DOMINANT ROLES OF TOTAL ACIDITY AND SULFATES DENSITY DETERMINING SULFATED ZIRCONIA CATALYST EFFICIENCY

Aleksandra ZARUBICA,[a,b*] Paula PUTANOV[c] and Goran BOSKOVIC[a]

[a]Faculty of Technology, University of Novi Sad, Blvd. Cara Lazara 1, 21000 Novi Sad, Serbia
[b]Faculty of Natural Sciences and Mathematics, University of Nis, Visegradska 33, 18000 Nis, Serbia
[c]Serbian Academy of Sciences and Arts, Knez Mihailova 10, 11000 Belgrade, Serbia

Sulfated zirconia catalysts are obtained from sulfated hydroxide, hydroxide and nitrate by the appropriate methods. Differences in properties of precursors and the applied calcination temperature induce various content of residual sulfate after calcinations considerably influencing total acidity of samples. Activity and selectivity of the catalysts are complex synergistic functions of the content of sulfates and related surface properties accompanying with the fraction of the tetragonal crystal phase, where total acidity and density of sulfates act as dominant factors. The best catalytic performances obtained in the case of the application of the catalysts originated from commercial sulfated zirconium-hydroxide and zirconium-oxynitrate were reached at the highest reaction temperature of 350ºC previously calcined at the lowest calcination temperature of 500ºC in the preparation procedure. The catalyst obtained from zirconium-hydroxide is characterized with the lowest amount of residual sulfates, thus resulted in inferior surface characteristics; consequently, its activity is the poorest.

INTRODUCTION

Strong legislative restrictions eliminated harmful substances that are, at the same time, characterized with high octane number (ON) from gasoline, and made the production of motor gasoline as a challenging task for refineries. Hydro-isomerization of straight C_5-C_7 paraffins producing high-ON components for gasoline blending is one possibility to solve ON-issue.[1] The reaction requires a bifunctional catalyst: a noble metal on an acidic support, *i.e.* chlorided alumina or zeolites. The former, however, faces environmental and expenses drawbacks, while the latter, although proved resistance to impurities, does not satisfy due to relatively low activity.[2] Therefore, an important challenge is to develop a new environmental friendly and active catalyst for the near future.

Solid acids like sulfated zirconia (SZ) are potential candidates for isomerization of light alkanes.[3] Zirconia modified with sulfates exhibits superior catalytic activity. The presence of sulfates increases stability of zirconia as well as a content of the most active tetragonal crystal phase.[4] Generally speaking, properties of SZ depend on the preparation method (type of precursor) and also an activation procedure.[5,6] Although a number on the methods and various zirconium compounds have been suggested for the preparation of SZ, still, there is no consensus in correlation of SZ activity with quality and content of sulfates as well as surface and structural properties.

In the present paper, series of the SZ catalysts were synthesized from different precursors by the appropriate preparation methods followed by the calcinations at different temperatures. Their catalytic activities were measured in the isomerization of *n*-hexane as the model reaction and results were correlated with surface and structural properties.

* Corresponding author: zarubica2000@yahoo.com

RESULTS

Specific surface area, volume fraction of zirconia crystal phases, content of remaining sulfates after calcination and surface density of sulfates are given in Table 1 for catalysts of different origin. Catalysts of the SZ-C and SZ-N series calcined at 500 or 600°C have values of the BET surface area above 100 m^2/g. On the contrary, samples of the SZ-H series show values of the BET surface area below 90 m^2/g.

Table 1

Specific surface area, crystal phase composition, content of remaining sulfates,
density of sulfates and pK$_a$ values in dependence on the catalyst origin and the temperature of calcination

Sample	Surface area (m^2/g)	Volume fraction of tetragonal / monoclinic phases (%)	Remaining sulfates after calcination (%)	Sulfates density per nm^2 of surface	pK$_a$
SZ-C-5	130	100	4.6	2.23	pKa < 0.8
SZ-C-6	103	93.3 / 6.7	3.9	2.38	3.3 > pK$_a$ ≥ 0.8
SZ-C-7	69	48.3 / 51.7	2.0	1.81	pK$_a$ > 3.3
SZ-H-5	82	100	2.2	1.72	3.3 > pK$_a$ » 0.8
SZ-H-6	68	71.9 / 28.1	2.3	2.12	3.3 > pK$_a$ » 0.8
SZ-H-7	67	27.3 / 72.7	1.8	1.69	3.3 » pK$_a$ »» 0.8
SZ-N-5	144	100	5.0	2.19	3.3 > pK$_a$ ≥ 0.8
SZ-N-6	117	80.3 / 19.7	3.7	1.96	3.3 ≥ pK$_a$ » 0.8
SZ-N-7	89	37.5 / 62.5	2.6	1.83	3.3 » pK$_a$ »» 0.8

