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Silica supported superacid isomerization catalysts

V.M. Benítez, Carlos R. Vera *, C.L. Pieck, F.G. Lacamoire, J.C. Yori, J.M. Grau, J.M. Parera

INCAPE, Instituto de Investigaciones en Catálisis y Petroquímica (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

Abstract

Oxoanion promoted ZrO_2 and TiO_2 catalysts are isomerization catalysts which are usually prepared in bulk form. High activation temperatures and low sintering resistance usually yield low surface area materials. The replication of the structure of these catalysts over silica was studied in this work as a means of increasing the number of available active sites. The acid activity was assessed by means of the test of isomerization of *cis*-butene.

The dispersion of tungsten-zirconia, tungsten-titania, boron-zirconia and boron-titania over silica was accomplished by sequentially impregnating Zr and Ti organic compounds and W and B inorganic salts. Supported ZrO_2 displayed the highest sintering resistance, crystallizing at 700 °C, while supported TiO_2 crystallized at a lower temperature, 550 °C. As a consequence, only supported zirconia could match the range of activation of WO_x species (700–800 °C) and a bimodal pattern of activity was found, with maxima at 550 and 750 °C when the W-ZrO_2/SiO_2 catalyst was used in the isomerization of *cis*-butene. W-TiO_2/SiO_2 was fairly inactive.

Keywords: Supported superacids; Silica; Tungsten-zirconia; *n*-Hexane; Isomerization

1. Introduction

Due to the restrictions on the content of aromatic hydrocarbons in gasoline and the gradual banning of MTBE, isomerization of short paraffins (C_5–C_6) has become a process of growing popularity as a supplier of octane points for the gasoline pool. The installed world capacity, which was 150,000 bpd in 1980, reached 1,000,000 bpd in 1995. The isomerization unit provides an increase of 15–20 points of RON and MON to straight-run naphtha. Apart from helping to decrease the amount of benzene in gasoline, the advantages over reforming are a greater yield of isoparaffins and lower cracking losses. The skeletal isomerization of short paraffins is catalyzed by solid materials of strong acidity. The first generation of catalysts were the Friedel–Crafts catalysts (Al halogenides) but their use was inconvenient because they were highly corrosive. Nowadays, most working plants use Pt/Cl-Al_2O_3 catalysts, that have good activity and selectivity at relatively low temperatures (T_{reac} = 110–135 °C). These catalysts are however very sensitive to impurities ($S < 0.5$ ppm, $H_2O < 0.1$ ppm), they cannot be regenerated, need high investments in equipment for protecting them and require a periodic injection of chlorine to maintain their activity. Chlorine produces corrosion problems. The new commercial processes that solve these problems use zeolite catalysts (e.g. Pt/H-mordenite) or superacid, oxoanion promoted catalysts, typically Pt/SO_4^{2-}-ZrO_2 (PtSZr) [1]. The zeolites provide robustness ($S < 30$ ppm, $H_2O < 20$ ppm) and can be regenerated, but have low activity (T_{reac} = 245–275 °C). PtSZr provides a moderate level of activity (T_{reac} = 150–180 °C) and a higher tolerance to impurities than Pt/Cl-Al_2O_3. Its regeneration is however questionable due to sulfur losses during coke burn-off at high temperatures. The catalyst is permanently deactivated in the event of a temperature runaway in the presence of H_2. The replacement of PtSZr by some other superacid catalyst of higher thermal stability is currently desired. For example, Pt/WO_3-ZrO_2 (PtWZr) is more thermally stable and has a greater selectivity to isomers [2]. However, WZr has lower activity

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* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068. *E-mail address:* cvera@fiqus.unl.edu.ar (C.R. Vera).

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and specific surface than SZr (WZr = 20–40 m^2/g; SZr = 120 m^2/g).

The improvement of the textural properties of oxoanion promoted catalysts is an important issue. Sulfate and tungstate do produce a textural promotion and the promoted catalysts have a preferential presence of the tetragonal structure, while the sintering resistance and the total area are higher than those of pure zirconia [3–5]. This is true only when the calcination does not produce the decomposition of the oxoanion layer. At temperatures higher than 700 °C, sulfate decomposes and the zirconia support sinters rapidly into the monoclinic form [6]. In any case, the temperature needed for maximum activity is high and decreases the area to small values.

