ISOMERIZATION OF N-BUTANE OVER Fe, Fe-Mn AND Ni PROMOTED SULFATED ZIRCONIA

E.A. GARCIA[†], M.A. VOLPE[‡], M.L. FERREIRA [‡] and E.H. RUEDA[†]

[†]*Dpto. de Química UNS, Avda Alem 1253-8000 Bahía Blanca-República Argentina*
ehrueda@criba.edu.ar
[‡] *PLAPIQUI - (UNS-CONICET) - Camino La Carrindanga Km 7 - CC 717, 8000 - Bahía Blanca - República Argentina*

Abstract—— The isomerization of n-butane was performed over Ni, Fe and Fe-Mn sulfated zirconia. Two preparation methods were employed differing in the sequence of promotion /sulfation steps. At 473K, for both preparation methods, Ni containing samples were the most active. The samples firstly promoted with Fe and Fe-Mn and subsequently sulfated were more active than the similar catalysts for which the promotion was carried out upon sulfation; a close contact between the promoter species and sulfate groups would be the origin of the enhanced activity. At 373 K, an induction period was observed. TPR results indicated that no loss of sulfur takes places and that a sintering of metal promoter species occurs during reaction. The deactivation of samples would be related to coke formation and the blocking of anion vacancies of the zirconia.

Keywords—**n-butane isomerization; promoted sulfated zirconia;**

I. INTRODUCTION

Sulfated zirconia (SZ) catalysts are potential substitutes to harmful acids such as HF, H_2SO_4 and chlorinated alumina used in the industrial process of n-butane isomerization. The activity of SZ was generally explained mainly on the basis of super-acidity (Corma and Martínez*, 1993)*. However, now it is generally accepted that the activity of SZ can be ascribed to a redox mechanism, which initiates n-butane isomerization (Chen *et al.*, 1993; Fărcaşiu *et al*, 1996; Mishra *et al.*, 2001).

The isomerization of n-butane over SZ is carried out at low temperature (293-473 K) to avoid the n-butane hydrogenolysis, thermodynamically favored at high temperatures. No high conversion has been obtained, since the reaction is kinetically restricted.

Transition metal promoted SZ has been reported to be more active for the isomerization of n-butane than the unpromoted SZ (Hsu *et al.* 1992; Jatia *et al.,* 1994; Adeeva e*t al.* 1995; Tabora and Davis*,* 1995; Coelho *et al.,* 1995). Different arguments have been invoked in order to explain such an improvement: i) an increase of the acid strength of the system and the creation of new catalytic sites (Hsu *et al.* 1992; Cheung and Gates, 1998; Lin and Hsu, 1992). ii) the formation of an un-saturated intermediate on redox active sites associated to the metals (Adeeva *et al.,* 1995; Tabora and Davis, 1995; Coelho *et al.*, 1995; Yamamoto *et al*., 1999; Wan *et al., 1996)*. iii) a non catalytic role of the metals as initiators of the reaction (Lange *et al. ,* 1996).

Wan *et al.* (1996) have proposed that a bifunctional mechanism is taking place on a redox metallic site close to an acid site. The interpretation of the catalytic results based on the existence of sites of different nature (redox and acid sites) has also been suggested (Rezgui, *et al.* 1998; Yamaguchi, 2001).

An induction period, followed by a rapid deactivation has been observed (Coelho *et al.,* 1996; Cheung *et al.,* 1995; Sayari *et al.,* 1997; Moreno and Poncelet, 2001; Hong *et al.,* 1999). It has been established that the surface concentration of the intermediates butene and carbenium ion increases and that the deactivation is related to coke formation. These authors have suggested that the deactivation could take place by a mechanism other than site blocking (Vera *et al.,* 1999).

In the present work we have studied the isomerization of n-butane to i-butane using SZ promoted with Fe, Mn and Ni. We have compared the catalytic pattern corresponding to catalysts prepared by two slightly different methods and we have tried to explain the observed differences. We have not studied nor the influence of sulfate concentration, neither the metal loading. The last parameter has been analyzed for some of us in a previous work (Garcia *et al.,* 2001) and it has been demonstrated that the best activity is achieved for a Fe and Mn loading of 1.5 and 0.7 wt % respectively. In this work we have carried out the entire catalytic tests following to the same activation treatment (calcination at 623 K), based on literature reports (Davis *et al.,* 1994; Wan *et al.*, 1996).

II. EXPERIMENTAL

A. Sample preparation

The zirconia was prepared from $Zr(OH)_4$ following the method developed by Chen *et al.* (1993). Zirconia hydroxide was synthesized by adding NH_4OH aliquots to a 0.4 M solution of $ZrOCl_2$ ($ZrOCl_2.8H_2O$ Riedel-de Haën). The solution was continuously stirred at room temperature up to pH 10.

