Catalysis Letters Vol. 102, Nos. 1–2, July 2005 (© 2005)
DOI: 10.1007/s10562-005-5199-1

Study of alumina-promoted $SO_4^{2-}/NiO/ZrO_2$ catalyst performance★

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Received 26 October 2004; accepted 16 February 2005

Improvement of the sulfated zirconia catalysts (SZN) was studied by adding different amounts of alumina as follows: 17.5, 29.8, 45.9, and 56wt %. Even though, alumina, is expect to promote higher specific area and increase the amount of acid sites, stability of the zirconia tetragonal phase, the active zirconia phase of the SZN catalyst isisomerization reaction was obtained for catalysts containing between 17.5, and 29.8wt % of alumina, which reflects the promotional effect of alumina. On the contrary, a strong reduction of this reaction rate is observed when higher amounts of alumina are added to the catalyst, which indicates the dilution effect of alumina.

KEY WORDS: alumina-promoted; sulfated zirconia catalyst; *n*-butane isomerization.

1. Introduction

Sulfated zirconia (SZ) as catalysts for *n*-alkanes isomerization, and alkylation is attributed to Holm and Bailey [1]. However, the first report of the SZ as an active catalyst for the conversion of butane to isobutane at low temperature (373 K) was published by Hino *et al.* [2], The lack of recognition and control of the variables affecting the catalytic activity produced serious variation of the catalytic activity [3–6]. Finally, studies on preparation methods contribute to identify, and consequently, control the catalytic activity, such as: contact time of the zirconia hydroxide with sulfuric acid, the drying and calcination time, and the temperature.

The high catalytic activity of SZ has been attributed to the superacidity, although the concept of superacid settled for Hammett's function H_o, has no the same meaning for solids than for liquid. The active centers for isomerization reaction and catalyst activity of SZ catalysts have been related to a combination of Brönsted and Lewis acid sites, as they are suppose to contribute to the concentration of surface intermediates (carbenium-like ions) during the isomerization reaction [7]. The active sites are related to a series of factors such as: (1) surface defects, (2) the presence of paramagnetic species, such as Zr^{3+} already detected by ESR technique [8], (3) the presence of the adequate crystallization phase, and (4) the crystallites sizes of the active phase. At low temperature, ZrO_2 crystallizes as a tetragonal metastable phase. Sulfation process contributes to the formation of small crystals of such phase, because transition temperature from tetragonal to monoclinic phase increases. Moreover, sulfation contributes to stabilize the catalyst at the reaction temperature (approximately 373 K) [9–11].

The catalyst activity decreases rapidly following a complex deactivation process [12]. Thus, in order to improve and maintain a high catalytic activity for a longer time, transition metals such as Fe, Mn, Ni are usually added (during the preparation process. The main effects on the catalytic activity are: (a) activation of hydrogen, (b) inhibition of coke formation and disproportionation reactions, and (c) modification of butane isomerization mechanism from monomolecular to bimolecular [13–15].The *n*-butane isomerization reaction is commonly used to evaluate the acid site density and strength of the catalyst.

Two reaction pathways (monomolecular and bimolecular) have been proposed for *n*-butane isomerization over SZ.5,12,16 However, Adeeva [17] indicated that isomerization of *n*-butane over SZ catalysts modified with other oxides occurs via an oligomeric intermediate, "an adsorbed carbenium ion", which confirms the bimolecular mechanism.

In addition, the catalytic activity of SZ catalyst could also be improved by adding small amounts of alumina [18–20]. Alumina as a catalyst diluent has been related to the improvement of catalytic activity, but also to catalyst chemical and structure modification. The primary effect is an increasing of the catalyst specific surface area. Structurally, alumina induces restrictions to the crystallite size growth, which limits the formation of large zirconia crystallites, and, at the same time, stabilizes the tetragonal crystal phase, the most active zirconia phase. Such influence on the ZrO_2 structure has

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★ This work is dedicated to the memory of Gabriel Aguilar-Rios, researcher at Instituto Mexicano del Petróleo and Professor at Instituto Politécnico Nacional. Who for more than 20 years contributed to catalysis science in Mexico.

only been reported for small amounts of Al_2O_3, 0–10wt % [19]. In this work higher amounts of alumina (17.5, 29.8, 45.9, and 56wt %) were used as diluent of the catalyst $SO4_4^{2-}/NiO/ZrO_2$. The performance of each catalyst was evaluated for the *n*-butane isomerization reaction, at 338 K, and 2.5 kg/cm^2 of pressure.

