ELSEVIER

Catalysis Today 51 (1999) 135–140

CATALYSIS TODAY

Saturation of aromatics and aromatization of C_3 and C_4 hydrocarbons over metal loaded pillared clay catalysts

Wei-Qiao Liu[a], Lin Zhao[a], Gui-Da Sun[a,*], En-Ze Min[b]

[a]*Fushun Petroleum Institute, Fushun 113001, China*
[b]*Research Institute of Petroleum Processing, Beijing 100083, China*

Abstract

Saturation of aromatics (benzene, xylene or mesitylene) over Pt (or Pd)/PLC catalysts and commercial Pt (or Pd)/γ-Al_2O_3 was studied. The results show that the benzene hydrogenation activity of Pt (or Pd)/PLC is similar to that of Pt (or Pd)/γ-Al_2O_3. Pt (or Pd)/PLC shows the shape-selectivity in the hydrogenation of xylene and mesitylene because of its regular larger pore structure. The bimetallic Pt–Pd/Al–PLC catalyst has a higher activity for hydrogen saturation and a stronger stability to sulfur poisoning. The study of C_3 and C_4 hydrocarbon aromatization over Zn/Al–PLC and Zn/HZSM-5 shows that the Zn/HZSM-5 has a much higher activity than the Zn/Al–PLC catalyst due to their characteristic difference in acidity. In addition, it is found that C_3 is mainly converted to benzene and C_4 to xylene over Zn/PLC, while both C_3 and C_4 are mostly converted to toluene over Zn/HZSM-5. Among the pillared clays, the Ga–PLC is most effective for aromatization. In order to improve the C_3 and C_4 aromatization property over Zn/Al–CLM, bimetallic catalysts were studied. Combining Ga^{3+} and Pt^{4+} improves the selectivity of aromatics as well as the total conversion. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Saturation of aromatics; Aromatization; C_3 and C_4 hydrocarbons; Pillared clay

---

1. Introduction

Pillared clays (PLC), which are also known as cross-linked smectites (CLS), are a relatively new class of molecular sieve-like materials with a large pore-size. Due to their high surface area, microporous structure and acidic properties, pillared clays have a potential interest as catalysts and adsorbents. We have made a study on the synthesis, acidity, pore structure and catalytic properties of pillared clays [1–4]. This paper presents the results of aromatics saturation and the C_3 and C_4 hydrocarbon aromatization over PLC loaded with metals.

2. Experimental

2.1. Catalyst preparation

In the present study, the γ-Al_2O_3 and HZSM-5 were supplied by Fushun Refinery no. 3's Catalyst Plant. The preparation of aluminium pillared clay (Al–PLC), which was also termed as Al–CLM (cross-linked montorillonite), was carried out as follows [3–7]. The starting mineral Ca–montmorillonite with a cation exchange capacity of 1150 mmol/kg produced in Linan of China was desiccated at 393 K for 48 h, cooled to room temperature and added to distilled water and stirred for 2 h. Then the clay slurry was added to Na–polystyrene cation exchange resin.

---

*Corresponding author.

PII: S0920-5861(99)00015-2

Exchange was carried out with continuous stirring for 72 h. The montmorillonite slurry with a clay particle size of less than or equal to 2 μm which was used for the pillaring experiments was separated by a classical gravity sedimentation method. The pillaring agent was prepared by adding 0.2 M NaOH solution into 0.2 M $AlCl_3$ solution slowly with continuous stirring. The OH/Al molar ratio of the pillaring agent was 2.5. The resulting solution was then aged at room temperature for seven days prior to use. Under vigorous stirring, the Al-pillaring agent was slowly added to the montmorillonite slurry. Reaction was then carried out at 343 K for 0.5 h with continuous stirring. Then, the resulting slurry was aged at room temperature for 12 h, followed by filtration and washing until free of Cl^- ions. Finally, the resulting solid was dried at 383 K and Al–CLM was obtained. When Ca–bentonite with a cation exchange capacity of 730 mmol/kg produced in Heishan of China was used as the starting material, the aluminium pillared bentonite (Al–CLB) was prepared by the same procedure as the preparation of Al–CLM. Ga–PLC which was also termed as Ga–CLM was synthesized by using the Ga-pillaring agent and the montmorillonite slurry with a clay particle size of less than or equal to 2 μm. The Ga-pillaring agent was prepared by adding 0.2 M NaOH solution into 0.2 M $GaCl_3$ solution slowly with continuous stirring. The OH/Ga molar ratio of the pillaring agent was 2.2. The mixture solution was then aged at room temperature for 0.5 h prior to use. The subsequent synthesis procedure is the same as that of Al–PLC.

