Catalysis Letters 15 (1992) 179–188

Effect of calcium addition on zinc aluminate spinel

M.A. Valenzuela [1,2], G. Aguilar [1], P. Bosch [2], H. Armendariz [1], P. Salas [1]
and A. Montoya [1]

[1] *Instituto Mexicano del Petróleo, Eje C. Lázaro Cárdenas 152, C.P. 07730 México, D.F., Mexico*
[2] *Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, 09340 México, D.F., Mexico*

The addition of calcium to zinc aluminate, prepared by coprecipitation methods, causes an increase in the specific surface area and a modification of the crystal morphology. However, the catalytic isobutane dehydrogenation properties remain unchanged. Careful characterization studies (XRD, TGA and SEM) indicate that calcium may be deposited on the zinc aluminate surface.

Keywords: Metallic oxide catalysts; coprecipitation of Al-Ca-Zn mixed oxide; isobutane dehydrogenation; N_2 physisorption; X-ray diffraction; thermal analysis; scanning electron microscopy

1. Introduction

Mixed oxides are physical or chemical combinations of two or more metallic oxides. As ceramics [1], catalysts [2], or electronic materials, they have found multiple applications in industry [3]. They are classified according to their framework geometries, i.e. spinels, perovskites or garnets. Their elemental composition may vary (solid solutions) or may be specifically determined by strict stoichiometric relationships [4].

Zinc aluminate spinel has been used as a catalyst and as a catalyst support [5–7]. This solid has low specific surface area, high thermal stability and is inert to water vapor. Other studies [8,9] have indicated that addition of calcium hydroaluminates has improved mechanical strength of materials and increased the specific surface area.

In the present work, the preparation of Al-Ca-Zn mixed oxides by the coprecipitation method is reported for the first time. The influence of the calcium content on the mixed oxide structure was also studied.

We employed N_2 physisorption, X-ray diffraction, thermal analysis, and scanning electron microscopy to characterize materials. Isobutane dehydrogenation was also utilized to examine the catalytic properties of the obtained solids.

2. Experimental

2.1. SAMPLE PREPARATION

Coprecipitations were performed from a mixed solution of Al, Ca, and Zn nitrates, with an initial pH of 2, through addition of a 20 wt% aqueous $(NH_4)_2CO_3$ solution until a pH of 7.5 was reached [10]. The obtained gels were dried at 110°C for 24 h and calcined in flowing air at 800°C for 8 h. The final composition of the solids is given in table 1.

2.2. CHARACTERIZATION TECHNIQUES

Chemical compositions were obtained by atomic absorption spectroscopy. The X-ray diffractograms were obtained using a D-500 Siemens diffractometer with a copper anode tube. The Cu K_α radiation was selected with a nickel filter. The specific surface areas of the samples were determined from the low temperature adsorption of nitrogen (BET method). TGA curves were measured with a TGS-2 type thermal analyzer (Perkin Elmer). The equipment was operated at a heating rate of 10°C/min in flowing air. A Jeol scanning electron microscope, equipped with Si-Li windows, was used to obtain the micrographs of the samples. The isobutane dehydrogenation reaction was performed in a conventional differential flow reactor coupled to a gas chromatograph. The reaction rate measurement was carried out at atmospheric pressure and 550°C. Feed stream of 40 ml/min was used, the composition being isobutane : helium = 1 : 1 ratio mixture and WHSV = 23 h^{-1}.