2. Experimental

2.1. Catalyst synthesis

The synthesis of the catalysts followed the classic two-steps procedure: an aqueous solution of ammonium hydroxide (J.T. Baker) (28 vol%), was added drop wise to a solution of $ZrO(NO_3)_2$ (Aldrich, 99wt %) until a pH of 9.5 was reached and a white $Zr(OH)_4$ precipitate was formed. The filtered precipitate was washed repeatedly with deionized water to a neutral pH, and dried overnight.

The SZN catalyst was prepared by adding $Ni(NO)_3*6\ H_2O$ (Aldrich, 99%) to a H_2SO_4 solution (J.T. Baker, 96 vol%) containing a fraction of precipitate $Zr(OH)_4$. The prepared sample was dried overnight at room temperature. This sample was separated and named: SZN catalyst.

Additionally, four alumina-promoted $SO_4^{2-}/NiO/ZrO_2$ catalysts were prepared by wet method, adding different amounts of boehmite (Catapal, Vista) (17.5, 29.8, 45.9, and 56wt %) to the SZN catalyst.

All samples were manually extruded to 1/8″ cylindrical particles with a peptizer (1/32 diluted HNO_3), and annealed at 948 K for 1 h in flowing air. The samples were labeled SZNA-X, were Z means zirconia, S sufate, N nickel, A alumina, and X is the alumina concentration.

2.2. Characterization techniques

The catalyst chemical composition was determined by Atomic Absorption Spectroscopy in a Perkin Elmer S-2380 apparatus. The sulfur content was determined by combustion in a LECO SC-44 apparatus. Specific surface area measurements were carried out in a Micromeritics Digisorb 2600 apparatus according to ASTM-D-3663.

X-ray diffraction patterns of the powder samples were recorded at room temperature using a CuK_α radiation Siemmens D500 diffractometer having theta–theta configuration and a graphite secondary-beam monochromator The diffraction pattern was recorded in the 20 range between 10 and 70 (20). Crystalline structures were refined with the Rietveld method, as following: a pattern is calculated from a series of structural parameters (cell, atomic coordinates, thermal motion), peak shape and width parameters (plus background, Lorentz-polarization correction), and compared to the observed data. The relative content and the crystallite size of ZrO_2 phases were determined by using the FullProf-V3.5d program [21].

The total acidity was measured by NH_3 titration in an Altamira AMI 2000 equipped with a thermal conductivity detector (TCD). Two hundred milligrams of each sample was pretreated under flowing N_2 at 773 K for 4 h. Then, the sample was cooled down to 423 K. Calibrated pulses of NH_3 were injected through a 6 port on-line valve until saturation of the sample was reached. The amount of NH_3 adsorbed by the sample was calculated by difference between the injected amount of NH_3 and the calculated amount of NH_3 from the TCD signals.

As for any oxide-bearing system, the surface activity was tested by the adsorption/desorption of pyridine vapors (py) at two temperatures: 323 and 573 K, respectively, [22]. The sample was evacuated up to 10^{-1} pa; maintained under nitrogen flow saturated with pyridine (2.14 mL/h) for 15 min. After that, the sample was outgassed at 10^{-1} Pa for 1 h at room temperature, and the infrared spectra were registered at two temperatures: 323 and 573 K. The characteristic bands of pyridine protonated by Brönsted acid sites appear at 1540 and 1640 cm^{-1}, while the bands of pyridine coordinated to Lewis acid sites appear at 1450 and 1620 cm^{-1}. From the intensity of such bands it is possible to calculate the Brönsted and Lewis acid sites of the catalyst. A 170-SX Nicolet spectrometer was used and Pyridine as probes molecule. Both, Brönsted and Lewis, can form on the surface of the catalyst; the nature and the strength of these acidic sites depend on different parameters such as: concentration of sulfates, adsorption of water, crystallite size of the zirconia active phase [4]. Moreover, the B/L ratio is affected by the increment of the temperature during its catalytic live.

