

The kinetics of citral hydrogenation over Pd supported on clinoptilolite rich natural zeolite

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Abstract

The liquid phase hydrogenation of citral has been investigated over Pd (2.42%) supported on clinoptilolite rich natural zeolite catalyst for different reaction conditions. The zeolite support did not affect the active metal properties. This was attributed to the large size of Pd particles on the support. High selectivity (90%) to citronellal was obtained at complete conversion of citral. The catalytic activity increased with reaction temperature (80, 100, 120 °C) following an Arrhenius behaviour, while selectivity remained constant for a given conversion. Selectivity to citronellal increased from 78 to 90% with increase in the amount of catalyst in the reaction solution (Citral/Pd mole ratio 293, 176 and 105). The spent catalyst regained its fresh activity and selectivity upon regeneration.

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1. Introduction

There are numerous studies on the selective hydrogenation of α , β unsaturated aldehydes [1,2]. Within the family of aliphatic unsaturated aldehydes, the hydrogenation of citral is important in production of intermediates for perfumes, fragrances and pharmaceuticals [3,4]. Citral has three sites of hydrogenation; a conjugate double bond, a carbonyl group and an isolated double bond. The reduction of citral can lead to a variety of products (Fig. 1) [5]. First step is the reduction of either the C=O bond or the conjugated C=C bond, to produce geraniol and nerol or citronellal, respectively. Consecutive reactions lead to citronellol and finally to 3,7-dimethyloctanol. Apart from these reactions, secondary processes of cyclisation or of reaction with the solvent (ethanol) can lead to other products like isopulegol or acetals of citronellal. The most important products, from the industrial point of view, are citronellal and citronellol.

The selective hydrogenation is a challenge since the C=C bond is more easily attacked than the C=O bond when a conventional heterogeneous catalyst is used. Therefore, many studies have been pursued to develop a suitable industrial catalyst that would be able to lead to a very high selectivity at total conversion [4,6–11]. However, the effect of reaction parameters on selectivity and the catalyst regeneration for a given catalyst are rarely studied.

The final selectivity of an active metal can be modified by using an adequate support [2,7,9,12], which interacts with the metal, or by adding a second component as a promoter [13–15]. Electronic effects and geometric effects have been suggested as the explanation for the improvement in selectivity to unsaturated alcohols. Zeolite supports introduce the possibility of metal–support interactions: active metals can be polarized by nearby cations or by metal support interaction [16]. Their use as catalyst support in hydrogenation reactions is not widely investigated. Blackmond et al. [2] reported the hydrogenation of 3-methyl crotonaldehyde over Pt, Rh or Ru metals supported on zeolites (NaY, KY) and on activated carbon. They found that the selectivity to unsaturated alcohols increased when

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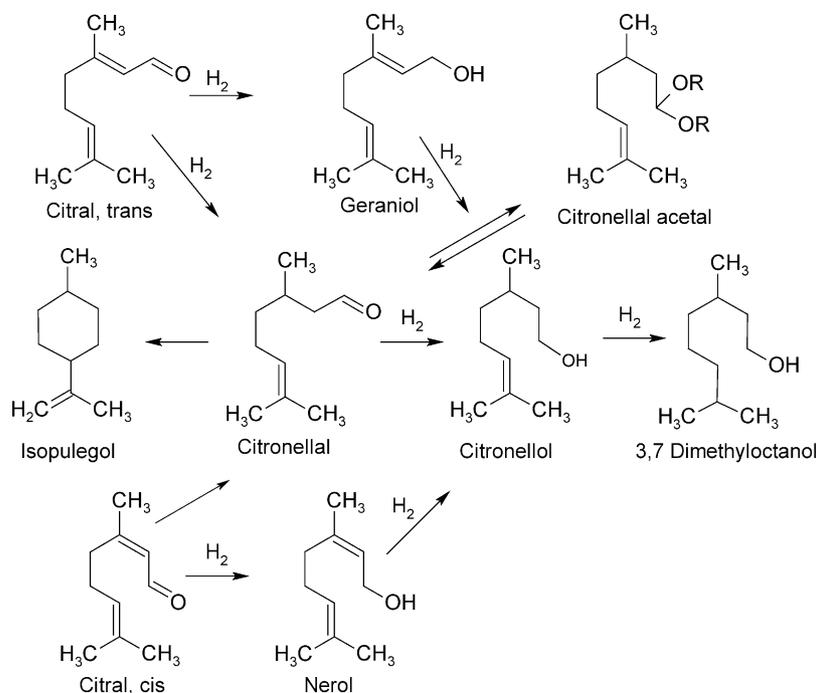