3. Results and discussion

In table 1 the chemical compositions, the specific surface areas (SA) and the pore volumes (PV) are given. Pure zinc aluminate (sample A) had a specific

Table 1
Chemical composition and textural properties of the calcined samples (800°C)

Sample	Composition (wt%)			SA (m^2/g)	PV (ml/g)
	Al_2O_3	CaO	ZnO		
A	55.6	–	44.4	20	0.15
B	56.2	2.5	41.3	36	0.19
C	56.8	4.2	39.0	51	0.24
D	57.8	8.9	33.3	65	0.21
E	60.1	17.7	22.2	85	0.12
F	64.5	35.5	–	103	0.32

surface area of 20 m^2/g, in contrast to the Al-Ca-O compound (sample F) which exhibited 103 m^2/g. If the zinc aluminate was loaded with 4.2 wt% of CaO (sample C) the specific surface area increased to 51 m^2/g. Moreover the bimodal pore size distribution, characteristic of $ZnAl_2O_4$ (sample A), became a narrow monomodal distribution centered at 50 Å, fig. 1.

Fig. 2 shows the X-ray diffraction patterns for all six materials. $ZnAl_2O_4$ was identified in zinc containing preparations. As the calcium content was increased the diffraction peaks broaden, indicating that the crystallite size diminished, in samples B through E. Even with CaO contents as high as 17.7 wt%, no CaO or any other calcium compound was detected. The diffractogram of the Al-Ca oxide (sample F), prepared under similar conditions, is shown for comparison.

Aluminum (Al^{3+}), calcium (Ca^{2+}) and zinc (Zn^{2+}) ionic radii are 0.45, 0.99 and 0.74 Å respectively. Calcium, therefore, was not expected to occupy sites in the zinc aluminate framework. If it were to substitute at a zinc position, a clear expansion of the lattice would be indicated by the cell parameters as the calcium content was increased. Hence, X-ray diffraction peaks would be shifted, as compared to a corundum (α-alumina) standard, fig. 3. As no shift in the $ZnAl_2O_4$ diffraction peaks was observed, fig. 3, the cell parameters do not vary with calcium content indicating that the calcium does not occupy sites in the $ZnAl_2O_4$ framework.

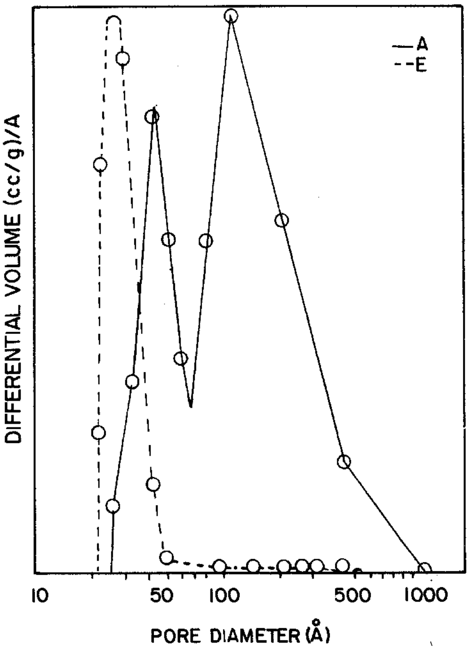


Fig. 1. Pore size distribution of (A) $ZnAl_2O_4$ and (E) Al-Ca-Zn-O samples.