2.3. Catalytic activity evaluation

The catalytic activity of solids was evaluated using *n*-butane isomerization reaction. The reaction was carried out in a stainless-steel fixed bed microreactor (7 mm of diameter, 150 mm of length) using 0.5 g powdered sample previously treated under flow air (30 cm^3/min) at 773 K for 1 h.

The operation conditions for all evaluation experiments were as follows: the *n*-butane (Matheson C.P.) flow was 2.5 mL/min, the temperature was fixed at 338 K, and the pressure at 2.5 kg/cm^2, which are below the critical conditions for the *n*-butane isomerization [23]. Under such thermal conditions, both compounds, *n*-butane and *i*-butane, are in gaseous phase, which minimizes the effects of the mass transfer with the catalyst. The reaction products were analyzed on-line in a Hewlett-Packard 5890 Gas Chromatograph equipped with a 3 m × 1/8″ packed column (Porasil C), and TCD detector. The calculated experimental error is approximately ±3%.

3. Results

Table 1 presents the physical and chemical characteristics of the catalysts. Chemical composition of all active components (ZrO_2, NiO, and SO_4) decreases as a diluting effect of the increase of the alumina concentration. Then, the ratios of ZrO_2 to NiO – about 87wt % – and ZrO_2 to SO_4 – about 7.2wt % – are conserved for all catalysts.

The total acid sites measured by TPD–NH_3 are higher for the alumina supported catalysts than for the SZN catalysts. Such result could be related to the intrinsic acidic properties of alumina. Moreover, by adding alumina, the specific area increased twice, from 99 to 199 m^2/g. However, the textural properties of the alumina supported catalysts are almost similar for all the samples, except for the SZNA-56. This last catalyst exhibits a smaller mean pore size, of 21 Å, instead of 50 Å reported for the other catalysts.

The Brönsted and Lewis acidity measured at 323 and 573 K are shown in table 2. In general, an increase in both Brönsted and Lewis acid sites were observed, except for the catalyst SZNA-17.5. The B/L ratio was maintained around 0.2 and 0.3 when the samples was outgassed at 323 K, while outgassing at 573 K the B/L ratio increased to 0.4 for the SZN and SZNA-29.5 catalysts; for the higher alumina concentration catalysts, SZNA-45.9 and SZNA-56.0, this ratio remained in 0.2 for both temperatures.

Figure 1 shows the X-ray diffraction patterns of the studied catalysts and table 3 shows the amounts of tetragonal and monoclinic zirconia phases and γ-alumina phases determined by Rietveld analysis of the diffractograms. In addition, the amount of the zirconia tetragonal phase was normalized related to the amount of the ZrO_2 of each catalyst and the results are also presented in table 3.

X-ray diffractogram of SZNA-17.5, with the lowest amount of alumina does not show the γ-alumina peaks; however, they appear when 29.8wt % or more alumina is added to the catalysts. The amount of γ-alumina refers to that crystalline alumina which apparently is not involved on the zirconia tetragonal phase stabilization; thus, the amount of the non-crystalline alumina – other than the γ-alumina – is related to the alumina involved on the stabilization of the zirconia tetragonal phase.

The ratio of this alumina versus the tetragonal phase, presented in table 3, is very similar: 0.3 for 17.5 and 29.8wt % of alumina and up to 0.5 for the highest amount of alumina, 56wt % added to the catalyst.