Fig. 1. Reaction scheme.

support was less acidic; the decrease in acidity results in greater electron density on the metal particles. In present study, Clinoptilolite rich natural zeolite was chosen as a catalyst support to investigate how it affects the Pd catalyst activity and selectivity. Some of the reactions catalysed by the natural clinoptilolite supported catalysts are the isomerization of linear hexane [17] oxidation of *m*-xylene [18] and the isomerization of α -pinene [19].

This work concerns the preparation and the characterisation of a Pd loaded natural zeolite rich in clinoptilolite, and the investigation of its application in citral hydrogenation. The role of support, the effects of reaction temperature and the catalyst amount on the product distribution, and the catalyst regeneration have been studied.

2. Experimental

2.1. Preparation and characterisation of catalysts

The support used in the preparation of the catalyst was natural zeolitic tuffs (Gördes-Manisa, Turkey). The zeolitic tuffs were ground and the particles having sizes between 100 and 400 mesh were taken. They were then refluxed in deionized water for 2 h and washed twice with deionized water to remove soluble impurities. This treatment was repeated twice. The washed samples were then dried overnight in an oven at 120 °C and used as a catalyst support.

Pd catalyst (Pd/NZ) was prepared by impregnation of the support with methanol solution of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Sigma, 10102-05-3). The sample was then dried overnight

at 120 °C prior to calcination under O_2 flow (200 ml/min) in a quartz tube at 430 °C for 2.5 h.

The natural zeolite and the catalyst were characterised by surface area analyser (Micromeritics ASAP 2010, nitrogen physico-sorption at 77 K), X-ray diffraction (Philips X'Pert Pro with Cu $\text{K}\alpha$ radiation), transmission electron microscope (JEOL-2000 FX), particle size analyser (Micromeritics Sedigraph 5100), elemental analyser (Varian Liberty II ICP-AES), scanning electron microscopy (Philips SFEG 30S SEM), thermal gravimetric analyser (Shimadzu TGA-51) and by differential thermal analyser (Shimadzu DTA-50).

2.2. Hydrogenation experiments

The liquid phase hydrogenation of citral was carried out in a stirred semibatch reactor (500 ml Parr reactor, 4575 Model). After transferring the calcined catalyst in to the reactor, the air inside the reactor was purged by pressurising the reactor up to 4 bar with He (99.999%) and evacuating it several times. The catalyst was reduced in situ under H_2 flow (60–80 ml/min) for 2.5 h at 400 °C. After that the reactor was allowed to cool down to the reaction temperature.

Reactant solution (200 ml of 0.1 M citral in ethanol) was degassed by sparging with high flowrate of hydrogen (99.999%) for about 15 min in a bubbling unit to remove dissolved oxygen prior to its injection into the reactor. Subsequently the reactor was pressurised to 6 bar and the stirrer was started. All reactions were conducted at 400 rpm and 6 atm, after preliminary tests showed that external mass

transfer limitations were negligible for this condition. The distribution of products was followed by repetitive sampling. The samples were analysed by gas chromatography (Shimadzu GC-17A) using a capillary column DB-225 (J&W, 30 m, 0.53 i.d.) and a flame ionisation detector. The reaction products were identified by GC–MS technique (Varian Saturn 2000). Content of individual components in the reaction mixture was determined by internal standardisation method (Cyclohexanone, Aldrich).