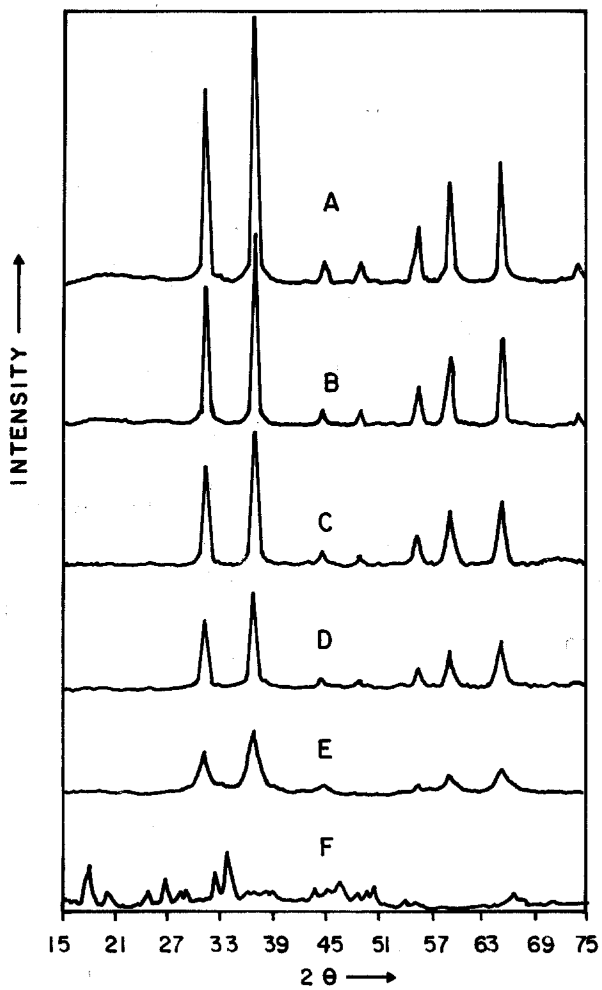


Fig. 2. X-ray diffraction patterns of the calcined samples. (A) $ZnAl_2O_4$, (B–E) Al-Ca-Zn-O, (F) Al-Ca-O.

Furthermore, the radial distribution functions of the zinc aluminate (sample A), and the 17.7 wt% Al-Ca-O compound (sample E) are identical, fig. 4. One would have expected, if small particles of calcium compounds were present, that several peaks, corresponding to the interatomic distances characteristic of these crystalline structures, would be superimposed on those of the $ZnAl_2O_4$. Even in the case of calcium present as an amorphous compound, peaks corresponding to the distances of the first and second neighbours would appear. It seems therefore, that a model having zinc aluminate with small particles, crystalline or not, of a calcium compound on its surface must be rejected. Instead, our results can be explained by the assumption of a thin calcium monolayer on the zinc

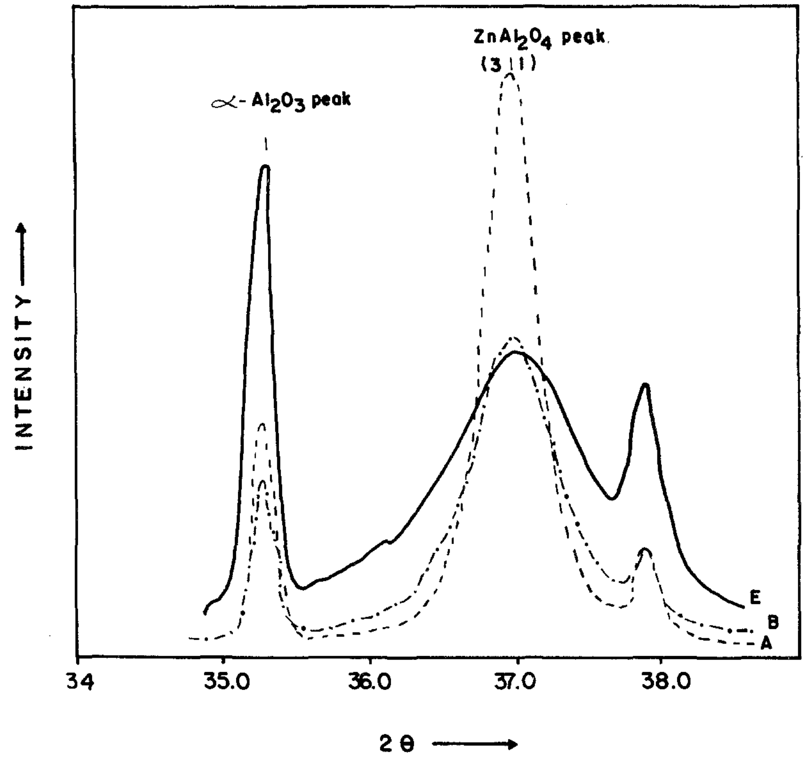


Fig. 3. X-ray diffraction patterns of (A) $ZnAl_2O_4$, (B, E) Al-Ca-Zn-O calcined samples.

aluminate surface, such that interatomic distances between calcium atoms and spinel atoms reproduce those of the pure $ZnAl_2O_4$. Such a model is similar to that proposed for Pt-Sn on alumina catalysts where tin seems to be deposited on the alumina surface (egg-shell model) [11].