Figure 2 shows the conversion of *n*-butane during the isomerization reaction, at different time on stream and using each of the tested catalysts: the SZN and the SZNA-X (X = 17.5, 29.8, 45.9, and 56.0), The decay of the catalytic activity is normally described by an exponential path; although, for some of the catalysts, the evolution of the conversion data, registered within the interval 1–5 h on stream, seems to be linear. Any deviation from this behavior is related to the alumina dilution effect and the loss of sulfate groups, which affects the structure of zirconia tetragonal phase. These catalysts are already known to be very labile [2,3].

Table 4 presents the isobutane formation rate of each catalyst calculated for one hour on stream, and related to the total amount of catalyst; to the zirconia tetragonal phase, and to the catalyst active phases: ZrO_2, NiO and SO_4^{2-}. These data are plotted in figure 3 for isobutane formation with respect to the zirconia tetragonal phase, and to the catalyst active phase (ZrO_2, NiO and SO_4^{2-}). The best performance is observed for the catalyst SZNA-29.8.

The selectivity towards isobutane is improved when metals such as nickel are incorporated to sulfated zirconia catalysts [12]. However, addition of alumina apparently amends the SZN catalysts selectivity; thus, fluctuations of selectivity within the interval 1–5 h on stream are lower (from 94 to 97 mol%) when alumina is included in the catalysts composition rather than in its absence (from 88 to 94 mol%).

4. Discussion

One of the expected benefits of alumina, used as support for Ni-sulfated zirconia catalyst, is to increase the catalysts specific area, as observed in table 1; thus, for the highest amount of alumina, 56wt %, added to the SZN catalyst, the specific area increases twice the original value. Additionally, alumina contributes to increases the overall acidity. Thus, the amount of the acidic sites, measured as mmol NH_3/m^2, also shows an important increase: up to 3.5 times the value of the SZN

Table 1
Chemical composition, textural and acidic properties of the SZN and SZNA-X catalysts

Catalyst	Chemical composition, wt %				Textural properties			
	ZrO_2	NiO	SO_4	Al_2O_3	Specific area (m^2/g)	Porous lume (cm^3/g)	Mean pore diameter (Å)	Acid sites, mmol NH_3/m^2
SZN	87	1	12	–	99	0.11	46.8	2.96
SZNA-17.5	71.8	0.8	9.9	17.5	117	0.13	46.8	8.07
SZNA-29.8	61.1	0.7	8.4	29.8	133	0.18	55.9	10.38
SZNA-45.9	47.0	0.6	6.5	45.9	177	0.11	52.3	8.12
SZNA-56.0	38.2	0.5	5.3	56.0	200	0.11	21.2	7.00

Table 2
Brönsted and Lewis acid sites measured as the adsorbed pyridine, mol of py/g

Catalyst	At T = 323 K					At T = 573 K				
	Brönsted	Lewis	Total	Total mol (py/m^2)	B/L ratio	Brönsted	Lewis	Total	Total mol (py/m^2)	B/L ratio
SZN	61	195	256	2.59	0.31	12	28	40	0.40	0.43
SZNA-17.5	32	144	176	1.50	0.22	0	39	39	0.33	0.00
SZNA-29.8	69	234	303	2.28	0.29	33	84	117	0.88	0.39
SZNA-45.9	75	424	499	2.82	0.18	28	144	172	0.97	0.19
SZNA-56.0	150	541	661	3.31	0.28	27	120	147	0.74	0.23

