

# Cesium concentration effect on Pt/Cs beta zeolite/ $\gamma$ -alumina catalysts for *n*-heptane conversion

G. Espinosa Sntamaaria<sup>a,\*</sup>, J.M. Bautista<sup>a</sup>, H. Silva<sup>a</sup>, L. Muñoz<sup>a</sup>, N. Batina<sup>b</sup>

<sup>a</sup> Instituto Mexicano del Petróleo, Catalizadores, Apdo. Postal 14-805, Eje Central Lázaro Cárdenas 152, 07730 México D.F., Mexico

<sup>b</sup> Depto. de Química, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. Postal 55-534, 09340 México D.F., Mexico

Received 25 June 2001; received in revised form 18 December 2001; accepted 4 January 2002

## Abstract

Catalytic behavior of platinum catalysts supported on Cs beta zeolite/ $\gamma$ -alumina, for *n*-heptane reforming reactions, was studied. Cs concentration in the beta zeolite varied from 0 to 0.84 wt.%, in order to neutralize Brönsted acid sites. Increase in Cs content leads to decrease cracking products, but without increase in the toluene selectivity. In the same study Cs beta zeolite catalysts were compared with pure  $\gamma$ -alumina supported platinum catalyst, showing high toluene selectivity. Selectivity towards isomerization products is favored with catalysts containing Cs beta zeolite, suggesting a bifunctional behavior of such catalyst in spite of Cs content. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Beta zeolite; Platinum; Bifunctional catalysts; Aromatization

## 1. Introduction

At industrial level, naphtha reforming catalysts are bifunctional, with metallic and acid functions. In such catalysts, acid function is traditionally provided by chlorided alumina. However, the chloride is lost from alumina in presence of humidity, weakening the acid function. In order to maintain the catalyst performance, addition of chloride compounds is required which is a difficult process to control [1,2]. Therefore, research on naphtha reforming catalysts is oriented to generate a more stable acid function than that obtained with chlorided alumina.

On past years, platinum catalysts supported on KL zeolite, have been extensively studied, showing successful results for *n*-hexane aromatization [3–5].

However, KL zeolite which possesses one-dimensional channel structure, with diameter of 0.7 nm, could be easily subject of rapid deactivation [6] and this system is very sensitive to sulfur poisoning [7], limiting its potential on industrial level. Studies on alternative zeolites for reforming processes, such as beta zeolite (commercially produced) have been developed. This large pore three-dimensional zeolite (maximum diameter of channels 0.75 nm) has been studied for paraffin isomerization [8–10], *n*-heptane and *n*-hexane aromatization reactions [11–13]. Smirniotis and Ruckenstein [13] and coworkers found that a catalyst formulated with 0.5 wt.% platinum supported on beta zeolite (acid form) shows a higher selectivity for isomerization reactions, in comparison with the catalyst of platinum supported on alumina. The addition of alkaline cations to the beta zeolite support was studied by Zheng et al. [14]; they found that platinum supported on beta zeolite exchanged with cesium cations shows important increase in the aromatization of *n*-hexane.

\* Corresponding author. Fax: +52-55-672-927.

E-mail address: gaespino@www.imp.mx.

(G. Espinosa Sntamaaria).

It has also been reported that beta zeolite supported platinum, in which the beta zeolite was exchanged with alkaline and earth alkaline cations, the Pt/Cs beta system has a similar behavior in *n*-heptane aromatization as the Pt/KL system [11]. This type of catalysts show from ammonia temperature-programmed desorption (NH<sub>3</sub>TPD) measurements, total acidity values in a relatively wide range. Comparative studies between Pt/KL and Pt/K beta [14], tested for *n*-hexane aromatization, have shown a high level of cracking products at high conversion rate, forecasting an inadequate performance as industrial catalyst. Although, it is already established that addition of alkaline and earth alkaline cations (i.e. Cs) improves the catalyst selectivity, still it is not clear how to control a desired acidity on catalysts to be prepared at industrial scale.