Fig. 5 shows the TGA curves for $ZnAl_2O_4$ (sample A), and the mixed oxides containing 8.9 and 35.5 wt% CaO (samples D and F respectively). Note that sample F does not contain zinc and does not exhibit the zinc aluminate structure. The major weight loss is observed in the 40–500°C range corresponding to surface sorbed and coordinated water. Al-Ca-Zn-O (sample D) and Al-Ca-O (sample F) retain a large amount of water and exhibit identical thermogravimetric behavior indicating that their surfaces are very similar. This is in agreement with the previously proposed model of Al-Ca-Zn-O preparations. Furthermore, these results suggest that when small crystals are covered by calcium (samples B to E) they do not grow any more. Calcium, probably, adsorbs hydroxyls and the particles repel each other. The structure as shown by the radial distribution function is the same as the $ZnAl_2O_4$ spinel. Scanning electron micrographs of the samples are shown in fig. 6. Zinc aluminate spinel (sample A), is comprised of irregular aggregates with a broad particle size

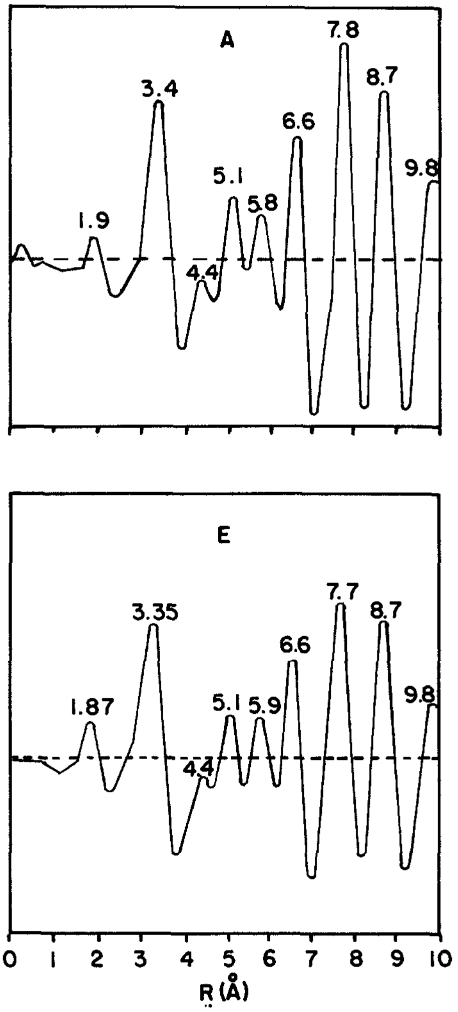


Fig. 4. Radial distribution curves of (A) $ZnAl_2O_4$, (E) Al-Ca-Zn-O samples.

distribution (1–50 μm). The Al-Ca-Zn-O coprecipitated solids (samples B and E) showed smaller uniform aggregates 1–5 μm in size. The Al-Ca-O preparation had a different morphology with aggregates that were irregular and compressed.

Finally, activity and selectivity to isobutene results for isobutane dehydrogenation are reported in table 2. All surfaces were catalytically equivalent for this reaction. At 550°C activity was very similar, although a maximum is found for sample C. Selectivity did not vary with calcium content. Calcium addition does not modify the nature nor the acidity of dehydrogenation active sites, the calcium layer is, indeed, very thin. Isobutane dehydrogenation over inert packing material (pyrex bed) resulted in no reaction up to 500°C.