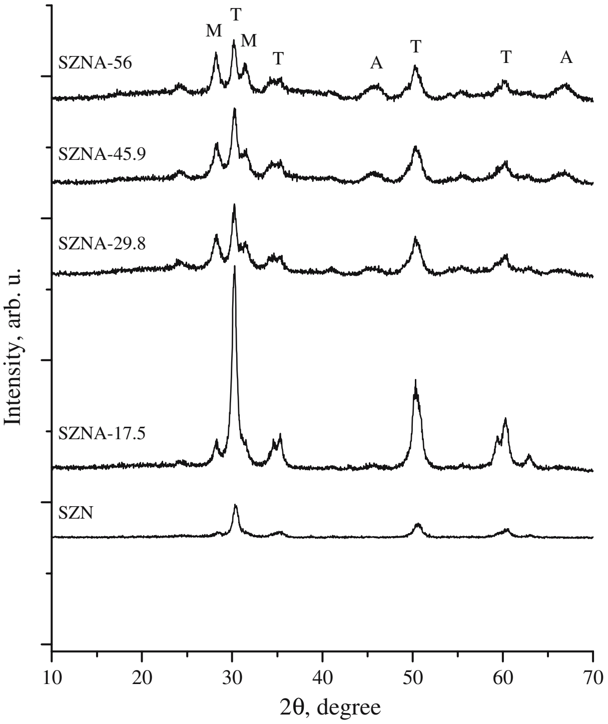

Figure 1. X-ray diffraction patterns of the catalysts evaluated in this study. (T corresponds to ZrO_2 tetragonal phase, M to ZrO_2 monoclinic phase and A to γ-alumina.)

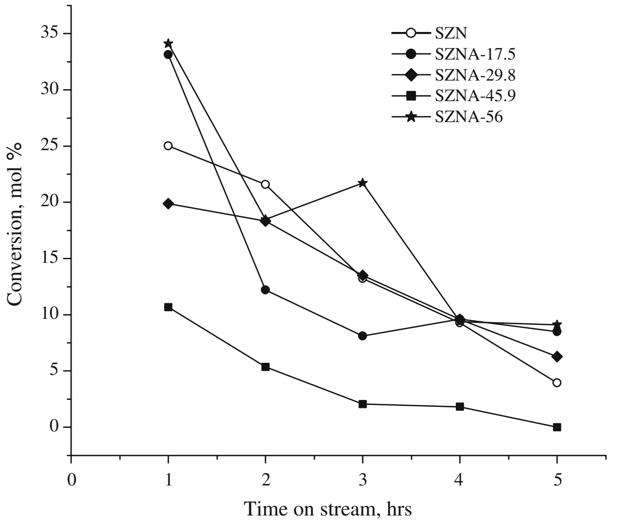

Figure 2. Conversion of *n*-butane versus time on stream for each catalyst.

catalyst; while the Lewis acid sites, measures at 373 K, also experiences a similar increase.

However, both increments are related to alumina presence, rather than to any new properties of SZN catalyst [24]. In fact, the increase in acid site density is attributed to the increase in alumina concentration, which contributes to an increase in Lewis type acid sites as shown in table 2. Nevertheless, the presence of sulfate groups on alumina surface also promotes the Brönsted acid sites formation. However, the strength of these acid sites formed on the alumina surface is not able to isomerize *n*-butane [25]. Then, no correlation between the py-acid sites and the catalysts activity was observed if the data in table 2 are revised. Nonetheless, if the variation of the *i*-butane formation rate calculated relative to catalyst active phase (ZrO_2, NiO, and SO_4^{2-}) is examined with respect to the amount of NH_3 acidic sites, an interesting relationship is observed in figure 4. The first part of the curve indicates the beneficial effect

Table 3
ZrO_2 crystal size and the amount of tetragonal, monoclinic phases and γ-alumina phases of the catalysts

Catalyst	Zirconia crystal size, (Å)		% of ZrO_2 phases		% γ-alumina	Normalized ZrO_2 tetragonal phase (wt %)	Amorphous alumina ZrO_2 tetragonal phase ratio
	Tetragonal	Monoclinic	Tetragonal	Monoclinic			
SZN	235.6	207.9	86.24	13.76	–	75.03	–
SZNA-17.5	148.4	137.0	91.63	8.37	0	65.79	0.3
SZNA-29.8	138.1	85.2	45.63	32.54	21.83	27.88	0.3
SZNA-45.9	175.0	137.0	46.12	19.77	34.11	21.68	0.5
SZNA-56.0	158.4	137.0	28.16	20.59	51.25	10.76	0.4