After calcination for 2 h at 773 K, the supports Al–PLC, γ-Al_2O_3 and HZSM-5 were respectively impregnated with solution of $Pt(NH_3)_4Cl_2$, $PdCl_2$, or $Zn(NO_3)_2$ at room temperature for 24 h, followed by drying at 383 K. The amount of Pt or Pd was 0.5 wt% and that of Zn was 5.8 wt% in the catalysts.

The bimetallic catalyst was prepared by impregnation of the above mentioned catalysts with another metal ion solution at room temperature for 24 h followed by drying at 383 K. Besides the above mentioned metal dipping solution, aqueous solution of $Ni(NO_3)_2$, $GaCl_3$, $H_2PtCl_6 \cdot 6\,H_2O$, or $Cr(NO_3)_3$ is also used as the dipping solution in this study.

More details on the preparation of the catalysts have been reported elsewhere [3–7].

2.2. *Catalyst characterization*

BET specific surface areas of the catalysts were measured via physisorption of nitrogen at 78 K on samples evacuated at 573 K for 4 h using a Micromeritrics ASAP 2400 type automatic porosimeter.

The basal spacing ($d_{0\,0\,1}$) of Al (or Ga)–PLC catalyst was obtained from X-ray powder diffraction (XRD) patterns recorded by a Japanese D/Max-RB X-ray diffractometer with Cu K_α radiation at 40 kV and 50 mA. During the analysis, scans was taken with a 2Θ size of 0.02° and a speed of 4°/min.

The temperature-programmed desorption of ammonia (NH_3-TPD) was performed in a flow system using helium as carrier gas. After heating at 773 K for 2 h the sample (0.1 g) was treated in a helium stream at 623 K for 1 h, then cooled to 393 K and maintained at 393 K for 0.5 h. After this treatment the samples were exposed to an NH_3 stream. The NH_3-TPD profile was obtained by heating the sample at a rate of 15 K/min under a 45 ml/min helium stream.

2.3. *Activity measurement*

The activity measurements of the aromatics hydrogenation saturation were carried out in a continuous flow fix-bed reactor system. The catalyst with particle size of 40–60 mesh (1.8 g) was pretreated in situ. The sample loaded with Pt was activated at 573 K for 3 h in an air stream and reduced at 773 K for 4 h in a hydrogen flow. The sample loaded with Pd was only reduced at 523 K for 4 h in a hydrogen flow. The testing conditions were as follows, hydrogen pressure 6.0 MPa, reaction temperature 493 K, WHSV 2 h^{-1}, the hydrogen/hydrocarbons volume ratio 800. The feed was a mixture containing 20 wt% benzene (or xylene or mesitylene) with 80 wt% *n*-hexane.

The catalytic reaction tests of C_3 and C_4 hydrocarbon aromatization were carried out with a pulse flow fix-bed reactor system. The catalyst with particle size of 40–60 mesh (0.2 g) was treated in an air flow at 673 K for 2 h, then reduced in a hydrogen flow at 773 K for 2 h and oxidated in an air flow at 773 K for 2 h. The amount of the reactants was 0.5 ml, and the reaction temperature was 773 K. The C_3 reactant gas contained more than 99 wt% propane with less than 1 wt% propylene. The C_4 reactant gas contained

Table 1
The results of benzene hydrogenation over the Pt (Pd)/Al–PLC catalysts

Catalyst	Benzene Conversion (%)	Yield (%)		Selectivity (%)	
		Cyclohexane	Methyl cyclopentane	Cyclohexane	Methyl cyclopentane
Pt/Al–CLM	97.47	95.80	1.67	98.29	1.71
Pd/Al–CLM	99.46	77.31	22.15	77.73	22.27
Pt/Al–CLB	94.56	93.97	0.59	99.37	0.63
Pt/γ-Al_2O_3	99.95	98.66	1.28	98.71	1.28
Pd/γ-Al_2O_3	99.89	81.28	18.61	81.37	18.63

Reactants: i-C_6 (4.84 wt%), n-C_6 (67.54 wt%), methyl cyclopentane (9.01 wt%) and benzene (18.59 wt%).