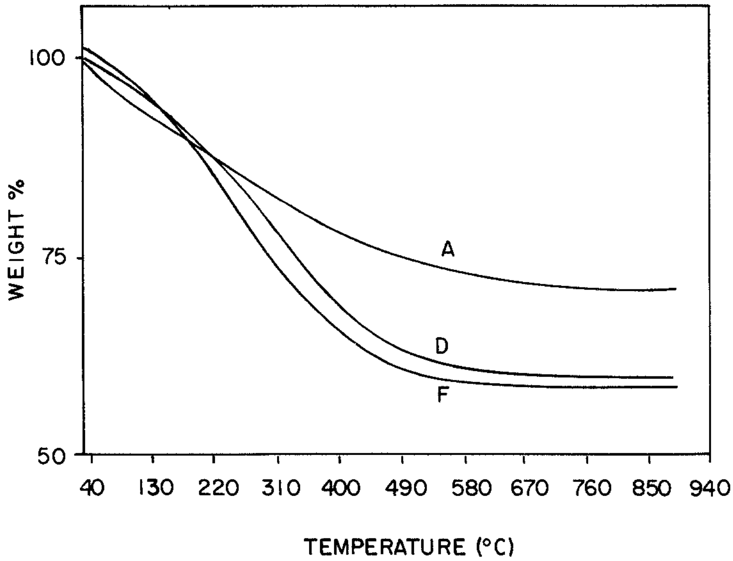


Fig. 5. Thermogravic analysis of (A) $ZnAl_2O_4$, (D) Al-Ca-Zn-O, (F) Al-Ca-O samples.

4. Conclusions

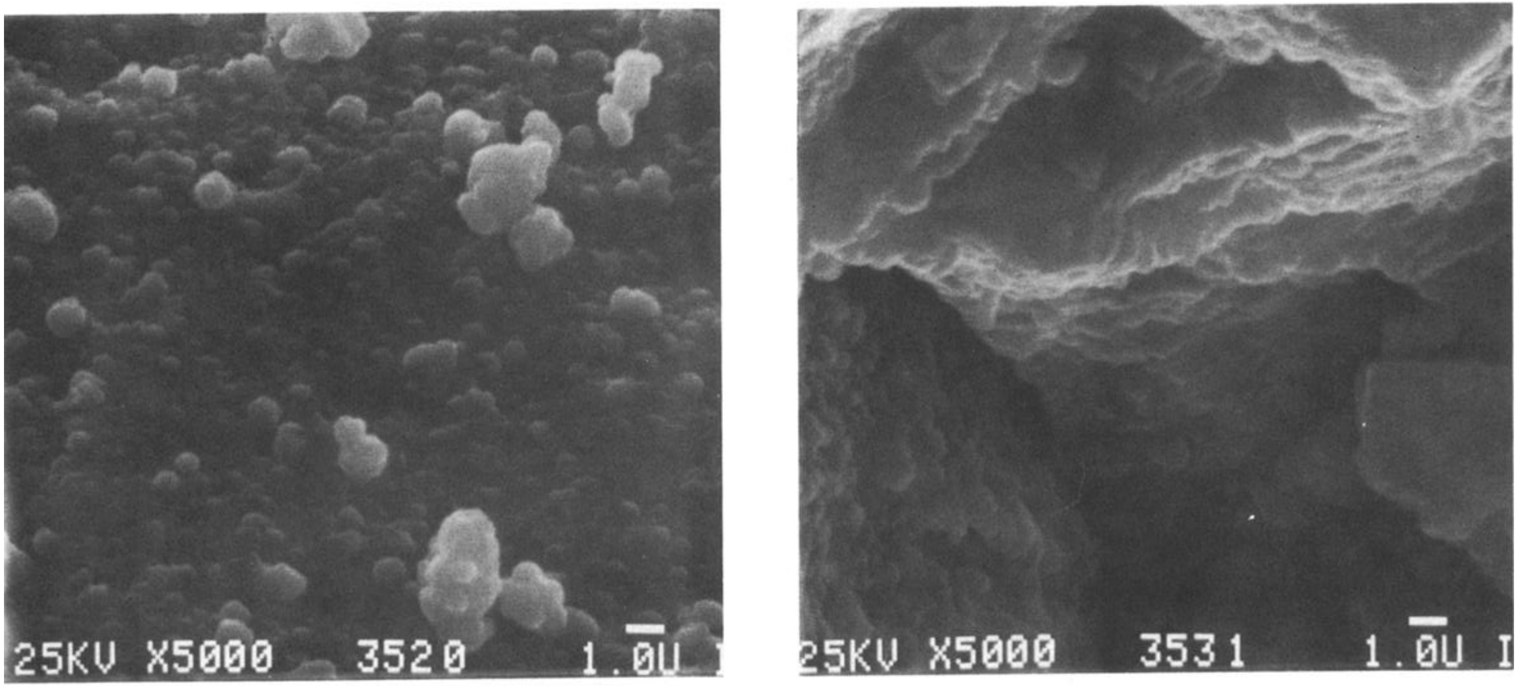
The coprecipitation of $ZnAl_2O_4$ with calcium oxide enhanced the specific surface area of the zinc aluminate. The pore size distribution was monomodal and centered at 50 Å diameter. The materials were reproducible; they consist of small particles whose core is $ZnAl_2O_4$ and whose surface is covered by calcium.