Two promoted-SZ series were prepared in all cases following the incipient wetness method. In one case, the zirconia support was treated with H_2SO_4 2N and then, the solid was dried for 24 h at 383 K. Promotion of SZ with the metal precursors was achieved by sequential incipient wetness impregnation by using appropriate amounts of aqueous solution of $Fe(NO_3)_3$, $Mn(NO_3)_2$ and $Ni(NO_3)_2$ as to obtain 1.5 wt% of Fe, 0.5 wt% Mn and 2.0 wt% of Ni.. For the case of the double promoted samples, the support was co-impregnated with both metal aqueous solutions. For all the cases the solid/liquid relation was 0.44 mL/g. The solids were calcined at 873 K for 4 h. These samples were named as: FSZ, FMSZ and NSZ, where F, FM and N mean Fe, Fe and Mn and Ni respectively. In the other series the promoters were fixed previously to the introduction of sulfates to the system. In this case a similar preparation procedure was followed and the samples were named as SFZ, SFMZ and SNZ.

The metal loading was measured by Atomic Absorption, while the sulfate concentration was determined over the calcined samples following the LECO method.

B. Catalytic Test

The n-butane conversion was measured for all the samples in a fixed bed reactor at 473 K and, for the series previously sulfated and then promoted the n-butane conversion was also measured at 373 K. The reactive mixture was 10% butane in N_2 (certified purity by Praxair). Approximately 100 mg of sample were pretreated in *situ* with chromatographic air at 623 K for 2 h. Then the temperature was lowered at 473 K or 373 K and the reactive mixture was admitted to the reactor, flowing at 20 mL/min. The space velocity was 2.8 g of butane per gram of catalyst per hour. The composition of the mixture after reaction was measured with a chromatograph Shimadzu GC 14B provided with a Chrom PAW 40/60 Mesh column and a TCD detector connected in line with the reactor. The conversions of butane (X%) and the selectivity to i-butane (S%) were measured approximately each 4 minutes, starting the measurements after 2 min of contacting the mixture with the catalyst.

C. Temperature Programmed Reduction (TPR)

Some samples were submitted to TPR experiments. Two kind of measurements were conducted: with fresh catalysts and with spent samples, after performing the reaction for 1 h at 473 K. Measurements were performed in a classical apparatus. The sample pretreatment was a calcination at 873 K, following by a purge in Ar at the same temperature. Then, the sample was cooled down to 300 K under Ar flow. Subsequently, a 10% H_2 in Ar mixture was admitted to the TPR reactor and the sample was heated at 10 K/min while the H_2 consumption was measured.

III. RESULTS AND DISCUSSION

A. Samples previously sulfated and then promoted.

The metal loading of the samples is presented in Table 1. The sulfate concentration was similar for all the samples (3.8–4.1 wt%).

A.1. Isomerization of n-butane at 473K

The variation of conversion of butane (X%) with time at 473 K is presented in Fig.1. In Table 1, some data from Fig. 1 are reported. It can be observed that the highest activity is obtained in the initial period. Immediately, a deactivation is observed. Focusing the attention on the initial activity, we observe that the promoted samples are more active than bare SZ. Regarding promoted samples, Ni containing sample presents the highest initial conversion value.

These results are in agreement with those from Yori and Parera (1996), who have studied the title reaction at 473 K over SZ catalysts promoted with Ni, Fe and Co. By the way, the specific rate obtained for FSZ in our work is 0.2 g of butane per hour per gram of catalyst; this value is similar to that calculated from the conversion values reported by Yori and Parera for a similar sample. An agreement is also found when comparing the initial specific rate corresponding to SZ in our work with the rate of a similar sample in the above-mentioned reference (0.14 and 0.11 g of butane per hour per gram respectively).

The conversion value after 1 h of reaction is taken as the residual activity of the samples. It can be observed in Table 1 that the residual activity of promoted catalysts is lower than the corresponding to SZ. This result indicates that the deactivation phenomena are notably enhanced in the former samples. The working hypothesis are: i) the transition metal enhances the coke formation, ii) a desulfation of zirconia occurs due to the pres-
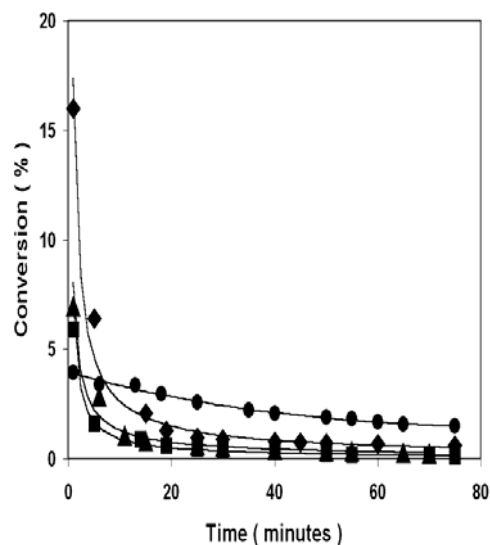

Fig. 1. Conversion of n-C_4 as a function of time at 473 K: (●) SZ; (▲)1.6% Fe, SZ; (■) 1.54% Fe, 0.76% Mn, SZ; (♦) 1.72% Ni, SZ.