3. Results and discussion

3.1. Catalyst characterisation

The natural zeolite was found to contain 63.07% SiO₂, 11.81% Al₂O₃, 1.61% CaO, 0.71% Fe₂O₃, 9.81% K₂O, 0.80% MgO, 0.98% Na₂O and 10.81% H₂O. This composition gave Si/Al ratio of 5.34, which is close to the ratios reported by Breck [20] and by Tsitsishvili et al. [21] for clinoptilolite rich natural zeolites. The water content was determined from TGA analysis. The mean diameter of the catalyst particles was determined as 66 μm and their Pd loading was found as 2.42 wt.% by ICP analysis.

The XRD patterns of the purified natural zeolite, zeolite calcined at 430 °C and the catalyst are given in Fig. 2. All the samples revealed characteristic peaks of clinoptilolite at 2θ degrees of 9.93, 22.48 and 30.18°. The XRD patterns of the catalyst showed also peaks of Pd at 2θ degrees of 40.114 and 46.661°. This showed that calcination and impregnation did not destroy the crystalline structure of the clinoptilolite. This result was also confirmed by SEM and TGA analysis. In the literature, it was reported that clinoptilolite exhibits thermal stability up to 700 °C [20]. The XRD peak intensities and widths were used to estimate mineral composition of the natural zeolite according to a method given in literature [22]. Natural zeolite was acquired to contain about 90%

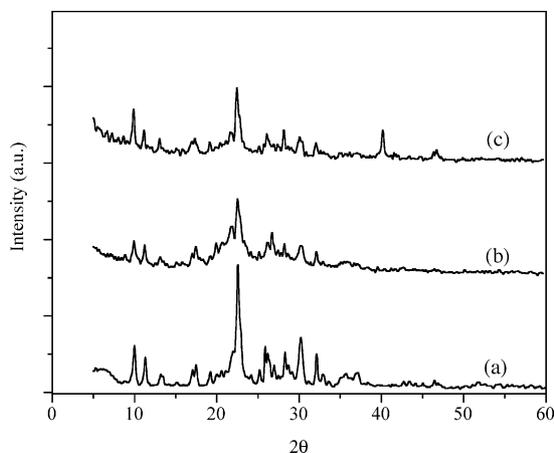


Fig. 2. X-ray diffraction patterns of: (a) natural zeolite, (b) natural zeolite calcined at 430 °C, (c) Pd/NZ catalyst.

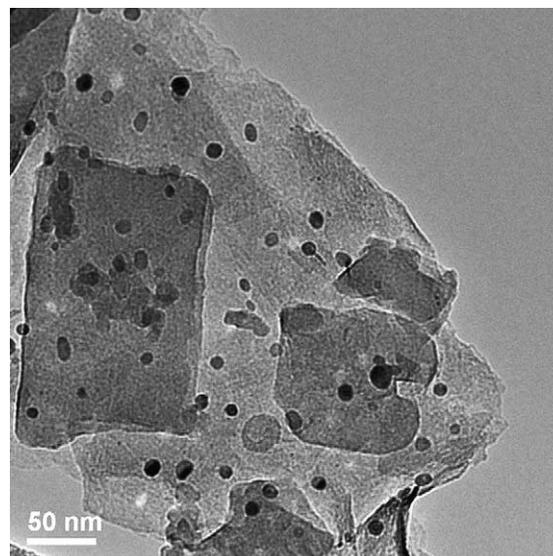


Fig. 3. TEM picture of the Pd catalyst.

clinoptilolite, 5–10% opal-CT (opal-cristobalit-tridimit), 1–2% feldspat and 1–2% quartz.

The electron micrograph of Pd catalyst is shown in Fig. 3. The Pd particles were well dispersed over the support and had a narrow size distribution. Their mean diameter was calculated as 9.4 nm. This large size of the Pd crystallite size suggested sintering of Pd particles. These particles should be exclusively localized on the outer surface of the zeolite crystallites.