In this work we present a study on platinum supported on beta zeolite/ $\gamma$ -alumina mixture, in which zeolite was exchanged with Cs cations at different levels, in order to optimize catalyst preparation process. The effect over its catalytic behavior was evaluated in *n*-heptane reaction used as reforming reaction model. The catalyst samples were characterized by NH<sub>3</sub>-TPD to determine the total acidity; H<sub>2</sub>-TPD was used to estimate the platinum dispersion and transmission electronic microscopy (TEM) for visualizing the position of platinum particles. Catalytic behavior of Cs beta zeolite catalysts was compared with that of  $\gamma$ -alumina supported platinum catalyst.

## 2. Experimental

### 2.1. Catalysts preparation

From an H beta zeolite sample (VALFOR CP 810B-75 from PQ Corporation) having 75 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, three parts were taken to be exchanged using CsOH solution. Cs concentration varied on two samples: one with 6.5 and 13 wt.% for the second one; these concentrations correspond to the stoichiometric quantity considering 1:1 Al: exchangeable H<sup>+</sup> molar ratio and twice of this amount, respectively. The third sample was not exposed to cation exchange.

After exchange, zeolites were filtered and washed using deionized water, dried and calcined at 550 °C for 3 h. Extrudates were prepared with exchanged

zeolites using Catapa1 B Boehmite (99% purity from Condea) as matrix and aqueous HNO<sub>3</sub>. The exchanged zeolites were mixed to have 10 wt.% concentration in extrudates after calcining at 550 °C for 3 h. Catalysts labeled as CZP-1 (lower Cs concentration) and CZP-2 (higher Cs concentration) were obtained from these supports. Platinum was loaded by ionic exchange, using Pt(NH<sub>3</sub>)<sub>4</sub>·(NO<sub>3</sub>)<sub>2</sub>, to obtain a concentration of 0.3 wt.% Pt in catalysts. Oxidation of platinum compound was carried out in air flow at 350 °C during 3 h. The same procedure was followed for extrudates containing zeolite in its acid form, (in the text marked as CZP-0). Pt reduction was achieved using hydrogen flow at 500 °C during 6 h, just before each evaluation run.

### 2.2. Reference catalyst

A catalyst without zeolite (CAP) was prepared from the same bohemite sample, using the same procedure described above for extrudates preparation. Platinum was loaded by wetness impregnation of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> in aqueous NH<sub>4</sub>OH. The thermal treatments for this sample were the same applied to catalysts containing zeolite as described above.

### 2.3. Characterization

Total acidity was obtained by NH<sub>3</sub>TPD using a ZA AMI-3 (Zeton Altamira Inc.) equipment. Metal contents of Pt and Cs, were determined by atomic absorption. Both properties, total acidity and metal content were determined employing standard methods.

Platinum dispersion was obtained from H<sub>2</sub>TPD measurements in a ZA AMI-3 system. The catalyst samples, previously reduced, were first pretreated in hydrogen flow at 500 °C during 1 h, afterward the temperature was decreased and hydrogen flow is changed by argon flow. At 100 °C the hydrogen adsorption is carried out passing a flow of H<sub>2</sub>/Ar (H<sub>2</sub>, 10%) for 30 min. Following, the system was purged to eliminate the hydrogen physical adsorption and the temperature was increased at a rate of 10 C/min with a gas flow rate of 30 cm<sup>3</sup>/min.

Beta zeolite crystalline structure was verified, after extrudates preparation with chemical and thermal treatments, by X-ray diffraction spectroscopy (XRD). Position and size of platinum particles were visualized

by TEM, using a Hitachi HD-2000 electronic microscope.

#### 2.4. Catalytic performance tests

For catalytic performance tests an all still unit was used, equipped with a fixed bed reactor and automated pressure and temperature controls; coupled to a Varian 3400 CX chromatograph, for on line reaction effluent analysis. The chromatograph is provided with FID detector and a 50 m capillary column coated with methylsilicon as a stationary phase. *n*-heptane (J.T. Baker 98 % purity) was used as reactive. Operating conditions were 15 H<sup>-1</sup> WHSV and H<sub>2</sub>/*n*-heptane molar ratio of 6. The temperature was set at 440 °C and the pressure was fixed to 2.5 and 10 kg/cm<sup>2</sup>.