Table 1: Metal loading, conversion and selectivity values at 473 K for samples previously sulfated and then promoted.

Sample	% Fe	% Mn	% Ni	X% inic[a]	X% res[b]	S%[c]
SZ$_2$	-	-	-	3.9	1.7	92
FSZ	1.6	-	-	7.0	0.3	69
NSZ	-	-	1.7	16.0	0.2	90
FSM	1.6	0.7	-	5.9	0.7	84

a) percentage of conversion measured after 1min under reaction; b) percentage of conversion measured after 30 min under reaction; c) percentage of selectivity to I-butane measured at a conversion value of 6-7% .

ence of the promoter, iii) a reduction of S^{6+} to S^{4+} is catalyzed by the promoter and, iv) the deactivation could be related with a blocking of anionic vacancies at the surface of zirconia (Vera e*t al.,* 1999).

We now come to consider the selectivity of the samples. Taking into account the selectivity measured at a conversion value of 6,7% (last column in Table 1) , the most selective catalyst is SZ.

This fact indicates that an intramolecular mechanism over sulfated zirconia takes place, as Garin *et al.* (1995) have suggested. The production of propane and pentane was mainly detected when promoted samples were used. This suggests that a bimolecular mechanism occurs over promoted samples.S% is nearly constant in time for SZ, while for the promoted samples it changes during the reaction. We have measured the dependence of %S with the i-butane conversion (Fig. 2). The residual selectivity (after 1 h of reaction) is lower than the corresponding to SZ.

A.2. Isomerization of n-butane a 373 K

The samples promoted upon their sulfation were tested at a relative low temperature, 373 K. The variation of the n-butane conversion with time on stream is shown in Fig. 3. The samples present an induction period. The increase of activity would be related to an augmentation of the surface concentration of butenes and carbenium ions (Moreno and Poncelet, 2001; Sommer *et al.,* 1997; Alvarez *et al. ,* 1997), which at the same time favor the coke precursors production. Finally the catalyst becomes deactivated.

When the highest conversions achieved by the different samples are compared, the following order of increasing activity is found: FMSZ> NSZ> FSZ.> SZ. The trend is not the same as the one observed at 473K where the most active sample was the NSZ. Since the activity of the samples results from a combination of several reactions (intra or intermolecular isomerization, coke formation, surface reconstruction, etc), the temperature governs the contribution of each of them to the overall activity.

It is interesting to note that the induction period of NSZ is longer than those of the other two promoted samples. This difference would be due to the nature of the catalytic surface of the promoters; the dehydrogenation reaction (and then the production of butenes) are catalyzed by Fe and Mn species, while the role of
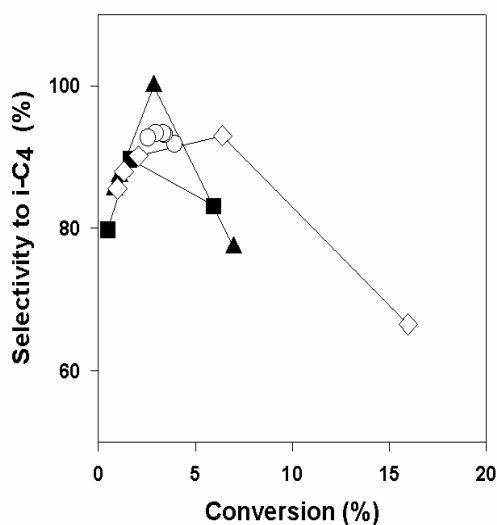

Fig. 2. Selectivity to i-C$_4$ as a function of conversion:: (●) SZ; (■)1.6% Fe, SZ; (▲) 1.54% Fe, 0.76% Mn, SZ; (♦) 1.72% Ni, SZ.
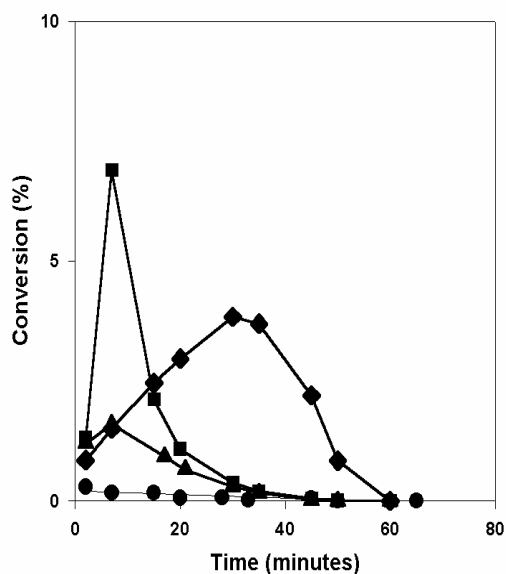