The textural characteristics of the catalyst determined from nitrogen adsorption are given in Table 1. The BET surface area and pore volume was very low compared to values reported in literature for natural zeolite (299 m²/g BET surface area and 0.122 cm³/g pore volume) where water vapour adsorption was used for the characterisation [23]. The results obtained in the present study are only for comparison purposes since only pore sizes of clinoptilolite that are large enough to allow nitrogen molecules to enter the pores were determined.

3.2. Hydrogenation tests

3.2.1. Influence of catalyst support

Fig. 4 displays temporal concentration profiles of citral and the products during hydrogenation reaction. The catalyst was highly selective to citronellal. The citral concentration exhibited a sustained exponential decrease with time. The

Table 1

Textural properties of the catalyst	
BET surface area (m ² /g)	35.2
Micropore area by t-plot (m ² /g)	17.2
External surface area by t-plot (m ² /g)	18.0
Median pore diameter by Horwath–Kawazoe (Å)	7.7
Pore volume (cm ³ /g)	0.049
Average pore diameter by BJH (Å)	76.4

main products initially formed were citronellal, and its acetal derivative. The evolution with time showed more citronellal formation while acetal amount remained constant. Small amounts (<2%) of geraniol, nerol, citronellol, and isopulegol were formed. Some traces of other by products such as 3,7-dimethyloctanol, 3,7-dimethyloctanal and 3,7-dimethyl-2-octenal were also detected (not shown in the figure).

High selectivity to citronellal (82%) was obtained for an overall citral conversion of 99.5%. It was ~90% when the reaction was performed with the higher amount of catalyst (the details are given in Section 3.2.3). The selectivities established by others were 88% over Pd/SiO₂-AlPO₄ [4], 70% over Pd/SiO₂ [11] and 87.5% over Pd/polymer and 67.5% for Pd/C [8]. The effect of zeolite support was reported by Maki-Arvela et al. [9]. A low selectivity to citronellol and citronellal (36%) was obtained over zeolite supported Ni catalysts (Ni/H-Y and Ni/NH₄-Y) [9]. However, with SiO₂ or Al₂O₃ supports, Ni catalyst was found to be very selective to citronellol and citronellal (>70%). With the zeolite support, hydrogenation products underwent transformations to other side products as the reaction proceeded. The main reactions taking place were cyclisation, dehydrogenation and cracking which have been reported to occur on Brönsted and Lewis acid sites. These reactions were not observed with the catalyst used in this study. Thus, it was suggested that the acid sites in the catalyst did not modify the active metal properties.

The presence of Fe as an impurity [4,24] and the electrostatic field produced by the constituent ions (e.g., Na, K) [13] being part of the zeolite structure was reported to improve the selectivity to unsaturated alcohols. In addition, electron transfer from acid sites in the zeolite to the active metals encapsulated by the zeolites was found to suppress the hydrogenation of C=C bond and favour the hydrogenation of C=O bond [2]. However, these beneficial metal support interactions were not observed in the present study. This could be attributed to the large size of the Pd particles, so that there was not a strong interaction (electron transfer) between the large metal particles and acid sites [25].

Acetilization is an acid catalysed reaction. Aumo et al. [8] have observed very high yields of acetal over Pd/C, reaching 52%. This was attributed to the catalyst acidity induced by chloride precursor used in the catalyst preparation. However, there are studies in which a chloride free precursor was used and still the formation of acetals was observed [8,13,26]. In the present study, the use of Cl precursor was avoided. The impurities in the catalyst support [8], the acid sites in the catalyst [9] and the acidity of the ethanol were also associated with acetal formation [8,26]. Further investigation is needed to determine what caused the acetal formation.