Volume fraction of crystal phases of all the samples calcined at 500°C, presented in Table 1, showed the presence of only tetragonal zirconia phase, while the increase of the calcination temperatures resulted in the appearance of tetragonal and monoclinic crystal phases in different ratios. The last prevail in catalysts pretreated at the highest temperature, *i.e.* 700°C ranging from 51.7% to 72.7% in dependence on the concrete catalyst origin.

Table 2

Initial catalyst activity and selectivity data as a function
of the precursor and both the calcination and the reaction temperatures

Sample	Conversion of *n*-hexane (%) / Selectivity to *i*-C$_6$ (%)		
	200 ºC	300 ºC	350 ºC
SZ-C-5	14.0 / 45.8	50.4 / 19.7	79.2 / 18.7
SZ-C-6	13.8 / 35.7	22.1 / 13.6	57.9 / 2.3
SZ-C-7	0	0	0
SZ-H-5	0	3.3 / 90.0	0
SZ-H-6	4.4 / 66.4	11.5 / 17.1	16.8 / 5.1
SZ-H-7	0	3.7 / 61.3	0
SZ-N-5	20.0 / 12.3	40.0 / 22.4	63.5 / 15.0
SZ-N-6	4.1 / 37.6	10.5 / 34.3	14.0 / 21.5
SZ-N-7	3.8 / 62.9	8.5 / 42.1	10.4 / 21.4

Catalyst SZ-C-5 exhibits maximal initial activities among all the catalysts at three applied reaction temperatures, Table 2. Selectivity to *i*-C$_6$ of the catalyst SZ-C-5 is substantial, all together resulting in the highest isomer yield, Table 2 and Figure 1. After exposure to calcination at 600°C, the catalyst sample from SZ-C series shows a preferential activity being almost two orders of magnitude greater at reaction temperature of 300°C comparing to other two catalysts samples of different origin calcined at the same temperature. There is no registered activity when catalyst

sample SZ-C-7 was tested regardless of the applied reaction temperature.

All the catalysts of the SZ-H series show relatively low catalytic activity, with the exception of the catalyst SZ-H-6, which demonstrates acceptable activities, even higher than in the case of the catalyst SZ-N-6, Table 2.

The catalyst sample calcined at 500ºC of the SZ-N series revealed comparable catalytic performances to those from commercially sulfated precursor (SZ-C). The most favorable calcination and reaction temperatures were the same for these catalytic series, *i.e.* 500 and 350ºC, respectively, what resulted with the highest isomer yield inside the actual catalytic series, given in Figure 1.
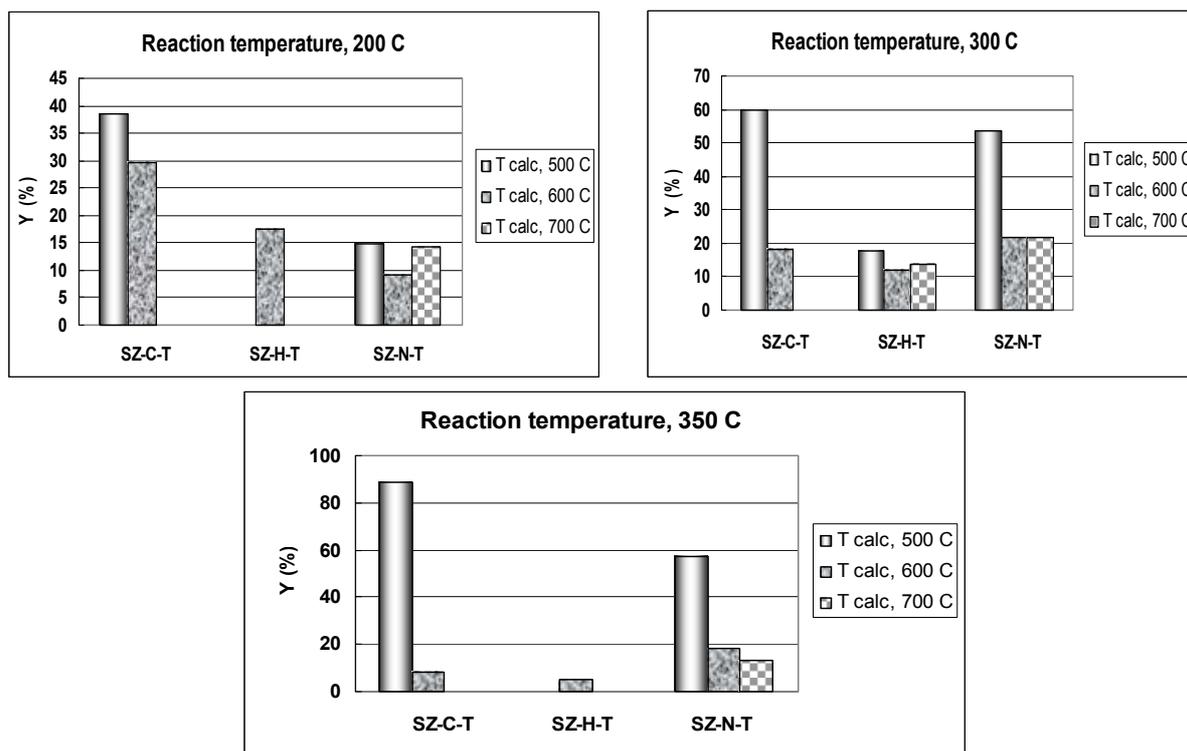