Conversion was calculated with the formula %  $X = 100 \times (\text{moles reactant consumed})/(\text{moles of initial reactant})$  [15]. Products distribution is reported in this work, grouping gaseous cracking products (propane, isobutane and *n*-butane (C<sub>3</sub>–C<sub>4</sub>)); for methane, it is worth to mention that it was not detected and ethane was detected only in traces; liquid cracking products (C<sub>5</sub>, C<sub>6</sub>) are not specified because each one is present in very low concentrations; isomerization products (*i*-C<sub>7</sub>) from *n*-heptane, 2,3-dimethylpentane, 3-methylhexane and 3-ethyl-pentane among the most abundant and as aromatization product, we only have toluene.

### 3. Results

Table 1 shows catalysts characterization results. Cs concentration in catalysts is lower than that expected (0.57 versus 0.65 wt.% for CZP-1 and 0.84 versus 1.3 wt.% for CZP-2) according to the amount added in zeolite, suggesting that uptake of Cs by zeolite under preparation conditions of catalysts is a limited

process. The mean diameter calculated from H<sub>2</sub>-TPD measurements is between 1.7 and 2.0 nm for all samples. Particle size is deduced from the hypothesis that one platinum atom chemisorbs one hydrogen atom in our standard conditions and that platinum particles are spherical. However, from these results it is not possible to know particles size distribution, which will be of special importance to consider very small platinum particles located inside the zeolite channels.

Fig. 1 shows the NH<sub>3</sub>-TPD profiles for all catalysts, which indicate that the total acidity is inversely correlated to the Cs content. The lowest acidity was obtained for catalyst without zeolite, as expected. Note that acidity of 220 μmol NH<sub>3</sub>/cat g, is a typical value for a γ-alumina catalyst type.

Fig. 2 shows a TEM image for the CZP-1 sample in which beta zeolite ordered structure can be appreciated in contrast to the alumina amorphous aspect. Platinum particles are preferably deposited on beta zeolite regions. Platinum particle sizes vary from 2 to 6 nm (as seen in the image), therefore being outside zeolite channels whose pore size is around 0.75 nm. This image can not reveal the presence of smaller particles into channel system for beta zeolite.

How and in which manner, presence of microcrystals are important and related to the catalyst activity, could not be estimated yet. It could be that most of catalytic activity is related to the fine Pt particles distributed along the zeolite channels. Further research is in progress.

Table 2 shows conversion and reaction products distribution at 10 and 360 min. Zeolite catalysts present higher conversions under the same operating conditions compared with activity on catalyst without zeolite (CAP). A significant fact to be outlined is that Cs beta-zeolite/γ-alumina extrudates, corresponding to CZP-1 support without platinum, showed no activity, therefore omitted on the results table.

Table 1  
Catalysts properties

Catalyst	Platinum (wt.%)	Cesium (wt.%)	Total acidity (μmol NH <sub>3</sub> /cat g)	Dispersion (%)	Platinum particle size (nm)
CAP	0.33	0.0	220	64	1.7
CZP-0	0.3	0.0	1105	51	2.0
CZP-1	0.27	0.57	618	55	1.8
CZP-2	0.32	0.84	460	52	1.9