Fig. 3. Conversion of n-C$_4$ as a function of time at 373 K: (●) SZ; (▲) 1.6% Fe, SZ; (■) 1.54% Fe, 0.76% Mn, SZ; (♦)SZ 1.72% Ni.

Nickel centers (like Pt ones) is limited to the activation of hydrogen (Yori and Parera, 1995).

Regarding the residual activity, for all the promoted samples the conversion was null after 1 h of reaction. This results is similar to that obtained at 473 K, showing that at 373 K the deactivation is also very important.

Let us compare our results with those of Moreno and Poncelet (2001). The calculated specific rate of these authors for a Fe promoted sample is 0.058 g of butane per h per gram of catalyst. This value is quite similar to the specific rate measured in our work for a similar sample: 0.062 g of butane per h per gram of catalysts. In disagreement with our work, the most active sample was FSZ, instead of the double promoted FMSZ. Probably this is due to differences in the promoters loading and in the preparation methods that have been proved to be very important in the catalytic performance.

With regards to the selectivity of the samples, it was nearly constant (95-100%). Thus, the highest yield to i-butane corresponds to SFMZ sample.

B. Samples previously promoted and then sulfated.
It is important to recall that in this case the transition metal was previously introduced and in the following step the sample was treated with H_2SO_4. As it can be observed in Table 2, the concentration of the promoter was similar to the other series. These coincidences strongly suggest that there exist an equal amount of sites available for the fixation of the metal species.

B.1. Isomerization of n-butane at 473K
Considering the initial activity the order of increasing conversion is: SZ< SFMZ< SFZ< SNZ. The X % values corresponding to SFMZ and SFZ are slightly higher than the values corresponding to the analogous samples FMSZ and FSZ. In this way, while SFZ presented a conversion of 11%, the sample FSZ showed a X% value of 7%. This result is rather difficult to explain, since with both preparation methods the same contents of metals and sulfate are obtained. We suggest that the activity improvement could be due to a higher dispersion of Fe species when the sulfates are fixed upon the introduction of the promoter.

Concerning the residual conversion, the unpromoted SZ sample is more active than the rest of the catalysts.

Once more, a remarkable deactivation process occurs over the promoted samples.

The dependence of the S% on conversion have shown the same trends as in the previous series: The selectivity varies with time on stream for the promoted catalysts and the most selective sample is SNZ.

C. Characterization by Temperature Programmed Reduction (TPR)
In order to find the origin of the catalytic difference between the two series and to explain the strong deactivation of the promoted samples a TPR study was conducted over fresh and spent FMSZ, SFMZ catalysts and on the fresh NSZ sample.

The TPR profiles of the fresh samples FMSZ (a), SFMZ (b), NSZ (c) and SZ (d) are shown in Fig. 5. All the samples show a peak related to the sulfate reduction. The temperature corresponding to the peak maximum is similar for all the promoted samples (808K), while for SZ it appears at a higher temperature (860 K).
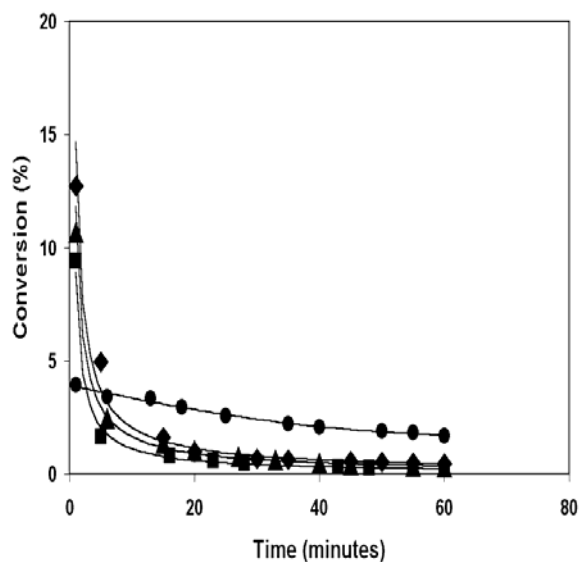

Fig. 4. Conversion of n-C_4 as a function of time at 473 K: (●) SZ; (▲) 1.6% Fe, SZ (■) 1.54% Fe, 0.76% Mn, SZ; (♦) 1.72% Ni, SZ.