Additional textural promotion could be obtained by adopting different synthesis methods for the zirconia gel. Some encouraging results have been found with WZr and SZr aerogels with high initial areas obtained by supercritical drying [7,8]. Mesoporous zirconias produced by cogellation with molecular templates have also been produced [9,10] but their structure is brittle or changes after calcination at high temperatures (400–500 °C).

The synthesis of superacid catalysts based on TiO_2 and ZrO_2 supported over silica and promoted with oxoanions (tungstate and borate) is studied in this work. The dispersion of these superacids over a high specific surface area support was aimed at augmenting the number of active sites. A sequential approach was used in the preparation: (i) synthesis of ZrO_2 and TiO_2 supported on a wide pore silica (ZrSi and TiSi samples); (ii) promotion of ZrSi and TiSi with W or B; (iii) calcination of these materials in order to obtain catalytic activity of the acid function; screening of the optimum temperature with the reaction test of isomerization of *cis*-butene.

2. Experimental

2.1. Catalysts preparation

Wide pore silica (300 $m^2\ g^{-1}$, 70 Å average pore radius) was supplied by Morton Thiokol. Silica supported zirconia (ZrSi) was prepared by multistep incipient wetness impregnation of the silica support with a solution of Zr *n*-propoxide (Fluka, ~70% in *n*-propanol) in *n*-hexane (Merck, pro analysis, 99%). The solutions prepared had a maximum concentration of 1:1 (v/v) and the number of impregnation steps was adjusted in order to achieve contents of 0.5, 1.0, 1.5 and 2.0 monolayers (*M*) of ZrO_2 over silica ($M = 8$ Zr atoms nm^{-2}), corresponding to 18, 30, 39 and 46% of ZrO_2 (see Table 1). Supported titania (TiSi) was prepared in the same fashion by incipient wetness impregnation of the silica support with a solution of $TiCl_4$ (Merck, Ti^{4+} chloride for synthesis, >99%) in *n*-hexane (50:50, v/v). A list of Ti weight contents is also included in Table 1.

The (W/Zr) and the (B/Zr) molar ratios used in the preparation were chosen in accord with previous reports on the preparation of tungsten-zirconia and boron-zirconia bulk catalysts and correspond to the ratios that produce the maximum activity in acid catalyzed reactions [11,12]. Tungsten in an amount sufficient to produce catalysts with a molar ratio $W/(W + Zr) = 0.07$ was deposited by successive impregnation to incipient wetness from an aqueous solution of ammonium metatungstate hydrate, $(NH_4)_6(H_2W_{12}O_{40})\cdot nH_2O$ (Fluka, purum, >85% WO_3) in a concentration of (1/10) its solubility limit (1 g in 10 ml, 20 °C). Boron was deposited by successive impregnations to incipient wetness from a boric acid solution adjusted to pH 10 with NH_4OH (Merck, pro analysis, 25% solution) and

Table 1
Zr and Ti contents of the silica supported ZrSi and TiSi samples

Catalysts	Content[a] (*M*)	Content (mass%)	
		Zr and Ti	ZrO_2 and TiO_2
ZrSi	0.5	15	18
	1.0	25	30
	1.5	33	39
	2.0	39	46
TiSi	0.5	11	14
	1.0	19	25
	1.5	25	33
	2.0	30	40

$W_{ZrO_2} = W_{SiO_2} \times S_g \times M \times \delta_{ZrO_2} \times \mathrm{MW}_{ZrO_2}$
$W_{Zr} = W_{ZrO_2} \times \mathrm{MW}_{Zr}/\mathrm{MW}_{ZrO_2}$