Table 4
Isobutane formation rate related of all catalysts and for one hour on steam

	I-butane formation rate (mol/g*s)*10^{-4}relative to:			Relative activity[a]
	Total catalyst	Zirconia tetragonal phase	Catalyst active phase (ZrO_2, NiO and SO4)	
SZN	1.806	2.407	1.806	1
SZNA-17.5	2.463	3.744	2.985	1.653
SZNA-29.8	2.391	8.576	3.406	1.886
SZNA-45.9	1.435	6.619	2.652	1.469
SZNA-56	0.771	7.165	1.752	0.970

[a] Relative activity was calculated as the ratio: isobutane formation rate of SZNA-X catalyst active phase/isobutane formation rate of SZN catalyst.

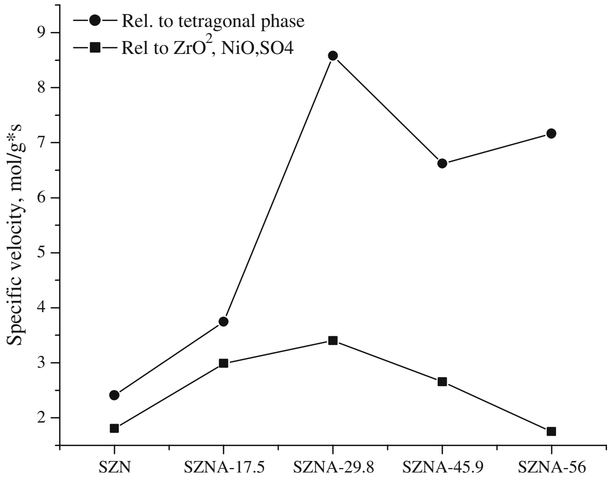

Figure 3. Variation of the isobutane formation rate with respect to zirconia tetragonal phase and the catalyst active phase (ZrO_{2-}, NiO and SO_4^{2-}).

of the alumina promotion, while increasing amounts of alumina are added to the SZN catalyst. The second part of the curve shows the effect of alumina dilution for alumina amounts higher than 29.8wt %; consequently, the specific activity decays even though the total NH_3 acidity increases. Apparently, when alumina is added to a SZN catalyst, the catalyst ability to donate a proton – the main participation of Brönsted acid sites to the reaction – should increase. *n*-Butane conversion has been related a high amount of the Brönsted sites of the superacid catalysts; B/L ratios of 1 or 0.5 were previously reported as the required condition for *n*-butane isomerization reaction [14].

However, the B/L ratios reported in table 2 are similar to those reported elsewhere for smaller amounts of alumina added to a SZ catalyst (B/L ratio of 0.27) [19]. Other researches pointed out that the enhancement of the catalytic activity following the addition of small amounts of alumina, or Ni or any other metal, to a superacid SZ catalyst is not related to any increment of the B/L ratio [14,19]. In addition, it is worth to note that our catalysts were prepared starting from a SZN catalyst with a B/L ratio of 0.31; this value is similar to that of the SZ starting material (B/L is 0.29) used in the experiments by Canton et al. [19]. Thus, for the alumina promoted SZN catalysts, some questions rise related to the benefits of such promotion on the *n*-butane conversion: are the Brönsted acid sites important for

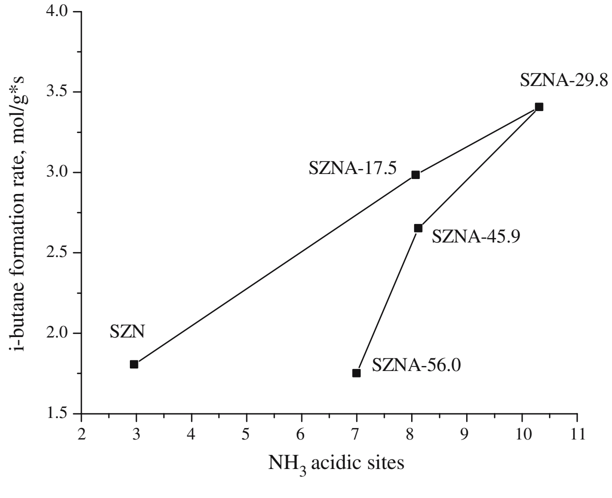

Figure 4. Variation of the *i*-butane formation rate calculated for the catalyst active phase with respect to the amount of the NH_3-acidic sites.

n-butane conversion? And also is the high acidity of catalysts synonymous of high catalytic activity? [8].