Table 2. Metal loading, conversion and selectivity values at 473 K for samples first promoted and subsequently sulfated..

Sample.	% Fe	% Mn	% Ni	X%[a]	X%[b]	S%[c]
SZ	-	-	-	3.9	1.7	93
SFZ	1.7	-	-	10.7	0.3	76
SNZ	-	-	1.9	12.7	0.5	93
SFMZ	1.7	0.7	-	9.4	0.2	85

a) percentage of conversion measured after 1min under reaction; b) percentage of conversion measured after 30 min under reaction; c) percentage of selectivity to I-butane measured at a conversion value of 6-7% .
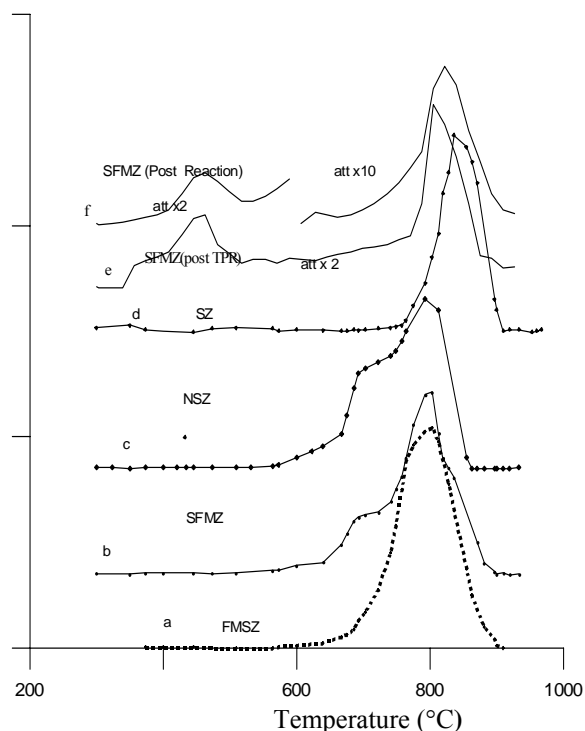
Fig. 5: TPR profiles of: a) FMSZ; b) SFMSZ; c) NSZ; d) SZ; e) 2nd TPR SFMZ; f) post reaction TPR of SFMZ. Attenuation: x10 for all the cases except for profile e) and for the first section of profile f) for which attenuation was x2

When FMSZ and SFMZ samples are compared (profile (a) and (b) respectively) the only difference is the presence of a shoulder on the low temperature side for the latter catalyst. It seems like in this sample two different sulfate species are present. We could ascribe the major consumption at 808 K to the reduction of SO_4^{2-} closely related to the zirconia meanwhile the shoulder at approximately 777 K could be associated with the reduction of a sulfate intimately associated with the promoter, perhaps iron sulfate (Garcia *et al.,* 2001; Strukul *et al.,* 1997; Alvarez *et al.,* 1996). Let us recall that in the preparation of SFMZ sample the acidification of zirconia was carried out after anchoring the promoter Fe and Mn. This sequence of impregnation would induce the formation of sulfate species in close contact to the metal promoter.

When the TPR characterization is connected with the catalytic results, which have indicated that SFMZ sample is more active than FMSZ catalyst, the straightforward conclusion is that the sulfate species closely related with the promoter is more active than the SO_4^{2-} associated to the zirconia.

The existence of certain amount of sulfate intimately associated to a promoter species is also suggested by the TPR profile of Ni containing sample (c profile in Fig. 5). The shoulder is more pronounced than in the case of SFMZ sample, and concomitantly the activity of NSZ is higher. Such Ni species could be highly dispersed NiO (Perez *et al.,* 1999). TPD NH_3 and pyridine adsorption

studies demonstrated that enhanced activity is not related to a higher acidity, but to a higher surface concentration of olefins when Ni is present, considering a bimolecular mechanism. XRD studies showed no evidence of bulk NiO, even at as high Ni loading as 5 %.

The reduction of the sulfates accomplished during the TPR experiments produces H_2S and thus originates a sulfur loss, in agreement with other studies (Xu and Sachtler, 1997; Dicko *et al.,* 1994).

The reduction of the Fe, Mn or Ni oxides was not detected in the TPR study. This result is similar to that found by Strukul et al. (1997). We could speculate that this fact indicates a high dispersion of the promoter oxide species. At this point it is interesting to observe the profile (e) in Fig. 5. This spectrum corresponds to a second TPR experiment carried out over SFMZ sample (the same batch from which the profile (b) has been obtained). Two interesting features are observed: the consumption assigned to sulfate reduction is five fold diminished and a small hydrogen consumption peak at approximately 500 K appears. The low sulfate loading in the solid would decreases the promoter-sulfate interaction, and thus the reduction of iron oxide species can be sensed. Certainly, this result does not correspond to a catalyst to be used or used in reaction, however it is indicative about the elevated iron dispersion achieved due to the high sulfate loading.