3.2.2. Effect of reaction temperature

The product distributions changed slightly with temperature (80, 100 and 120 °C) for a given conversion (Figs. 4 and 5). In the beginning, citronellal and citronellal acetal

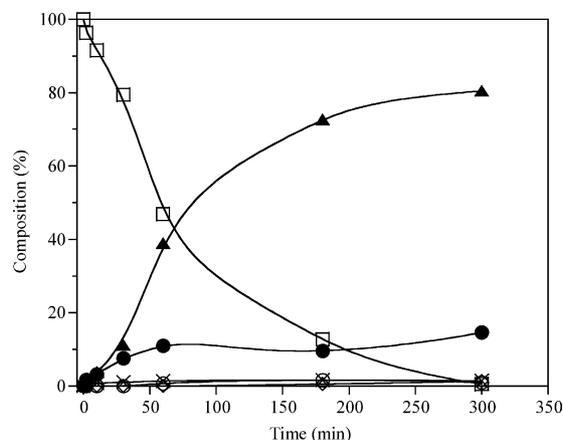


Fig. 4. Product distribution over Pd/NZ catalyst with 250 mg cat. at 80 °C. Citral (□), citronellal (▲), citronellol (◇), isopulegol (○), nerol + geraniol (×), citronellal acetal (●).

were the main products. Citronellal formation prevailed with the reaction time up to complete conversion of citral. Formation of small amounts of citronellol, geraniol and nerol was also observed. The major product was citronellal at all the temperatures studied and the maximum selectivity to citronellal was around 82%. Citronellal was converted to

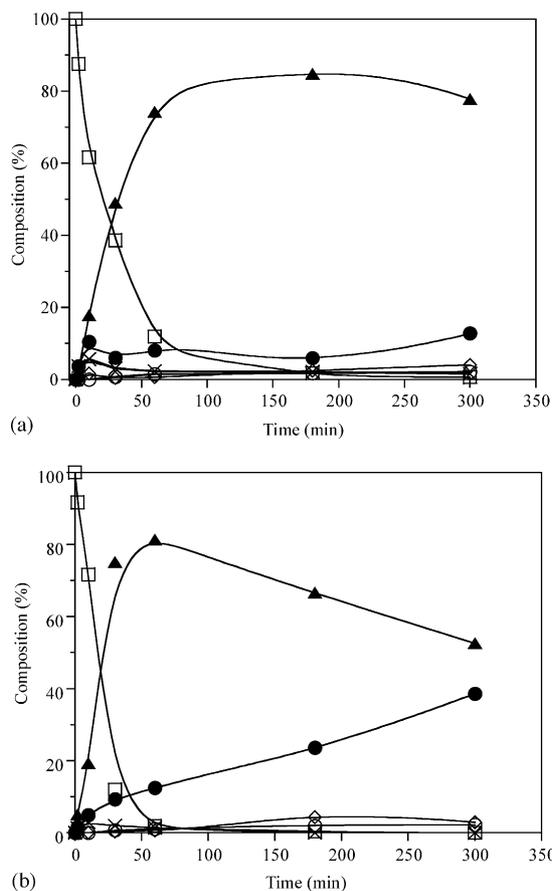


Fig. 5. Product distribution with reaction temperature for 250 mg cat.: (a) at 100 °C, (b) at 120 °C. Citral (□), citronellal (▲), citronellol (◇), isopulegol (○), nerol + geraniol (×), citronellal acetal (●).

Table 2
Initial reaction rates for different reaction conditions

Reaction temperature (°C)	Catalyst amount (mg)	Initial reaction rate (mmol/g _{Pd} s)
80	250	0.65
100	250	1.06
120	250	1.62
80	150	0.71
80	400	0.79

the citronellal acetal once all the citral was consumed. This indicated that adsorption of citronellal on to the surface was inhibited by the strong adsorption of citral.

The initial reaction rates were calculated from the slope of the linear region of the plots of conversion versus time (Table 2). The initial reaction rate increased significantly with temperature following an Arrhenius behaviour with an activation energy of 6.6 kcal/mol. This implied that the reaction was not internal diffusion limited. Internal diffusion effects were tested by applying Weisz Prater parameter. Weisz Prater parameter was calculated as 0.10 for the highest initial activity (1.62 mmol/g_{Pd} s), which assured the absence of significant internal diffusion limitations [27]. Similar effect of temperature on reaction products and initial

rates were observed by Singh and Vannice [28] over Pt/SiO₂ and Pt/TiO₂ catalysts.