Fig. 1 – Initial yield performances of catalysts SZ-C, SZ-H and SZ-N
as a function of both the calcination and the reaction temperatures.

DISCUSSION

All the catalyst samples of the series SZ-C and SZ-N calcined at two lower temperatures have high BET surface areas, greater than usually reported in the literature for SZ with the same temperature history.[7,8] Samples of the series SZ-H maintain low surface area, regardless of the temperature pretreatment altitude, as it was previously stated,[9] Table 1.

The SZ-H catalyst is characterized with the most unfavorable crystal phase structure at the elevated calcination temperatures, having the lowest fraction of tetragonal phase among all the catalysts, Table 1. At the same time, this catalyst exhibited the lowest initial conversion, Table 2. In contrast, the prevailing crystal phase structure of SZ synthesized on the basis of two other precursors (SZ-C and SZ-N) demonstrates values, which more favorably affected their activity in the reaction of *n*-hexane isomerization.

Comparing surface, textural and structural properties of catalysts, Table 1, with their catalytic efficiency, Table 2 and Figure 1, some correlations might be imposed. Firstly, it is obvious that there is the direct proportion between the fraction of the tetragonal zirconia phase in samples and their activity. Secondly, the amount of sulfates remained upon calcination of samples can be correlated with the catalytic efficiency. Even more, it seems that a critical minimal density of sulfates on SZ surface is responsible for the catalytic activity. Thirdly, a total acidity plays the vital role determining the catalytic efficiency.

The present FTIR spectra of fresh samples give valuable data concerning acidic centers of catalysts

and their nature, Figure 2. In the O-H stretching region (3300-3800 cm^{-1}), only catalysts SZ-C-5 and SZ-N-5 show a two-band pattern. The main broad band having maximum at about 3450 cm^{-1} comes from acidic OH groups, while a tail-band at higher frequency (3630 cm^{-1}) corresponds to OH groups of the highest acidity.[10] This FTIR two-band pattern is already established as exclusive characteristic of the zirconia tetragonal crystal phase.[10] This claim is consistent with the present XRD results, Table 1, that showed the presence of only tetragonal phase in the mentioned samples (SZ-C-5 and SZ-N-5) being consenquently the most active ones.