Summing up, the transition metal promoters modify the reducibility of the sulfate groups, due to a close proximity metal-sulfate. In the light of the TPR results, we suggest that a relationship between the reducibility of the sulfate and the catalytic activity for the title reaction exists. In other words, the existence of a well-dispersed phase of oxides as small particles in intimate contact with sulfate species on zirconia should be considered. After reaction, sintering and formation of higher aggregates of promoter oxides changes the TPR profiles.

The TPR profile of SFMZ after reaction at 473 K is shown in Fig. 5, profile (f). From the comparison of the spent and fresh samples (profile f and b respectively), two differences are observed: a small peak at around 500 K has appeared and the shoulder of the main peak has been eliminated in the profile of the spent sample. The consumption at 500 K would be associated to the reduction of iron oxide, indicating that sulfate-iron interaction has been lost during the reaction. Furthermore, the shoulder elimination would also be indicating that the iron-sulfate close contact has been destroyed. Regarding the main peak, associated to sulfate reduction, it is similar to the peak corresponding to the fresh catalyst (note that in both profiles b and f the attenuation was the same). This fact indicates that neither sulfate loss nor changes in sulfur oxidation state has occurred during the isomerization of butane. Then, these events are not the origin of the deactivation of the sample. This result is in agreement with Kim *et al.* (2000) who have not observed loss or migration of sulfur during the reaction.

We have not studied the coke formation. However, we have observed that the coloration of the spent samples is black, while fresh catalysts are light gray. It is worthnoting that promoted used samples are darker than used unpromoted SZ catalyst. This simple observation indicates that the coke deposition is a more extended process in promoted than over unpromoted zirconia. When the spent catalysts were submitted to a treatment in Ar at 873 K, we have observed a change in the coloration of the sample: from black to light gray, which would indicate that the deposition of carbon is eliminated at high temperature, even under inert gas flow. A similar result was obtained by other authors (Vera *et al.,* 1999) , who have established that the coke deposit can be removed by stripping with an inert gas at sufficiently high temperature. However, they have observed a reduction of SO_4^{2-} to SO_2, which was not our case. We could argue that the deactivation phenomena are related to a loss of the interaction between the metal promoter and the sulfate group and, concomitantly a diminution of promoter high dispersion takes place. Besides, it could be considered that over promoted catalysts, due to hydrogen spillover from metal promoter to sulfated zirconia surface, the formation of high amounts of olefins responsible for the anionic vacancies blocking is enhanced. This interpretation seems a sensible basis on which the marked deactivation of promoted samples can be explained.

According to this hypothesis, a pre-reduction treatment would create anion vacancies before sulfation. It seems plausible that this system would be initially the most active. Recently it has been published that pre-reduction of the bare zirconia samples (before sulfation) with H_2 increases the catalytic activity in n- butane isomerization of SZ (Vera *et al.,* 2002). A maximum rate was found at a pre-reduction temperature of 823-873 K. A TPR peak in this zone was assigned to the removal of lattice oxygen and the creation of lattice defects in bare zirconia. A weaker dependence of catalytic activity on density or kind of surface OH groups on zirconia (before sulfation) was found. In line with this, Occelli *et al.,* (2001) have found that oxidized Cu-SZ is inactive and gains its isomerization activity only after reduction in H_2. It has been proposed that the function of the Cu^0 in the reduced catalyst is to remove oxygen from the zirconia support to form CuO and oxygen-deficient Zr atoms, which initiates the isomerization reactions of n-alkanes at low temperatures.

IV. CONCLUSIONS

All the promoted samples are more active than SZ. We suggest that the close proximity of the promoter with SO_4^{2-} is related with the enhancement of activity. At 473K the promoting effect of Ni on SZ is more prominent than that corresponding to Fe and Fe-Mn. In the case of Fe containing samples, slight variation in the preparation procedures would introduces changes in the promoter dispersion and thus would modify the catalytic pattern of the samples. A strong deactivation of pro-

moted samples is observed, which is due to neither a loss of sulfur nor a S massive reduction. The deactivation is related with a loss of the strong promoter-SO_4^{2-} interaction with a prompt formation of carbonaceous deposits, probably related to changes in anionic vacancies concentration at surface.