ZrO_2 monolayer surface density $= \delta_{ZrO_2} = 8\,\mathrm{Zr\,nm^{-2}}$
$\mathrm{MW}_{ZrO_2} = 123.22\,\mathrm{g\,mol^{-1}}$
$\mathrm{MW}_{Zr} = 91.22\,\mathrm{g\,mol^{-1}}$
$\%\mathrm{Zr} = W_{Zr} \times 100/(W_{SiO_2} + W_{ZrO_2})$
$\%\mathrm{ZrO_2} = W_{ZrO_2} \times 100/(W_{SiO_2} + W_{ZrO_2})$

$W_{TiO_2} = W_{SiO_2} \times S_g \times M \times \delta_{TiO_2} \times \mathrm{MW}_{TiO_2}$
$W_{Ti} = W_{TiO_2} \times \mathrm{MW}_{Ti}/\mathrm{MW}_{TiO_2}$

TiO_2 monolayer surface density $= \delta_{TiO_2} = 10.5\,\mathrm{Ti\,nm^{-2}}$
$\mathrm{MW}_{TiO_2} = 123.22\,\mathrm{g\,mol^{-1}}$
$\mathrm{MW}_{Ti} = 91.22\,\mathrm{g\,mol^{-1}}$
$\%\mathrm{Ti} = W_{Ti} \times 100/(W_{SiO_2} + W_{TiO_2})$
$\%\mathrm{TiO_2} = W_{TiO_2} \times 100/(W_{SiO_2} + W_{TiO_2})$

[a] $M = 1$ monolayer.

with a concentration equal to (1/10) its solubility limit (1 M in water, 20 °C). The amount was regulated in order to get a molar ratio B/(B + Zr) = 0.3. After impregnation, the catalysts were dried at 110 °C overnight in a stove. They were named WZrSi, BZrSi, WTiSi and BTiSi. The catalysts were calcined at different temperatures in an air stream ($10\,\mathrm{ml\,min^{-1}\,g_{cat}^{-1}}$) and then tested with the reaction test of *cis*-butene (Matheson, >99%) in order to determine the optimum range for the generation of acid sites. For comparison, bulk catalysts of tungsten-zirconia (WZr), boron-zirconia (BZr), tungsten-titania (WTi) and boron-titania (BTi) were prepared following the same procedure of impregnation and with the same values of W/Zr and B/Zr molar ratios. $Zr(OH)_4$ was prepared according to Ref. [3].

For the preparation of titanium hydroxide, $TiCl_4$ (Merck, 99%, yellow liquid) was used as starting material and when not used it was kept in a dessicator. Since the dissolution of $TiCl_4$ in water is explosively exothermic and generates orthotitanic acid, a calculated amount of $TiCl_4$ was dissolved in distilled water in an ice-water bath in order to produce a 2 M solution. The solution was acidified to pH 2 with drops of concentrated ClH to promote the hydrolysis. This aqueous solution was then placed in a temperature-controlled bath at 30 °C. Maintaining at the same temperature for 1 h, the solution was treated with 2.5 M dilute NH_4OH until the pH value was 10. The reaction conditions were maintained for a period of 1 h. The precipitated titanium hydroxide/hydrous titanium oxide ($TiO_2{\cdot}nH_2O$) was separated from the solution by using filtration and then it was repeatedly washed with distilled water to remove chloride ions. The hydrous oxide was then dried at 110 °C overnight. The powder was finally compacted and shaped into pellets in a press.

In order to be used in the catalytic reaction tests and in most of the characterization experiments, all samples were ground in a mortar and sieved to 35–80 meshes.

2.2. Characterization

Textural properties were measured by N_2 sorptometry at the temperature of liquid nitrogen. X-ray diffraction spectra were measured in a Shimadzu XD-1 equipment, using Cu Kα radiation filtered with Ni and scanning the $2\theta = 15–75°$ range. The acidity of the catalysts was measured by thermodesorption of pyridine (TPD) in a dynamic equipment with flame ionization detection. The samples (50 mg) were first stabilized in flowing nitrogen ($40\,\mathrm{ml\,min^{-1}}$, 110 °C, 1 h) and then the temperature was raised to 600 °C with a heating rate of $10\,°\mathrm{C\,min^{-1}}$. The total amount of acid was determined by integration of the TPD trace.