3.2.3. Effect of the catalyst amount

Citral hydrogenation was performed for three different amounts of catalyst (150, 250 and 400 mg) in the reaction solution corresponding to the citral/Pd mol ratios of 293 (Fig. 6a), 176 (Fig. 4), and 105 (Fig. 6b), respectively. As the catalyst amount increased, the time needed for complete conversion of citral decreased. The initial reaction rates were almost constant for different catalyst amounts (Table 2). This reinforced that there was no transport limitation from the gas phase to the liquid phase [29]. Product distribution changed with the catalyst amount and the maximum selectivity to citronellal increased from 78 to 90% as citral/Pd ratio in the reacting solution increased. The citronellal was converted to citronellal acetal once all the citral was converted to citronellal, as observed in the other tests.

3.2.4. Catalyst re-use

The catalyst re-use was tested by recycling the catalyst used at 80 °C (spent catalyst) for another test under the same conditions without any pretreatment. The catalytic activity of the spent catalyst dropped significantly; the conversion obtained was 33% compared to 99% for the fresh catalyst. However, the spent catalyst regained its fresh activity and selectivity after it was regenerated under the same conditions used for the preparation of the fresh catalyst.

4. Conclusions

Natural zeolite supported Pd catalyst has been investigated in citral hydrogenation. The zeolite support did not modify the product distribution. The catalyst primarily hydrogenated the conjugated C=C bond and showed very poor activity for the hydrogenation of the isolated C=C and C=O bonds. The highest selectivity obtained was ~90% for citronellal at complete conversion of citral. The selectivity remained almost constant with temperature and increased with decrease in citral/Pd ratio. The spent catalyst regained its fresh activity and selectivity after being regenerated.

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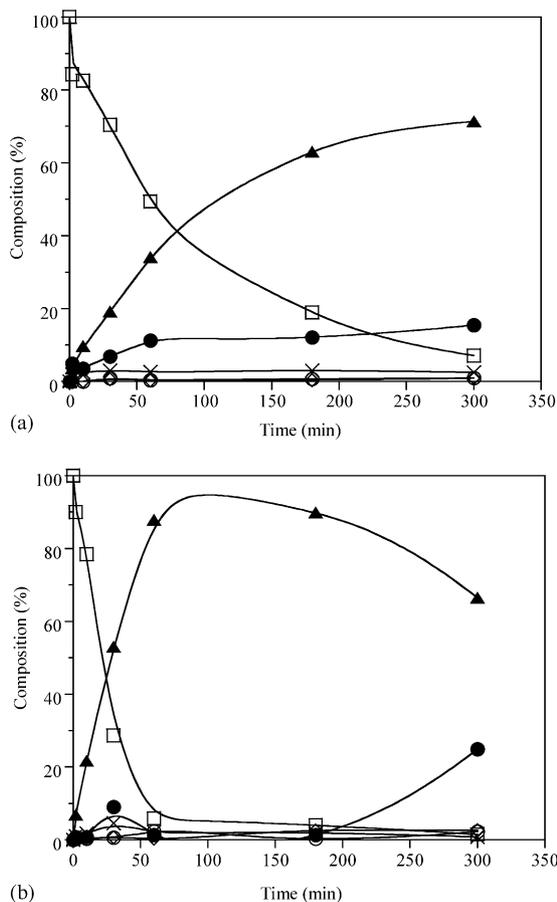


Fig. 6. Product distribution with different catalyst amounts at 80 °C, (a) 150 mg, (b) 400 mg. Citral (□), citronellal (▲), citronellol (◇), isopulegol (○), nerol + geraniol (×), citronellal acetal (●).