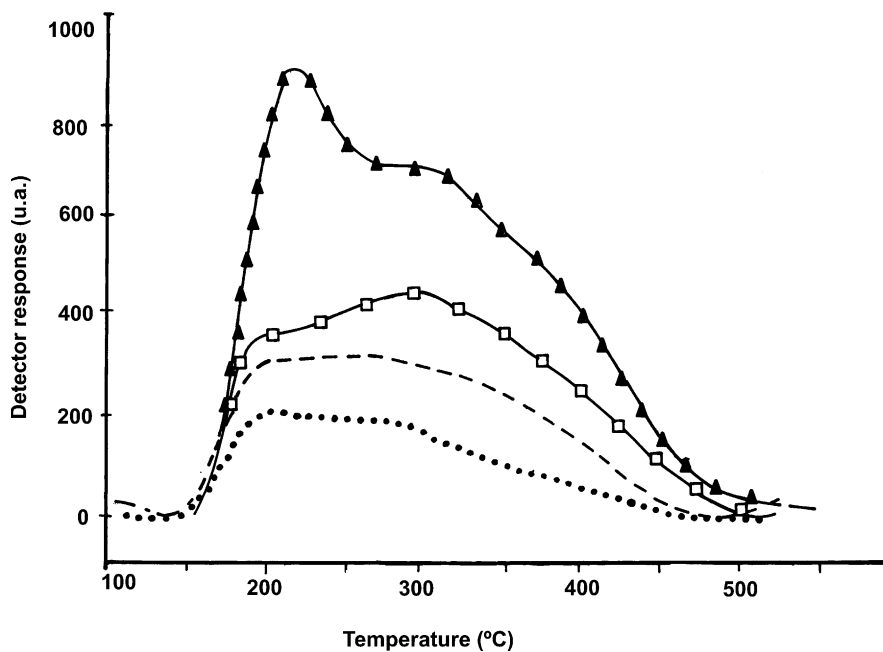


Fig. 1. NH<sub>3</sub>TPD profiles of studied catalysts (●) CAP; (---) CZP-2; (□) CZP-1 and (▲) CZP-0.

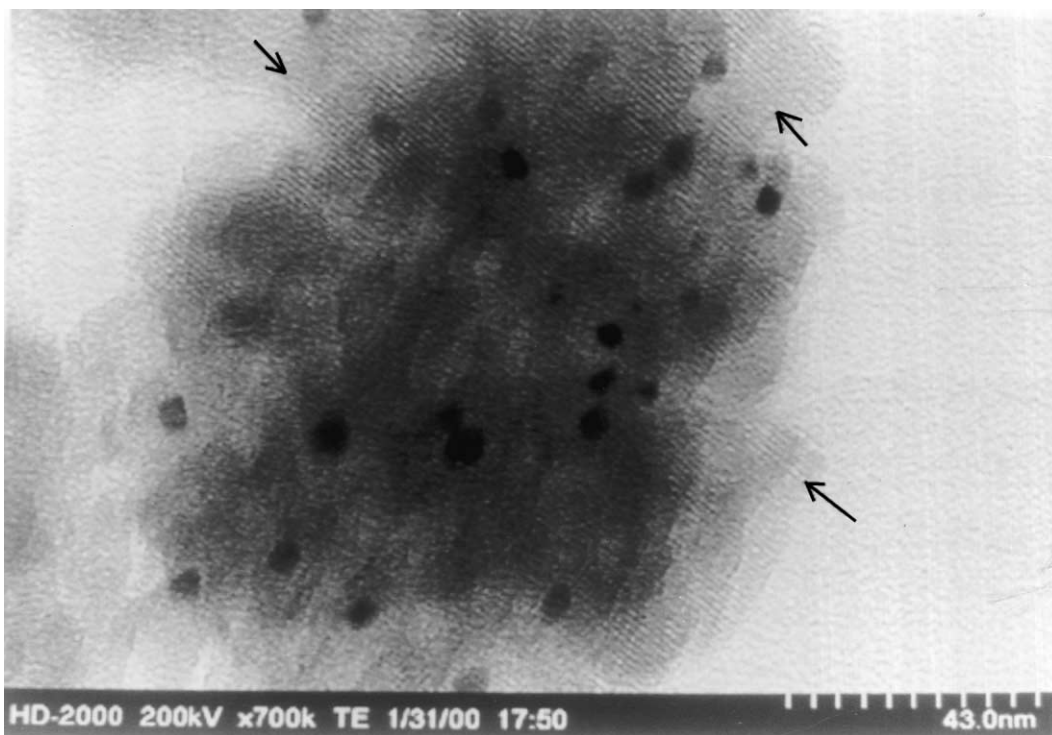


Fig. 2. STEM image of CZP-1 sample, the arrows point out the beta zeolite channel structure.