2.3. Test reaction

The reaction of *cis*-butene (Matheson, 99%) was carried out in pulse mode (0.3 ml C_4 per pulse, $10\,\mathrm{ml\,min^{-1}}$ N_2 carrier gas, reaction temperature = 70 °C, catalyst mass = 0.30 g, total pressure = 0.1 MPa).

While supported catalysts were calcined at several temperatures in order to search the optimum pretreatment conditions, bulk catalysts (WZr, WTi, BZr and BTi) were calcined at the temperatures that are known to produce the best catalysts for acid-catalyzed reactions, i.e. 800 °C for the tungsten-promoted catalysts and 600 °C for the boron-promoted ones [13,14].

3. Results and discussion

3.1. Surface area, pore size and crystal properties

With respect to the uncalcined, pure oxides and hydroxides, SiO_2 had a specific surface area of $340\,\mathrm{m^2\,g^{-1}}$, $Zr(OH)_4$ had $224\,\mathrm{m^2\,g^{-1}}$ and $Ti(OH)_4$ had $74\,\mathrm{m^2\,g^{-1}}$. Calcination reduced the area of ZrO_2 to $64\,\mathrm{m^2\,g^{-1}}$ at 600 °C and to less than $40\,\mathrm{m^2\,g^{-1}}$ at 800 °C. In the case of TiO_2 calcination at 600 °C reduced the area to $43\,\mathrm{m^2\,g^{-1}}$ and to $25\,\mathrm{m^2\,g^{-1}}$ at 800 °C.

Fig. 1 shows the pore size distributions of the ZrSi catalysts dried at 110 °C with different Zr loadings. As a consequence of the pronounced drop of the pore volume (V_g, area under the curve) and the smoother variation of the specific surface area (S_g, Fig. 2), the center of the distribution is displaced to lower pore diameter (d_p) values as the ZrO_2 load increases, a fact that can be inferred from Wheeler's formula $r_p = 2V_g/S_g$. In the case of the uncalcined ZrSi samples, some microporosity was created in the 2 nm zone and its contribution to S_g counterbalanced to some degree the loss of surface area produced by the loading of the pore volume. In spite of this, the area of the ZrSi samples dried at 110 °C ($280–320\,\mathrm{m^2\,g^{-1}}$) was lower than the area of the free silica support.

Calcination at high temperatures reduced the area to smaller values as can be seen in Fig. 2 for both the ZrSi and TiSi supports. The surface area decrease was mainly related to the sintering of ZrO_2 and TiO_2 particles and the blocking of pores by crystals, because the area of the original silica

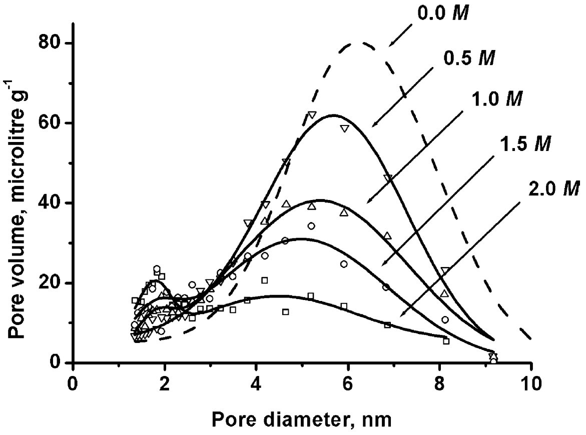

Fig. 1. BJH pore size distribution. ZrSi samples with different Zr contents (expressed as number of monolayers) and dried at 110 °C.