REFERENCES

Adeeva, V., J.W. de Haan, J. Jänchen, G.D. Lei, V. Schünemann, L.J.M. van de Ven, W.M.H. Sachtler and R.A. van Santen, "Acid sites in Sulfated and Metal-Promoted Zirconium Dioxide Catalysts," *J. Catal.*, **151,** 364-372 (1995).

Alvarez, W.E., H. Liu and D.E. Resasco, "Comparison of the different promoting effects of Fe-Mn, Ni and Pt on the n-butane isomerization activity of sulfated zirconia catalysts," *Appl. Catal. A: Gen.*, **162**, 103-119 (1997).

Alvarez, W.E., H. Liu, E.A. García, E.H. Rueda, A.J. Rouco and D.E. Resasco, "n-Butane isomerization on Ni-promoted sulfated zirconia catalysts," *Studies in Surface Science and Catalysis,* **101,** 553-563 (1996).

Chen, F.R., G. Coudurier, F.J. Joly and J.C. Vedrine, "Superacid and catalytic properties of Sulfated Zirconia," *J. Catal.,* **143**, 616-626 (1993).

Cheung, T.K. and B.C. Gates, "Sulfated Zirconia and Iron- and Manganese-Promoted Sulfated Zirconia: Do they Protonate Alkanes," *Top. Catal.,* **6**, 41-47 (1998).

Cheung, T.K., J.L. D'Itri and B.C. Gates, "Low–Temperature Superacid Catalysis: Reactions of n-Butane Catalyzed by Iron-and Manganese-Promoted Sulfated Zirconia," *J. Catal.,* **151**, 464-466 (1995).

Coelho, M.A., D.E. Resasco, E.C. Sikabwe and R.L. White, "Modification of the Catalytic Properties of Sulfated Zirconia by addition of Metal Promoters," *Catal. Lett.*, **32**, 253-262 (1995).

Coelho, M.A., W.E. Alvarez, E.C. Sikabwe, R.L. White and D.E. Resasco, "Induction of Activity and Deactivation of Fe, Mn-Promoted Sulfated Zirconia Catalysts," *Catal. Today,* **28**, 415-429 (1996).

Corma, A. and Martínez, A., " Chemistry, Catalysts, and Processes for Isoparaffin -Olefin Alkylation-Actual Situation and Future-Trends," *Catal.Rev. Sci.Emg.*, **35**, 483-570 (1993).

Davis, B.H., R.A. Keogh and R. Sirinivasan, "Sulfated zirconia as a hydrocarbon conversion catalyst," *Catal. Today,* **20**, 219-256 (1994).

Dicko, A., X. Song, A. Adnot and A. Sayari, "Characterization of Platinum on Sulfated Zirconia Catalysts

by Temperature Programmed Reduction," *J. Catal.*, **150**, 254-261 (1994).

Fărcaşiu, D., A. Ghenciu and J. Qi Li*, "The Mechanism of Conversion of Saturated Hydrocarbons Catalyzed by Sulfated Metal Oxides: Reaction of Adamantane on Sulfated Zirconia," *J. Catal., 158*, 116-127 (1996).

García, E. A., E.H. Rueda and A.J. Rouco, "Sulfated zirconia catalysts promoted with Fe and Mn: Mn effect in the Fe dispersion," *Appl. Catal. A., 210*, 363-370 (2001).

Garin, F., L. Seyfried, P. Girard, G. Maire, A. Abbdulsamad and J. Sommer, "A Skeletal Rearrangement Study of Labelled Butanes on a Solid Superacid Catalyst: Sulfuric Acid Treated Zirconium Oxide," *J. Catal., 151*, 26-32 (1995).

Hong, Z., K.B. Fogash and J.A. Dumesic, "Reaction Kinetic-Behavior of Sulfated-Zirconia Catalysts for Butane Isomerization," *Catal. Today,* **51**, 269-288 (1999).

Hsu, C.Y., C.R. Heimbuch, C.T. Armes and B.C. Gates, "A Highly Active Solid Superacid Catalyst for n-Butane Isomerization: a Sulfated Oxide containing Iron, Manganese and Zirconium," *J. Chem. Soc. Chem. Commun.*, 1645-1646 (1992).

Jatia, A., C. Chang, J.D. MacLeod, T. Okubo and M.E. Davis, "ZrO$_2$ promoted with sulfate, iron and manganese: a solid superacid catalysts capable of low temperature n-butane isomerization," *Catal. Lett.*, **25**, 21-28 (1994).

Kim, S.Y, J.G. Goodwin Jr. and D. Galloway, "n-Butane isomerization on sulfated zirconia: active site heterogeneity and deactivation," *Catal. Today,* **63**, 21-32 (2000).

Lange, F.C., T.K. Cheung and B.C. Gates, "Manganese, Iron, Cobalt, Nickel and Zinc as Promoters of Sulfated Zirconia for N-Butane Isomerization," *Catal. Lett.*, **41**, 95-99 (1996).