Besides, in the S=O stretching region (1340-1440 cm^{-1}), the samples of catalysts from series SZ-C-T and SZ-N-T calcined at the lowest temperature, show a transmittance band having more or less typical maximum at about 1400 cm^{-1}, Figure 2. The broadening of this band (SZ-C-5) and a shift to low frequency side (SZ-N-5) might be caused by a surface heterogeneity reflected also in unequal dispersion of acid sites on the surface of catalysts. Higher frequency component of this band in the S=O stretching region is assigned to pyrosulfates groups.[10] It is known from previously reported catalytic tests for isomerisation reaction that conversion of *n*-butane depends on an amount of these pyrosulfates groups.[11] In the present results, catalysts that exhibited the best efficiency had pyrosulfates groups as active acidic centers..
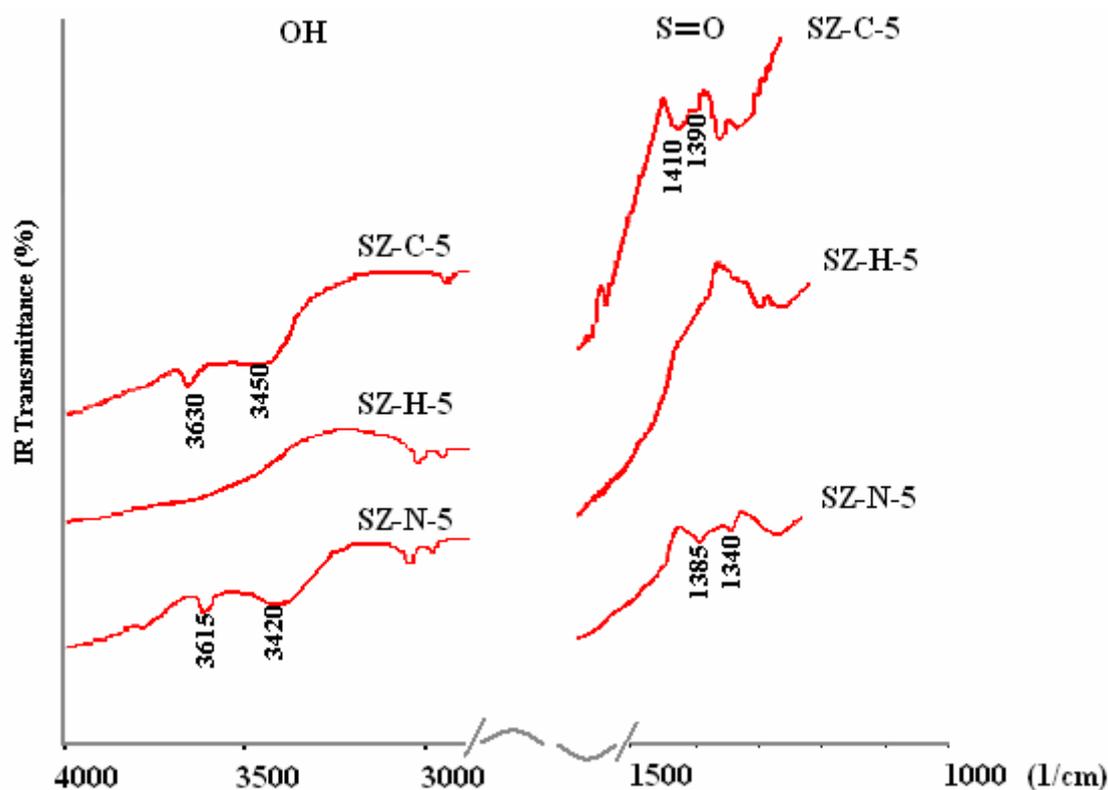

Fig. 2 – FTIR spectra of sulfated zirconias in the OH (left side) and sulfate stretching region (right) depending on the catalyst origin.

Both of these groups, Figure 2, are absent in the SZ-H-5 catalyst, which is therefore distinguished by the worst catalytic efficiency.

All the mentioned properties of the catalysts do not play independent roles but acting together determine the corresponding final catalytic features. The presented activity results comprised experiments performed in He as carrier gas, while no activity was observed using H$_2$, Table 2. The reaction tests were carried out for as long as activities were recorded. In the absence of hydrogen, *i.e.* autoregeneration conditions, a fast deactivation occurs due to the coke accumulation that was reported in the preceding articles.[9,12] Active catalysts exhibited the initial activities already after 5 min of the time-on-stream (TOS),

and the TOS varied from 30 to 120 min depending on the tested catalyst.[12]

The most favorable catalytic efficiency achieved in the case of the catalyst SZ-C-5 among all the catalysts samples can be explained by the highest total acidity ($pK_a < 0.8$) and density of sulfates, Table 1 and Figure 1. Besides, the restricted presence of pyrosulfates groups attached to tetragonal crystal phase contributed the catalyst to be quite active, Figure 2 and Table 2. The surface density of sulfates is highly influenced by textural properties of the catalyst, *i.e.* heterogeneity of surface. In addition to the other features, this catalyst is characterized with great S_{BET} and the best porosity structure.