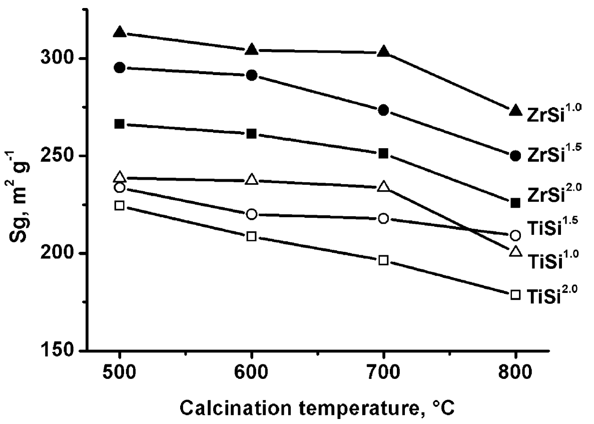

Fig. 2. Specific surface area (S_g) as a function of the calcination temperature: (▲) ZrSi$^{1.0}$; (●) ZrSi$^{1.5}$; (■) ZrSi$^{2.0}$; (△) TiSi$^{1.0}$; (○) TiSi$^{1.5}$; (□) TiSi$^{2.0}$.

support remains essentially unchanged upon calcination ($\approx$315 m^2 g^{-1} at 800 °C). In spite of the sintering, the available surface area of the ZrSi and TiSi supports is very high, much higher than that of the bulk ZrO_2 and TiO_2 supports after being calcined at 600–800 °C. The magnitude of the S_g values also indicates that for most ZrSi samples, a seemingly good degree of dispersion was achieved, because agglomeration and pore blocking would produce a drastic loss of surface area that did not occur.

In the case of the TiSi samples, the achieved dispersion was apparently lower, because the S_g values after drying the samples at 110 °C (240–275 m^2 g^{-1}) were lower than those of the ZrSi samples. The variation of S_g with the calcination temperature (T_c) was similar to that of ZrSi and as a consequence, the final area values of the TiSi catalysts were always lower than those of the ZrSi ones.

The similarities in the S_g–T_c pattern are repeated in Fig. 3, which contains results related to the crystal growth of both ZrSi and TiSi. As indicated by the intensity of the XRD signal, the absolute crystal growth is similar for both series of catalysts. In comparison to the ZrSi samples, the TiSi samples have initially bigger TiO_2 crystals at 500 °C and consequently end up with bigger crystals after being treated at 800 °C. The higher dispersion of the ZrO_2 crystals with respect to the TiO_2 crystals correlates with the higher S_g values of the ZrSi samples.

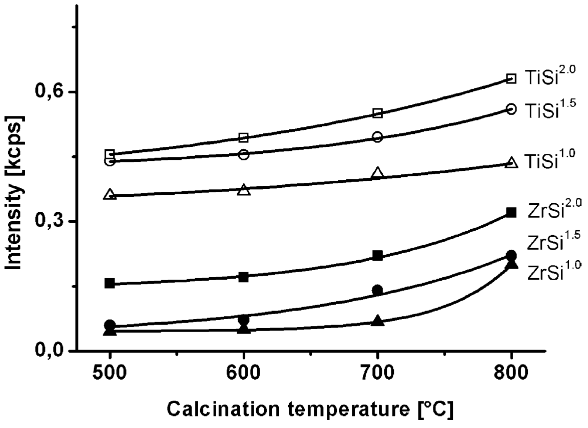

Fig. 3. XRD intensity of the main peak ($2\theta = 30.5°$ for ZrO_2 and $2\theta = 25°$ for TiO_2) as a function of the calcination temperature: (▲) ZrSi$^{1.0}$; (●) ZrSi$^{1.5}$; (■) ZrSi$^{2.0}$; (△) TiSi$^{1.0}$; (○) TiSi$^{1.5}$; (□) TiSi$^{2.0}$.

In all samples, the thermal stability of the supported crystal was high, especially in the case of the TiSi ones. ZrO_2 crystals had a small size at 500 °C but they increased their volume 300% after calcination at 800 °C. The TiO_2 crystals of the TiSi samples had a much bigger size at 500 °C than their ZrSi counterparts but only had a maximum volume growth of 35%.

As indicated by the dominant peak at $2\theta = 30°$ (spectra not shown) due to the presence of the tetragonal phase and the absence of peaks at 28.5° attributed to monoclinic zirconia, silica supported zirconia crystallized exclusively in the tetragonal phase which is the catalytically active phase for acid catalyzed reactions [4]. The discrimination between the anatase and rutile phases of titania was made by measuring the intensity of the peak at $2\theta = 25.4°$ attributed to the $\langle 1\,0\,1 \rangle$ reflection of the anatase phase and the intensity of the peak at about $2\theta = 28.0°$ attributed to the $\langle 1\,1\,0 \rangle$ plane of rutile. Anatase was the only phase found in all the TiSi samples.

