
Benzene	0.84	0.03	0.08			
CH	36.94	19.01	49.56			

pressure and unfavorable for high reaction temperature. The operating window for 100% conversion for the pressure of 101 kPa is below 500 K, which is much narrower than that operated at higher reaction pressures. The effect of H_2/HC ratio on the catalytic performance of B25-WPtNH⁺ is shown in Table 5. As shown in Fig. 4, as benzene partial pressure decreased with increasing H_2/HC ratio, benzene conversion increased slightly but OB number dropped. The best catalytic performance was obtained at H_2/HC molar ratio of around 6, giving a maximum MCP/CH ratio of 3.6 and maximum OB number of 101.5.

The thermodynamic equilibrium curve of isomerization of CH is shown in Fig. 5. The ΔG of CH isomerization is +0.96 kcal at 298 K. Due to positive ΔG , the MCP/CH ratio at thermodynamic equilib-



Fig. 4. Catalytic performance of zeolite beta supported platinum catalyst by ion exchange at various H₂/HC ratio (catalyst: B25-WPtNH⁺; temperature: 523 K, pressure: 2068 kPa, WHSV: 2 h⁻¹ g/g-catalyst).



Fig. 5. Thermodynamic equilibrium MCP/CH ratio.



Fig. 6. Effect of reaction temperature on the catalytic performance of B25-WPtNH⁺, pressure: 2068 kPa, WHSV: $2 h^{-1} g/g$ -catalyst, H2/HC (molar ratio: 6).

rium increases with increasing reaction temperatures. In contrast, the ΔG of paraffin isomerization is negative and temperature does not favor DMB yield [28].

Since benzene hydrogenation is highly exothermic leading to large rise of reactor temperature. CH isomerization in series with benzene hydrogenation is favorable by thermodynamics. The temperature rise arisen from heat of reaction can be used to promote CH isomerization and thus OB number of the reaction products. Therefore, bi-functional catalyst Pt/beta could be effective in benzene hydrogenation -CH isomerization cascading reaction system. The effect of reaction temperature on the catalytic performance of B25-WPtNH⁺ is shown in Fig. 6. While benzene conversion remained 100% in the reaction temperature range of 483 K and 523 K, MCP/CH ratio and also cracking gas yield increased with increasing reaction temperatures. Over B25-WPtNH⁺, the MCP/CH ratio reached thermodynamic equilibrium ratio of 3.0 at reaction temperature of around 520 K. As a result, maximum OB number appeared at around 513 K in the compromise between liquid yield and MCP/CH ratio.

4. Conclusions

Zeolite supported platinum catalysts for benzene hydrogenation and cyclohexane (CH) isomerization into methyl-cyclopentane (MCP) were studied; particularly the effect of catalyst preparation procedures was examined. It was found that Pt/zeolite prepared from Pt(NH₃)₄(NO₃)₂ precursor with wet solution procedure in general showed higher MCP/CH ratio, lower C4- gas yield and higher octane barrel (OB) than that prepared with H₂PtCl₆ precursor by dry impregnation procedure. The difference in catalytic performance associating with various preparation procedures is attributed to the effect of platinum location as a result of electrical force exerted by alumina anions. Ion exchange of $Pt(NH_3)_4(NO_3)_2$ precursor would introduce platinum into zeolite channels through attraction force between cationic platinum species and alumina anions. On the other hand, anionic platinum species generated from H₂Pt(OH)₆ and H₂PtCl₆ precursors are repelled by alumina anions in zeolite framework. Thus, preparing from anionic platinum precursors by dry impregnation procedure, platinum tends to locate on zeolite external surface. Preparing with cationic precursors by dry impregnation procedure, platinum could be heterogeneously distributed on zeolite.

CH isomerization can compensate partially the OB loss from benzene hydrogenation. Furthermore, the temperature rise arisen from the reaction heat of benzene hydrogenation favors CH isomerization. It was found that in terms of OB number of reaction products, Pt/beta was more effective than Pt/mordenite and Pt/ZSM-5. Pt/ZSM-5 suppressed the CH isomerization and the formation of MCP product, which can be attributed to the product shape selectivity of ZSM-5. On the other hand, Pt/beta prepared from cationic platinum precursor $Pt(NH_3)_4(NO_3)_2$ showed the highest MCP/CH ratio reaching thermodynamic equilibrium and the highest OB number.

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