It seems that, as soon as small $ZnAl_2O_4$ spinel particles precipitate, they are covered by calcium. This calcium layer adsorbs, probably, hydroxyls and the particles, then, repel each other, no further sintering or particle growth is observed.

However, the catalytic properties were not modified by calcium. The nature nor the acidity of the dehydrogenation sites were altered. Hence, this calcium modified spinel should be useful to prepare metal supported catalysts. The metal dispersion, as the surface area value is high, should be improved.

Acknowledgement

PB thanks Victor Hugo Lara for his technical work in X-ray diffraction measurements. MV thanks Emma Garcia Figueroa for her work to obtain the SEM images.



(E)

(F)

Fig. 6. SEM images. (A) $ZnAl_2O_4$, (B–E) Al-Ca-Zn-O and (F) Al-Ca-O calcined samples.

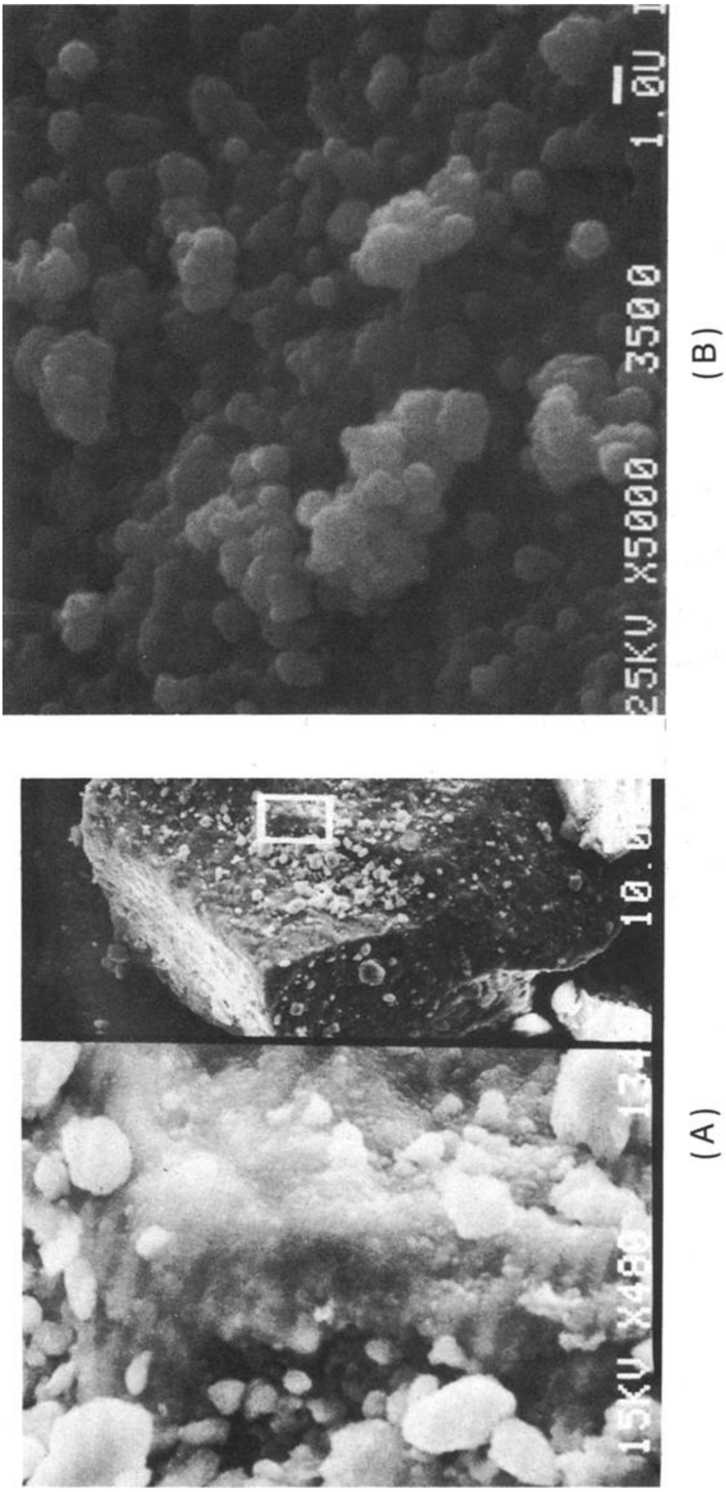


Fig. 6 (continued).

Table 2
Catalytic activity in isobutane dehydrogenation ($T = 550°C$, $iC_4/He = 1$, WHSV = 23)

Sample	Activity (10^6 mol/g s)	Selectivity (mol%)
A	6.7	57
B	6.7	57
C	8.5	59
D	7.2	57