Table 2

*n*-Heptane conversion and selectivity over Pt loaded Cs beta zeolite  $\gamma$ -alumina catalysts

	Conversion (mol%)		Selectivity to products (mol%)							
	10	360	C3–C4		C5–C6		<i>i</i> -C7		Toluene	
Time (min)	10	360	10	360	10	360	10	360	10	360
Catalyst										
CZP	97	89.1	80.3	65.1	3.4	4.9	7.2	20.8	8.8	8.8
CZP-1	82.7	73.5	42.7	31.7	8.6	6.6	36.5	51.5	12.3	10.1
CZP-2	67.1	56.7	24.3	14.0	11.7	8.7	56.7	70.1	7.2	7.0
CAP	13	10	11.0	10.0	9.7	8.8	40.7	34.8	22.9	28.3

Conditions: WHSV =  $15 \text{ H}^{-1}$ ,  $\text{H}_2/\text{Hc}$  molar ratio of 6.  $T = 440^\circ\text{C}$  and  $P = 2.5 \text{ atm}$ .

For zeolite catalysts, a direct correlation is found with catalysts total acidity, inversely correlated with Cs concentration. Cracking products increase in the same sense, being evident the zeolite acidic action as active part on catalyst, however, toluene selectivity reflects no clear tendency.

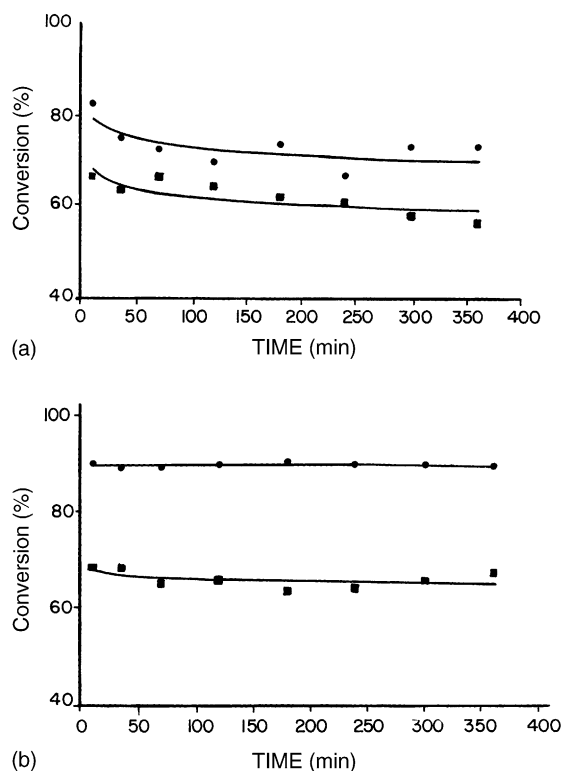


Fig. 3. *n*-Heptane conversion over Pt/Cs beta zeolite- $\gamma$ -alumina catalysts as function of reaction time, at  $T = 440^\circ\text{C}$ ,  $\text{H}_2/\text{Hc} = 6$ . (a) Curves at  $P = 2.5 \text{ atm}$  (●) CZP-1; (■) CZP-2 catalyst; (b) curves at  $P = 10 \text{ atm}$  (●) CZP-1; (■) CZP-2 catalyst.

Initial deactivation suffered by catalysts, affects cracking reactions in higher grade, being  $\text{C}_7$  isomerization products favored by this effect. In catalyst with higher neutralization grade, (CZP-2) we have also higher selectivity towards isomerization products from the beginning of the reaction. Nature of deposited coke on this type of catalysts and the way it acts within deactivation, is still being studied.

In order to define pressure influence, tests were run at  $10 \text{ kg/cm}^2$ , which is a pressure closer to that of industrial operation [16]. Fig. 3 shows conversion variation curves for reactions at 2.5 and  $10 \text{ kg/cm}^2$  pressure. Table 3 shows products distribution results. No results are reported for the not neutralized catalyst, considering the high cracking grade obtained under such conditions.

As pressure is increased, initial deactivation is reduced, but increment in light products is observed in the most acid catalyst. On the other hand, CZP-2 catalyst shows lower cracking level, but toluene is reduced in both cases.

#### 4. Discussion

Analyzing differences in products distribution, it is noticeable that catalysts containing beta zeolite present higher tendency to favor isomerization and cracking reactions, in contrast to what is observed in catalyst without zeolite, CAP sample, which is more selective to toluene. Acidity shown in CAP account for its cracking activity. It is known [17], that acid sites may be activated on  $\gamma$ -alumina at high temperatures by a dehydroxylation mechanism.