The reason for beneficial activity of the catalyst SZ-C-6 is not only a high total acidity but also a high dispersion of sulfates groups as active centers. An exposure of the catalyst SZ-C-X to both, higher calcination and reaction temperatures, *i.e.* 600ºC and 350ºC, respectively, reduced the yield of isomers, Figure 1. The maximal achieved conversion of the catalyst SZ-C-6 is even 58%, Table 2, but the yield performance is rather low due to a very low selectivity.

No activity in the case of the catalyst SZ-C-7 is somewhat curious and speaks of a complexity of the active phase formation in SZ catalysts. Namely, the lowest total acidity ($pK_a > 3.3$) and relatively low density of sulfates caused by low specific surface area have the dominant negative impact on the catalytic activity, no matter what the beneficial structural properties were. However, our finding is completely opposite to the opinion of other authors reported that tetragonal crystal phase is main factor influencing catalytic activity.[13]

The previously described poor catalytic performance of the catalyst SZ-H series, Table 2 and Figure 1, is in line with low amount of remained sulfates and resulted surface properties, which are mainly in the region of low total acidity, Table 1. The registered catalytic performance of the sample SZ-H-6 can be explained by the highest density of sulfates in the SZ-H series compensating unfavorable fraction of the tetragonal crystal phase. Therefore, this is additional evidence of our conclusion that structural benefit is not the unique or major factor determining catalytic activity. As the result, the activity of the catalyst SZ-H-6, as well as the yield of isomers, Figure 1, are relatively acceptable, but still almost a half of the yield reached in the case of the most favorable sample SZ-C-6 in the group of the catalysts calcined at 600ºC.

Positive catalytic performance of the catalysts of SZ-N series, the authors elucidated by the significant content of remaining sulfates after calcination, the presence of pyrosulfates in the case of the SZ-N-5 catalyst as addition to the other valuable physical-chemical features. The advantageous behavior of the catalyst pretreated at the highest temperature (SZ-N-7) comparing to the corresponding samples of other series might be related to higher total acidity and density of sulfates, Table 1, resulted from greater amount of sulfates remained after calcination.

The picture of the product distribution is similar in the case of all the tested catalysts, regardless of their origin, showing a lack of highly desirable di-branched isomers, *i.e.* 2,2- and 2,3-dimethyl-butanes. The major products are methyl-pentanes, while the abundance of the cracked products (including i-C_4 and i-C_5) possibly originated from the reaction mechanism over carbonium ion[12,14] attached to the catalyst, which could also act as acidic center.[15]

EXPERIMENTAL

Catalysts preparation and methods for characterization

Three types of SZ catalysts were prepared from materials of different origin applying the appropriate steps required to obtain the particular sample in the sequence of synthesis. The following precursors were used: sulfated zirconium-hydroxide, SO_4-$Zr(OH)_4$ (Aldrich); zirconium-hydroxide, $Zr(OH)_4$ (97%, Aldrich) and zirconium-oxynitrate, $ZrO(NO_3)_2 \cdot xH_2O$ (Aldrich), all leading to catalysts SZ-C, SZ-H and SZ-N, respectively. Different steps were carried out for each sample, like calcination for the first catalyst, sulfation and calcination for the second, and precipitation (with 25% NH_4OH), followed by sulfation of the obtained hydroxide and its calcination in order to get the third catalyst series. The sulfation was realized by wet-impregnation using 0.5M H_2SO_4 for the intended content of sulfates (4 mas.%). The subsequent calcination was performed at different temperatures for 3 h in the synthetic air flow of 25 cm^3/min. Consequently, total of nine SZ-catalyst samples were obtained, denoted as: SZ-C-T, SZ-H-T or SZ-N-T, where T (T = 5, 6 or 7) stands for the applied calcination temperature: 500, 600 or 700ºC, respectively.

Specific surface area was investigated by the BET procedure following low temperature N_2 adsorption on Micromeritics ASAP 2010 apparatus. X-ray diffraction analysis (XRD) (Philips APD-1700 diffractometer with Cu-anticathode and monochromator) was used for determination of the zirconia crystal structure. The remaining content of sulfates upon calcination was measured by thermogravimetric analysis (TG) on a Baehr STA 503 instrument in the dynamic air conditions. The density of sulfates was calculated using the obtained TG results and values of the S_{BET}, while related acidic properties were evaluated by the color changes of Hammett indicators covering the range of pKa values from +3.3 to +0.8. The nature of sulfates groups was studied by Fourier transformed infrared spectrophotometry by means of Thermo Nicolet Nexus 670 FTIR spectrophotometer.