E	6.9	60
F	6.6	57

References

[1] J. Jimenez-Becerril, P. Bosch and S. Bulbulian, J. Nucl. Mat. 185 (1991) 304.

[2] P. Bosch, A. Montoya, I. Schifter and J.M. Dominguez, J. Mol. Catal. 54 (1989) 263.

[3] Tecno-Japan 23 (1990) 15.

[4] P. Courty and C. Marcilly, *Preparation of Catalysts* (Elsevier, Amsterdam, 1976) p. 119.

[5] A. Kiennemann, H. Idriss, J.P. Hindermann, J.C. Lavalley, A. Vallet, P. Chaumette and P. Courty, Appl. Catal. 59 (1990) 165.

[6] G.P. Chernyuk, L.I. Chelyadin and Y.S. Mazurenko, Neftekhimiya 16 (1976) 683.

[7] M.E. Olbrich and J.H. Kolts, *AICHE Spring Nat. Meet.*, New Orleans, April 6–10 1986.

[8] E.Z. Golosman, V.I. Yakerson, I.A. Mamaeva and F.H. Boerskaya, Kinet. Catal. 17 (1976) 392.

[9] A.L. Klyachko, G.I. Kapustin, M.I. Dashevskii, E.Z. Golosman, V.I. Yakerson and A.M. Rubinshtein, Kinet. Catal. 20 (1979) 996.

[10] M.A. Valenzuela, G. Aguilar, P. Salas, H. Armendariz, R. Silva and G. Del Toro, *12th Iberoamerican Symposium on Catalysis* (1990) p. 455.

[11] S.R. Adkins and B.H. Davis, J. Catal. 89 (1984) 371.