56 wt% butane, 38 wt% butene and 6 wt% C_1–C_3 hydrocarbons.

The reactants and products were analyzed on-line using a gas chromatography equipped with a 50 m long quartz capillary column and an integrator (HP3394A).

3. Results and discussion

3.1. Saturation of aromatics

The benzene saturation activities of the various catalysts are shown in Table 1. Clearly, the benzene hydrogenation activity of PLC loaded with Pt or Pd is similar to that of the Pt (or Pd)/γ-Al_2O_3 catalyst used in industry. When the benzene content in the feed is about 20 wt%, the benzene content in the product can be reduced to below 1 wt%. This shows that the benzene saturation activity of Pt (or Pd)/Al–CLM is not superior to that of Pt (or Pd)/γ-Al_2O_3.

Table 1 also shows that the selectivity for cyclohexane over Pd/Al–CLM is lower than that over Pt/Al–CLM. The selectivity for methyl cyclopentane shows a trend which is the reverse of that for cyclohexane. The reason is that the metal with a stronger hydrogenation function is able to increase the acidity of the bifunctional catalyst. The difference in catalytic activity between Pt/Al–CLM and Pt/Al–CLB is caused by the difference in surface area (see Table 2) and acidity [8] between Al–CLM and Al–CLB.

Table 2
The physical features of the catalysts

Catalyst	SA (m^2/g)	$d_{0\,0\,1}$ (nm)	Pore volume (ml/g)
Pt/Al–CLM	142	1.78	–
Pt/Al–CLB	121	1.77	–
Zn/Al–CLM	198	1.78	0.11
Zn/Ga–CLM	206	1.88	0.12
Zn/HZSM-5	260	0.58 (pore diameter)	0.14
Pt/γ-Al_2O_3	215	–	0.44

The results of the xylene and mesitylene saturation over the PLC type catalysts loaded with precious metals (see Tables 3 and 4) show that their hydrogenation activity for large aromatic molecules is

Table 3
The results of xylene hydrogenation

Catalyst	Conversion (%)			C_8N[a] Selectivity (%)
	Benzene	Ethylbenzene	Xylene	
Pt/Al–CLM	100	100	100	94.34
Pd/Al–CLM	100	100	100	89.37
Pt/γ-Al_2O_3	100	36.32	14.06	94.12

[a] C_8N=C_8 cycloalkane.

Reactants: i-C_6 (4.83 wt%), n-C_6 (67.24 wt%), methyl cyclopentane (8.57 wt%), benzene (0.49 wt%), ethylbenzene (4.35 wt%) and xylene (14.51 wt%).

Table 4
The results of mesitylene hydrogenation

Catalyst	Conversion (%)		Psa[a] selectivity (%)
	Benzene	Mesitylene	
Pd/Al–CLM	100	100	77.32
Pd/γ-Al_2O_3	71.16	6.10	77.10

[a] Psa: Products of hydrogenation saturation of mesitylene (except cyclohexane).

Reactants: i-C_6 (3.75 wt%), n-C_6 (70.01 wt%), methyl cyclopentane (9.27 wt%), benzene (3.19 wt%), and mesitylene (13.77 wt%).

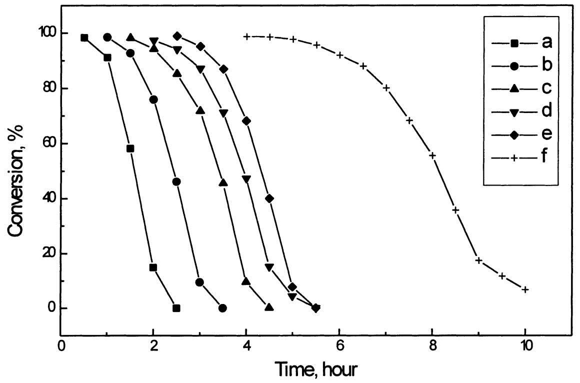


Fig. 1. The behavior of the sulfur-resistance of the various catalysts in the benzene hydrogenation saturation reaction. Catalyst: (a) Pd (0.5 wt%)/Al–CLM, (b) Pt (0.5 wt%)/Al–CLM, (c) Pd (1.2 wt%)/Al–CLM, (d) Pt (1.2 wt%)/Al–CLM, (e) Pt (0.5 wt%)/γ-Al_2O_3, and (f) Pt (0.3 wt%)–Pd (0.9 wt%)/Al–CLM. Reactants: a mixture containing 19.89 wt% benzene with 80.11 wt% *n* (*i*)-hexane and methyl cyclopentane to which 100 ppm thiophene was added. Testing conditions: hydrogen pressure 6.0 MPa, reaction temperature 493 K, WHSV 2 h^{-1}, hydrogen/hydrocarbons volume ratio 800.