Table 3  
*n*-Heptane conversion and selectivity over Pt loaded Cs beta zeolite  $\gamma$ -alumina catalysts

	Conversion (mol%)		Selectivity to products (mol%)							
			C3–C4		C5–C6		<i>i</i> -C7		Toluene	
Time (min)	10	360	10	360	10	360	10	360	10	360
Catalyst										
CZP-1	90.9	89.7	58.3	61.5	12.2	9.3	25.2	23.4	5.3	4.4
CZP-2	68.8	67.8	19.3	22.6	11.8	10.3	63.0	62.7	5.8	4.3

Conditions: WHSV = 15 H<sup>-1</sup>, H<sub>2</sub>/Hc molar ratio of 6. *T* = 440 °C and *P* = 10 atm.

However, acidity level in CAP is the lowest and its products distribution differs from obtained with zeolite catalysts. Therefore, we suppose that any contribution from platinum deposited on  $\gamma$ -alumina, on the catalytic behavior in the series of tested catalyst is not significant. Moreover all catalysts were prepared from the same boehmite and any effect from  $\gamma$ -alumina acidity is equivalent to all samples.

It has been considered that catalysts of platinum supported on L zeolite, exchanged with alkaline or alkaline earth cations, represent that its acid function is inactive, being identified as monofunctional catalysts. However, for catalysts containing beta zeolite, this situation may not be established because their selectivity for skeletal isomerization and cracking, despite of alkaline cations nature [11,14,18]. In this study we also found a higher selectivity for isomerization and relatively high selectivity to cracking in our catalysts despite of the quantity of Cs, which is the cation that we supposed as the more likely to promote *n*-paraffin aromatization from previous reports [11–14].

Concerning dehydrocyclization reactions, results show higher levels for CZP-1 than for CZP-2, following a similar trend as cracking reactions, i.e. increasing with the catalyst total acidity, but in CZP-0, which is the more acidic, relatively lower selectivity is observed for the aromatization product. Results published for *n*-hexane aromatization [19] employing several zeolites, show a decrease in benzene formation with catalyst acidity increase; in other words, the acidity is relatively deleterious for dehydrocyclization reaction.

Studies performed by Sachtler and co-workers [20,21] suggested the possibility to regenerate Brønsted acid sites when reducing platinum with hydrogen, however, the extent in which this effect can be produced, has not been thoroughly studied. The partial

regeneration of Brønsted acidity could explain the fact that even with Cs excess in CZP-2 catalyst, its activity level, cracking and isomerization reactions reflect an important contribution of bifunctional mechanism. For CZP-1 (support alone) no activity is observed previous platinum incorporation. Unfortunately in pyridine adsorption FTIR spectra that we carried out, no Brønsted acid sites were detected in CZP-1 neither in CZP-2 to verify this phenomena in our tested samples.

On the other hand, platinum was found in the TEM images, forming very large particles deposited on the external surface of the zeolite crystals. A relatively poor dispersion has been reported when ionic exchange is employed in incorporating platinum, despite of thermal treatments [14,22]. It seems unlikely that particles having a size above of 0.75 nm may remain inside channels. Therefore, a further investigation is necessary to optimize the size of platinum particles in these systems.

#### 4.1. Pressure effect

Naphtha reforming process, commonly operate at hydrogen pressure between 10 and 15 atm, when using chlorided alumina supported platinum catalysts. High hydrogen pressure has an important effect when minimizing catalyst deactivation, as carbonaceous precursors compounds are hydrogenated. However, thermodynamically, pressure does not favor aromatic products formation, which require low hydrogen pressure in order to dehydrogenate the six carbons rings.

This situation may not be considered independently from the role played by catalyst within reaction. The CZP-1 catalyst having low Cs concentration and possibly acidity partial regeneration, shows an im-

portant effect with pressure. Cracking is increased resulting in a low liquid components yield. In contrast to results obtained at 2.5 kg/cm<sup>2</sup>, a slight increase in cracking products is observed at 10 kg/cm<sup>2</sup>. It seems that high hydrogen pressure favors coke precursors hydrogenation cleaning active sites. With CZP-2 catalyst, pressure has no important effect over cracking products, but it responds toward dehydrocyclization reactions in the sense expected by the thermodynamic.