Catalysts activity measurements

The isomerization of *n*-hexane was used as the test reaction to probe activity and selectivity of catalysts. The reaction conditions were as follows: 200-350°C, atmospheric pressure, the molar ratio of carrier gas He/H_2 and *n*-C_6 was 15.5 at the constant partial pressure of *n*-C_6 of 60.5 mbar, and modified space velocity (MSV) $6 \cdot 10^{-2}$ mmol *n*-C_6/g_{cat}·min. As a rule 0.5 g of a fresh catalyst sample was loaded into the quartz microreactor and *in situ* activated at 500°C for 1 h in the synthetic air flow of 20 cm^3/min by-passing the saturator. The reaction products were on-line separated on the 30 m long PONA GC-capillary column and analyzed by gas chromatograph (GC-HP 5890, Series II) equipped with a FID detector. The activity of catalyst was classified as the conversion of *n*-hexane normalized by the number of C-atoms of the products. The selectivity of catalyst was calculated as the sum of mono-branched and di-branched C_6-isomers. Finally, the yield of the isomers was calculated as the multiplication of the conversion, selectivity data and MSV value.

CONCLUSIONS

Highly active pyrosulfates groups are limitedly presented in the SZ catalysts based on the commercially sulfated zirconia and oxynitrate. This finding is linked with the nature of precursor, its porosity structure and the performed method of sulfation. Different density of sulfates originated from the heterogeneity of the surface, is also influenced by the history of precursor and the method of synthesis, *i.e.* incipient wetness technique by sulfuric acid in the present study. In addition to the previous conclusion, a variety of removal of sulfates depended on a mechanism of their incorporation and linkage into zirconia matrix. The catalytic efficiency can be dominantly ascribed to both the total acidity and dispersion of acid sites with different acidic strength despite the positive status of the other physical-chemical properties of the catalytic material.

REFERENCES

1. I.E. Maxwell, J.E.Naber and K.P. De Jong, *Appl. Catal. A: General.*, **1994**, *113,* 153-173.
2. G. Boskovic, R. Micic, P. Pavlovic and P. Putanov, *Catal. Today.*, **2001**, *65,* 123-128.
3. T. Yamaguchi, *Appl. Catal. A: General.*, **2001,** *222,* 237-246.
4. J.M. Parera, *Catal. Today.,* **1992,** *15,* 481-490.
5. G.D. Yadav and J.J. Nair, *Micropor. & Mesopor. Mater.,* **1999,** *33,* 1-48.
6. A. Corma, J.M. Serra and A. Chica, *Catal. Today.*, **2003**, *81*, 495-506.
7. M. Benaissa, J.G. Santiesteban, G. Diaz, C.D. Chang and M. Jose-Yacaman, *J. Catal.,* **1996,** *161,* 694-703.
8. K. Fottinger, G. Kinger and H. Vinek H, *Appl. Catal. A: General.*, **2004**, *226*, 195-202.
9. A.R. Zarubica, M.N. Miljkovic, E.E. Kiss and G.C. Boskovic, *React. Kinet. Catal. Lett.,* **2007**, *90,* 145-150.
10. O.V. Manoilova, R. Olindo, C.O. Areán and J.A. Lercher, *Catal.Comm.*, **2007**, *8*, 865-870.
11. X. Li, K. Nagaoka, L.J. Simon, R. Olindo and J.A. Lercher, *J. Catal.*, **2005**, *232*, 456-466.
12. A. Zarubica, P. Putanov and G. Boskovic, *J. Serb. Chem. Soc.,* **2007**, *72*, 679-686.
13. M. Signoretto, F. Pinna, G. Strukul, G. Cerrato and C. Morterra, *Catal. Lett.,* **1996**, *36*, 129-133.
14. P.A. Jacobs and J.A. Martens, "Introduction to Zeolite Science and Practice", Elsevier Amsterdam, *Stud. Surf. Sci. Catal.*, **1991,** *58,* 445-450.
15. T. Buchholz, U. Wild, M. Muhler, G. Resofszki and Z. Paál, *Appl. Catal. A: General*, **1999**, *189*, 225-236.