Lin, C.H. and C.Y. Hsu, "Detection of Superacidity on Solid Superacids; a New Approach," *J. Chem. Soc. Chem. Commun.*, 1479-1480 (1992).

Mishra, H.K., A.K. Dalai, K.M. Parida and S.J. Bej, "Butane isomerization over persulfated zirconia," *Appl. Catal A: Gen., 217*, 263-273 (2001)

Moreno, J.A. and G. Poncelet, "n-Butane isomerization over transition metal-promoted sulfated zirconia catalysts: effect of metal and sulfate content," *Appl. Catal. A: Gen.*, **210**, 151-164 (2001).

Occelli, M.L., D.A. Schiraldi, A. Auroux, R. Keough and B.H. Davis, "Effects of Copper on the Activity of Sulfated Zirconia Catalysts for N-Pentane Isomerization", *Appl. Catal. A: Gen., 209*, 165-177 (2001).

Pérez, M., H. Armendáriz, J.A. Toledo, A. Vázquez, J. Navarrete, A. Montoya and A. García, "Preparation of Ni/ZrO$_2$-SO$_4^{2-}$ catalysts by incipient wetness method: effect of nickel on the isomerization of n-butane," *J. Mol. Catal. A:*, **149**, 169-178 (1999).

Rezgui, S., A. Liang, T.K. Cheung and B.C. Gates, "Methane Conversion to Ethane in the Presence of Iron-Promoted and Manganese-Promoted Sulfated Zirconia," *Catal. Lett.*, **53**, 1-2 (1998).

Sayari, A., Y. Yang and X. Song, "Hydrogen Effect on N-Butane Isomerization over Sulfated Zirconia-Based Catalysts," *J. Catal.*, **167**, 346-353 (1997).

Sommer,J., R. Jost and M. Hachoumy, "Activation of small alkanes on strong solid acids: mechanistic approaches," *Catal. Today,* **38**, 255-390 (1997).

Strukul, G., M. Signoretto, A. Minesso, F. Pinna, C. Morterra and G. Cerrato, "Low Temperature Isomerization of Butane: A Comparison between ZrO$_2$-SO$_4^{2-}$ and Fe-Mn/ZrO$_2$-SO$_4^{2-}$ Catalysts," *Abstr. Pap. Amer. Chem. Soc.*, **214**, 729-733 (1997).

Tábora, J.E. and R.J. Davis, "Structure of Fe, Mn-Promoted Sulfated Zirconia Catalyst by X-Ray and IR Absorption Spectroscopies," *J. Chem. Soc. FaradayTrans.*, **91**, 1825-1834 (1995).

Vera, C.R., C.L. Pieck, K. Shimizu, C.A. Querini and J.M. Parera, "Coking of SO$_4^{2-}$- ZrO$_2$ Catalysts During Isomerization of N-Butane and its Relation to the Reaction-Mechanism," *J. Catal.*, **187**, 39-49 (1999).

Vera, C.R., C.L. Pieck, K. Shimizu and J.M. Parera, "Tetragonal Structure, Anionic Vacancies and Catalytic Activity of SO$_4^{2-}$- ZrO$_2$ Catalysts for N-Butane Isomerization," *Appl. Catal. A: Gen.*, **230**, 137-151 (2002).

Yamaguchi T., "Alkane isomerization and acidity assessment on sulfated ZrO$_2$," *Appl. Catal.A: Gen.*, **222**, 237-246 (2001).

Yamamoto,T., T. Tanaka, S. Takenaka and S. Yoshida, "Structural Analysis of Iron and Manganese Species in Iron-and Manganese-Promoted Sulfated Zirconia," *J. Phys. Chem. B*, **103**, 2385-2393 (1999).

Yori, J.C. and J.M. Parera, "Preparation of Pt/SO$_4^{2-}$-ZrO$_2$ by incipient wetness impregnation: Infuence of the sulfur concentration in the isomerization of n-butane," *Appl. Catal. A: Gen.*, **129**, L151-L156 (1995).

Yori, J.C. and J.M. Parera, "n-Butane isomerization on metal –promoted sulfated zirconia", *Appl. Catal. A: Gen.*, **147**, 145-157 (1996)

Wan, K.T., C.B. Khouw and M.E. Davis, "Studies on the Catalytic Activity of Zirconia Promoted with Sulfate, Iron and Manganese," *J. Catal.*, **158**, 311-326 (1996).

Xu, B.Q. and W. Sachtler, "Reduction of SO$_4^{2-}$ Ions in Sulfated Zirconia Catalysts," *J. Catal.*, **167**, 224-233 (1997)