higher than that over the Pt (or Pd)/γ-Al_2O_3 catalysts. When the content of xylene or mesitylene in the feed is about 15 wt%, both reactants show 100% conversion over Pt (or Pd)/Al–CLM whereas the conversion of C_8-aromatics over Pt/γ-Al_2O_3 is 50.38% and that of mesitylene over Pd/γ-Al_2O_3 is only 6.10%. The reason of the higher activity of Pt (or Pd)/PLC is that the PLC has a larger pore size structure (see Table 2). The larger molecule reactants can more easily diffuse into the PLC pores and more reactant molecules may contact the active sites. Indeed the larger basal space of PLC matches the molecular size of the transition state of the large molecules. As a result, Pt (or Pd)/PLC shows high catalytic activity for the hydrogenation of large aromatic molecules. γ-Al_2O_3 has not such regular large pore structure, and consequently the catalytic activity of Pt (or Pd)/γ-Al_2O_3 for the saturation of large aromatic molecules is low.

The sulfur-resistance of the various catalysts is shown in Fig. 1. The test was carried out using a feed stock with 100 ppm thiophene. From Fig. 1 it can easily be seen that for benzene hydrogenation the sulfur-resistance of Pt/γ-Al_2O_3 is superior to that of Pt (or Pd)/PLC. In order to improve the sulfur-resistance of PLC loaded with precious metals, bimetallic Pt–Pd/Al–CLM catalysts were prepared and tested. The results indicate that the second metal in the catalysts can remarkably increase the stability to sulfur poisoning and Pt–Pd/Al–CLM with Pt 0.3 wt% and Pd 0.9 wt% clearly has the best sulfur-resistance.

3.2. Aromatization of C_3 and C_4 hydrocarbons

In Tables 5 and 6 the results of the C_3 and C_4 hydrocarbon aromatization over Zn/Al–CLM, Zn/Ga–CLM and Zn/HZSM-5 are presented. These results show that the aromatization activity of Zn/PLC is lower than that of Zn/HZSM-5, due to the difference in the acidic properties. The profiles of NH_3-TPD of Zn/Al–CLM and Zn/HZSM-5 are shown in Fig. 2. It can be seen that two kinds of acidic sites exist in both catalysts. Peak I shows the weak acidic sites and peak II shows the strong acidic ones. According to the position of the two peaks, it is clear that the strengths of the two kinds of acidic sites of Zn/HZSM-5 are stronger than those of Zn/Al–CLM. According to the area of peaks, it is clear that the strong acidic capacity dominates in the case of Zn/HZSM-5, whereas for Zn/Al–CLM the weak acidic capacity is dominating.

Table 6 shows that C_3 is mainly converted to benzene and C_4 is mainly converted to xylene over the Zn/PLC catalysts. Both C_3 and C_4 hydrocarbons are

Table 5
The C_3 and C_4 hydrocarbon aromatization properties

Catalyst	C_3 hydrocarbons			C_4 hydrocarbons		
	Conversion (%)	Selectivity of aromatics (%)	Yield of aromatics (%)	Conversion (%)	Selectivity of aromatics (%)	Yield of aromatics (%)
Zn/Al–CLM	16.86	27.40	4.62	51.49	46.96	24.18
Zn/Ga–CLM	24.17	40.34	9.75	56.89	51.45	29.27
Zn/HZSM-5	49.01	57.30	27.89	92.52	52.66	48.72

Table 6
The aromatics yield of C_3 and C_4 hydrocarbon aromatization

Catalyst	Yield of products of C_3 aromatization (%)					Yield of products of C_4 aromatization (%)				
	Benzene	Toluene	Ethyl-benzene	Xylene	Cracking-products	Benzene	Toluene	Ethyl-benzene	Xylene	Cracking-products
Zn/Al–CLM	4.14	0.48	0	0	3.67	2.34	8.89	1.37	11.58	20.26
Zn/Ga–CLM	8.64	1.11	0	0	6.25	3.63	10.85	1.90	12.89	21.71
Zn/HZSM-5	6.69	14.50	0.83	3.90	14.87	12.70	23.18	2.76	10.08	31.88