References

- [1] P. Gallezot, D. Richard, *Catal. Rev.-Sci. Eng.* 40 (1998) 81.
- [2] D.G. Blackmond, R. Oukaci, B. Blanc, P. Gallezot, *J. Catal.* 131 (1991) 401.
- [3] L.P. Tianen, P.M. Arvelaand, T. Salmi, *Catal. Today* 48 (1999) 57.
- [4] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, A. Porras, F.J. Urbano, *J. Catal.* 172 (1997) 46.
- [5] T. Salmi, P.M. Arvela, E. Toukonitty, A.K. Neyestanaki, L. Tainen, L. Linfords, R. Sjöholm, E. Laine, *Appl. Catal. A: Gen.* 196 (2000) 93.
- [6] J.N. Coupe, E. Jordao, M.A. Fraga, M.J. Mendes, *Appl. Catal. A: Gen.* 199 (2000) 45.
- [7] R. Malathi, R.P. Viswanath, *Appl. Catal. A: Gen.* 208 (2001) 323.
- [8] J. Aumo, J. Lilja, P. Maki-Arvela, T. Salmi, M. Sundell, H. Vainio, D.Y. Murzin, *Catal. Lett.* 84 (2002) 219.
- [9] P. Maki-Arvela, L.-P. Tainen, M. Linblad, K. Demirkan, N. Kumar, R. Sjöholm, T. Ollonqvist, J. Vayrynen, T. Salmi, D.Y. Murzin, *Appl. Catal. A: Gen.* 241 (2003) 271.
- [10] S. Galvagno, C. Milone, A. Donato, G. Neri, *Catal. Lett.* 18 (1993) 349.
- [11] U.K. Singh, M.A. Vannice, *J. Catal.* 199 (2001) 73.
- [12] U.K. Singh, M.A. Vannice, *J. Mol. Cat. A: Chem.* 163 (2000) 233.
- [13] B. Bachiller-Baeza, I. Rodrigues-Ramos, A. Guerrero-Ruiz, *Appl. Catal. A: Gen.* 205 (2001) 227.
- [14] G. Neri, L. Mercadante, C. Milone, R. Pietropaolo, S. Galvagno, *J. Mol. Catal. A: Chem.* 108 (1996) 41.
- [15] I.M.J. Vilella, S.R. Miguel, C.S.M. Lecea, A. Linares-Solano, O.A. Scelza, *Appl. Catal. A: Gen.* 281 (2005) 247.
- [16] A.P. Jansen, R.A. van Santen, *J. Phys. Chem.* 94 (1990) 6764.
- [17] K.I. Patrylak, F.M. Bobonich, Y.G. Voloshyna, M.M. Levchuk, V.M. Solomakha, L.K. Partrylak, I.A. Manza, O.M. Taranookha, *Catal. Today* 65 (2001) 129.
- [18] A. Allhaverdiev, S. Irandoust, Y.D. Murzin, *J. Catal.* 185 (1999) 352.
- [19] O. Akpolat, G. Gündüz, F. Ozkan, N. Beşgün, *Appl. Catal. A: Gen.* 265 (2004) 11.
- [20] D.W. Breck, *Zeolite Molecular Sieves*, Wiley-Interscience, 1974.
- [21] G.V. Tsitsishvili, T.G. Andronikashvili, G.N. Kirov, *Natural Zeolites*, 1st ed., Ellis Horwood Limited, New York, 1992, p. 40.
- [22] F. Esenli, I. Kumbasar, *Clays Clay Miner.* 46 (1998) 679.
- [23] F. Cakicioglu, S. Ulku, *Micropor. Mesopore. Mater.* 77 (2005) 47.
- [24] L. Mercadante, G. Neri, C. Milone, A. Donato, S. Galvagno, *J. Mol. Catal. A: Chem.* 105 (1996) 93.
- [25] P. Canizares, A. de Lucas, F. Dorado, A. Duran, I. Asencio, *Appl. Catal. A: Gen.* 169 (1998) 137.
- [26] P. Maki-Arvela, L.-P. Tainen, A.K. Neyestanaki, R. Sjöholm, T.-K. Rantakyla, E. Laine, T. Salmi, D. Yu Murzin, *Appl. Catal. A: Gen.* 237 (2002) 181.
- [27] P.B. Weisz, *Z. Phys. Chem.* 11 (1957) 1.
- [28] U.K. Singh, M.A. Vannice, *J. Catal.* 191 (2000) 165.
- [29] C.N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, Krieger Publishing Co., New York, 1981.