## 5. Conclusions

Platinum supported on a mixture of beta zeolite/ $\gamma$ -alumina catalysts are very active in *n*-heptane reforming reaction and show selectivity to isomerization and cracking products better than to aromatization products, suggesting a bifunctional mechanism. An important effect from acidity is present on catalysts with high Cs concentration, indicating that its influence in neutralizing acidity is limited. The system behavior is more likely to be a beta zeolite supported platinum than  $\gamma$ -alumina supported platinum, in other words, we can suppose that alumina is an inert matrix in these systems.

## Acknowledgements

The TEM images were obtained at Electron Microscope Department of Nissei Sangyo America LTD., Hitachi Scientific Instruments.

## References

- [1] J.M. Grau, E.L. Jablonsky, C.L. Pieck, R.J. Verderone, J.M. Parera, *Appl. Catal.* 36 (1988) 109.
- [2] R.S. Brown, J. Matsuoka, S. Aizawa, K. Fujiwara, T. Takase, Y. Shioya, New chloride removal catalyst in CCR Unit, in: Proceedings of the Annual Meeting of NPRA 2001, 18–20 March 2001, AM-01-50.
- [3] J.R. Bernard, in: L.V.C. Rees (Ed.), Proceedings of the Fifth International Zeolite Conference, Napoli, Heyden, London, 1980, p. 686.
- [4] G.J. Jacobs, W.E. Alvarez, D.E. Resasco, *Appl. Catal. A: Gen.* 206 (2001) 267.
- [5] A.E. Schweizer, US Patent 4,992,401 (1991).
- [6] M.M.J. Treacy, *Micro. Meso. Mat.* 28 (1999) 2:271.
- [7] T.R. Hughes, W.C. Buss, P.W. Tamm, R.L. Jacobson, in: Y. Murakami, A. Ijima, J.W. Ward (Eds.), Proceedings of the 7th International Conference on Catalysis, Kodansha, Tokyo, 1986, p. 725.
- [8] J.K. Lee, H.K. Rhee, *Catal. Today* 38, 2 (1997) 235.
- [9] H.Y. Chu, M.P. Rosynek, J.H. Lunsford, *J. Catal.* 178 (1998) 352.
- [10] F. Vaudry, F. Di Renzo, F. Fajula, P. Shulz, *J. Chem. Soc., Faraday Trans.* 94 (1998) 617.
- [11] F.J. Maldonado-Hodar, M.F. Ribeiro, J.M. Silva, A.P. Antunes, F.R. Ribairo, *J. Catal.* 178 (1998) 1.
- [12] W. Zhang, P.G. Smirniotis, *Appl. Catal. A: Gen.* 168 (1998) 113.
- [13] P.G. Smirniotis, E. Ruckenstein, *J. Catal.* 140 (1993) 526.
- [14] J. Zheng, J.L. Dong, Q.H. Xu, J. Liu, A.Z. Yan, *Appl. Catal. A* 126 (1995) 141.
- [15] J.J. Carberry, *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York, 1976.
- [16] C.N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980, p. 250.
- [17] D.S. Maciver, H.H. Tobin, R.T. Barth, *J. Catal.* 2 (1963) 485.
- [18] S. Siffert, J.L. Schmitt, J. Sommer, F. Garin, *J. Catal.* 184 (1999) 19.
- [19] L.X. Dai, Y. Hashimoto, H. Tominaga, T. Tatsumi, *Catal. Lett.* 45 (1997) 107.
- [20] I.L.M. Kustov, D. Ostgard, W.M.H. Sachtler, *Catal. Lett.* 9 (1991) R.
- [21] D.J. Ostgard, L. Kustov, K.R. Poepelmeier, W.M.H. Sachtler, *J. Catal.* 133 (1992) 342.
- [22] G. Jacobs, W.E. Alvarez, D.E. Resasco, *Appl. Catal.* 206 (2001) 267.