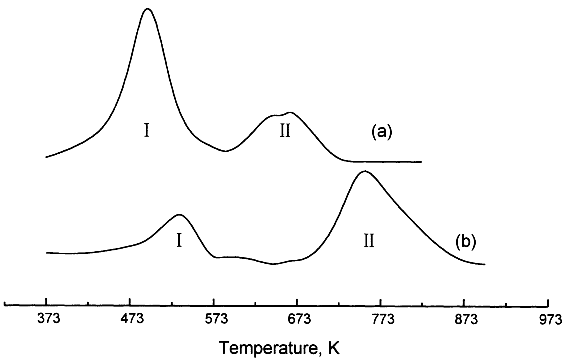
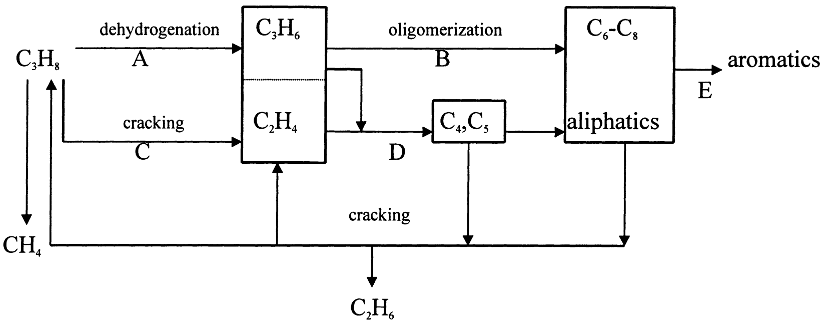


Fig. 2. The profiles of NH_3-TPD of Zn/Al–CLM and Zn/HZSM-5 after pretreatment: (a) Zn/Al–CLM, (b) Zn/HZSM-5. The pretreatment conditions are given in Section 2.

mostly converted to toluene over Zn/HZSM-5. These results are due to the different acidic properties and different pore structure of these two catalysts. It is worth noting that the large pore structure of Zn/PLC is capable of shape-selective catalysis.

According to the products of the C_3 and C_4 hydrocarbon aromatization, the main reaction pathways of propane to aromatics may be summarized as follows [9].



For the Zn/HZSM-5 catalyst, due to the bi-functional property by the presence of acidity and metal, propane gives C_2H_4 and C_3H_6, which oligomerize in the zeolite channels. The oligomerized products either give smaller molecules via cracking or aromatics via dehydrocyclization (dehydrogenation and cyclization). The main reaction paths for aromatization are the path C–D–E and A–B–E.

Owing to the weak acidity of PLC, the cracking activity of Zn/PLC is much less than that of Zn/HZSM-5. Thus, propane gives more C_3H_6 and less C_2H_4, and the dehydrocyclodimerization of propane (path A–B–E) is the main reaction path of propane to aromatics. So propane is selectively converted to benzene over Zn/PLC. Similar results were obtained by Bradley and Kydd [10] in a study on the dehydrocyclodimerization of propane over Ga–PLC and Ga–HZSM-5 catalysts.

In the aromatization of C_4 hydrocarbons, these reaction paths of C_4 hydrocarbons to aromatics are similar to those of propane to aromatics. For the Zn/PLC catalysts, the dehydrocyclodimerization (path A–B–E) is the main reaction path of C_4 hydrocarbons to aromatics. Due to the larger content of butene in C_4

hydrocarbons and the higher cracking behavior of butane and butene compared to propane (see Table 6), C–D–E is also an important reaction pathway. Toluene is a remarkable product of C_4 hydrocarbons to aromatization over Zn/PLC, resulting in a much higher conversion and aromatics selectivity of C_4 hydrocarbons compared to propane.