The amount of the zirconia tetragonal phase of the promoted catalyst diminishes as a consequence of dilution with alumina. The isobutane formation rate trends, shown in figure 3, show a maximum at 29.8wt % of alumina, which indicates the promotional effect of alumina; at higher amounts of alumina the dilution effect is evident from the loss of the catalytic activity (figure 4).

When the X-ray diffractogram of the SZNA-17.5 is examined, no peaks corresponding to 6γ-alumina are observed; thus, we suppose that, in this case, all alumina added to the SZN catalyst is occupied to stabilize the tetragonal phase of zirconia which explains the lack of γ-alumina in the X-ray diffractogram. Thus, the difference between alumina added to the catalysts and the γ-alumina measured by X-ray diffraction corresponds to the amorphous phase involved in the stabilization of the zirconia tetragonal phase.

The major benefit of alumina is related to the formation and stabilization of zirconia crystallites and specially the tetragonal crystal phase [19]. However, sulfate ions also participate in the formation and stabilization of the zirconia active phase. The crystallite size of the zirconia tetragonal phase apparently is related to the catalyst acidity: the smallest size corresponds to the highest amount of NH_3 acidic sites, as figure 5 shows. It is worth to note in table 3, that, the smaller crystal size of the tetragonal phase was observed for SZNA-29.8 catalyst; which explains why the SZNA-29.8 catalysts exhibits the highest *i*-butane formation rate relative to the tetragonal phase and for 1 h on stream. However, the SZNA-17.5 catalysts exhibits the best *n*-butane conversion for all the TOS's; this could be explained as the consequence of the promotional effect of alumina which gives, in this case, a more stable material.

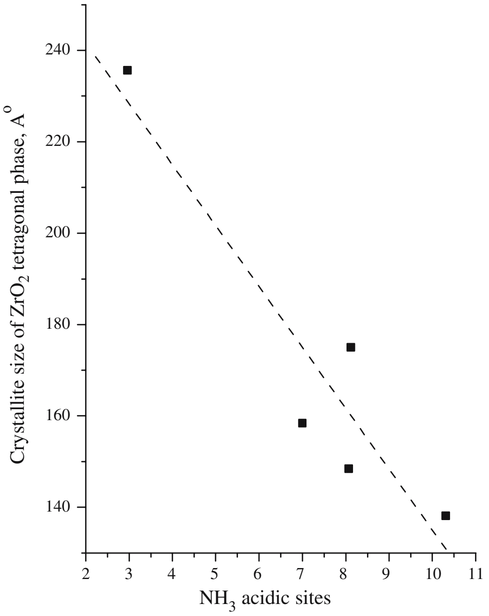

Figure 5. Relationship between crystallite size of zirconia tetragonal phase and the amount of NH_3-acidic sites.

5. Conclusions

The ZrO_2/SO_4^{2-}/NiO catalyst promoted with high amounts of alumina was evaluated for *n*-butane isomerization reaction. The catalytic performance was related to the amounts of alumina and their effects on the catalyst structure, texture, amount of acid sites and zirconia tetragonal phase. When the *i*-butane formation ratios of the catalysts are examined, the best performance is observed of SZNA-29.8 material. Thus, for catalysts containing 17.5 and 29.8wt % the added alumina promoted the catalyst properties, while more alumina only dilutes the catalyst. When alumina is used as diluent, apparently, the enhacement of the catalytic activity depends on the Zirconia tetragonal phase concentration and the size of its crystallites, both related to the amounts of total acidic sites, and sulfate ions.

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