Besides the acidity of the catalyst and the content of alkene in the feed stock, the difference in pore structure between PLC and HZSM-5 can also cause the differences in selectivity. Table 2 shows that the Zn/PLC catalysts have a larger pore size than the Zn/HZSM-5 catalyst. The regular larger pore structure of the Zn/PLC catalysts is suited to the formation of C_8 aromatics, because of the space in the porous pathway of PLC is big enough for the formation of the transition state cyclocompound for C_8 aromatics. The dynamic diameters of *p*-xylene, *m*-xylene and *o*-xylene are 0.58, 0.63 and 0.64 nm, respectively, and the pore diameter of Zn/HZSM-5 is only 0.58 nm. So there is space-limitation for the formation of the transition state cyclocompound for *m*-xylene and *o*-xylene and for the diffusion of *m*-xylene and *o*-xylene in the pores of the Zn/HZSM-5 catalyst. The results of the product analysis show that, in the aromatization of C_4 hydrocarbons, *p*-xylene is obtained without *m*-xylene and *o*-xylene for the Zn/HZSM-5 catalyst whereas mixed xylenes are obtained for the Zn/PLC catalysts.

In order to improve the C_3 and C_4 hydrocarbon aromatization property, a second metal component (1 wt%) such as Ni^{2+}, Cr^{3+}, Ga^{3+} or Pt^{4+} was added, respectively, to the Zn/Al–CLM catalyst (containing 5.8 wt% of Zn) to change its surface properties. The results are presented in Table 7. Comparing Table 7 with Table 5, it becomes clear that Ga and Pt improve the aromatization activity for C_4. The stronger the n-type semiconductor feature of ZnO, the higher the dehydrogenation activity of ZnO. The introduction of Ga (or Pt) to the Zn/Al–CLM catalyst is able to promote the n-type semiconductor feature of ZnO, so the aromatization property of Zn/Al–CLM is improved.

Table 7
The C_4 hydrocarbon aromatization property over bimetallic catalysts

Catalyst	Conversion (%)	Selectivity of aromatics (%)	Yield of aromatics (%)
NiZn/Al–CLM	58.94	36.19	21.33
CrZn/Al–CLM	51.79	45.66	23.65
GaZn/Al–CLM	56.23	56.91	32.00
PtZn/Al–CLM	64.41	54.20	34.91

4. Conclusions

Owing to the larger pore structure of PLC, the Pt (or Pd)/PLC catalysts show much higher catalytic activity for the hydrogenation of large aromatic molecules. Because of the larger pore structure and the weak acidity of PLC, the Zn/PLC catalysts are selective in the aromatization of C_3 and C_4 hydrocarbons, that is, propane is remarkably converted to benzene and C_4 hydrocarbons are mainly converted to xylene over the Zn/PLC catalysts. The second metal (Pd or Pt) in Pt (or Pd)/Al–PLC can remarkably increase the sulfur-resistance and the second metal (Pt or Ga) in Zn/Al–PLC is able to improve the aromatization activity.

Acknowledgements

The authors are grateful to professor Yu-Qing Gao in Daqing Petroleum Institute and to all our colleagues of the industrial catalysis group in the Fushun Petroleum Institute for their long term contribution in this work. The project is supported by China Petrochemical Corporation (SINOPEC).

References

[1] Z.H. Liu, G.D. Sun, Stud. Surf. Sci. Catal. 24 (1985) 493.
[2] G.D. Sun, F.S. Yan, H.H. Zhu, Z.H. Liu, Preparation of catalysts IV, Stud. Surf. Sci. Catal. 31 (1987) 649.
[3] G.D. Sun, F.S. Yan, Z.H. Liu, Fushun Shiyou Xueyuan Xuebao 11 (1986) 36.
[4] G.D. Sun, F.S. Yan, Z.H. Liu, Fushun Shiyou Xueyuan Xuebao 12 (1986) 74.
[5] V.N.P. Arulekar, J. Hightower, Appl. Catal. 35 (1987) 249.
[6] T.J. Pinnavaia, M.-S. Tzou, S.D. Landau, R.H. Raythatha, J. Mol. Catal. 27 (1984) 195.
[7] T.J. Pinnavaia, M.-S. Tzou, S.D. Landau, J. Am. Chem. Soc. 107 (1985) 4783.
[8] G.H. Liu, Ph.D. Thesis, Research Institute of Petroleum Processing, Beijing, the People's Republic of China, 1988.
[9] H. Kitagawa, Y. Sendoda, Y. Ono, J. Catal. 101 (1986) 12.
[10] S.M. Bradley, R.A. Kydd, J. Catal. 142 (1993) 448.