In summary, ZrSi and TiSi share a common sintering pattern as a function of the calcination temperature. The final state of dispersion is determined by the initial dispersion obtained during the step of controlled hydrolysis of the Ti and Zr alkoxide precursors.

The promotion with B and W reduced the available surface area of ZrSi and ZrTi even further. The negative effect on S_g was more pronounced than in the case of the loading of the original silica support with ZrO_2 and TiO_2, especially on the XYSi$^{2.0}$ samples (X = W and B; Y = Zr and Ti) which had final specific surface areas lower than 150 m^2 g^{-1}. The problem on the samples of high zirconia content was related to the high amount of promoter that these samples needed in order to maintain the B/Zr, W/Zr, B/Ti and W/Ti ratios.

3.2. *cis*-Butene reaction

This is a reaction that does not demand a high acid strength and involves both weak and strong acid sites. It was used here to make a screening of the temperature of calcination and to determine in which range of preparation conditions the maximum amount of acid sites was generated. An active phase content of 1.5 monolayers was chosen for the screening because some preliminary experiments indicated that catalysts with a content of active phase of 1.5 monolayers were on average the most active ones (Fig. 5).

The results of Fig. 4 indicate that the most active catalysts were BTiSi and WZrSi. The activity of WTiSi was particularly low. It had maximum conversion at 500 °C but higher calcination temperatures (T_c) only produced a drop in activity. The activity of BZrSi was similar to that of

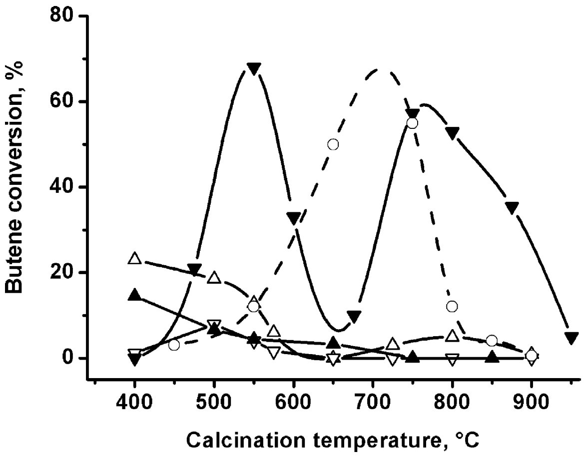

Fig. 4. Activity in the *cis*-butene reaction as a function of the calcination temperature. 1.5 monolayers promoter content. Initial conversion. (▼) WZrSi$^{1.5}$; (△) BTiSi$^{1.5}$; (▲) BZrSi$^{1.5}$; (▽) WTiSi$^{1.5}$; (○) WZr.

WTiSi, with practically the same initial conversion of *cis*-butene at 500 °C. However, the highest value was obtained at 400 °C and the activity decreased monotonically as the temperature was increased. The highest activity was displayed by WZrSi$^{1.5}$, which had a peculiar bimodal conversion pattern with two maxima at 550 and 750 °C. This pattern was associated to the increase in catalytic activity due to elimination of chemisorbed water (acting as an adsorbed Lewis base) in the range $T_c = 400$–600 °C and to the formation of new WO_3–ZrO_2 acid sites during crystallization of ZrO_2 at $T_c > 700$ °C. Both phenomena competed against the loss of active sites by sintering. The total amount of acid sites of the WZrSi$^{1.5}$ catalysts was measured by pyridine TPD after calcination at four different temperatures, 500, 550, 650 and 750 °C. The acid amounts were 1.0, 1.01, 0.32 and 0.81, on a relative basis (taking the total acidity of WZrSi$^{1.5}$/500 as unity). The variation of the total acidity follows the variations in the conversion in the *cis*-butene reaction, a fact that seems to indicate that the activity is related to the total number of acid sites.

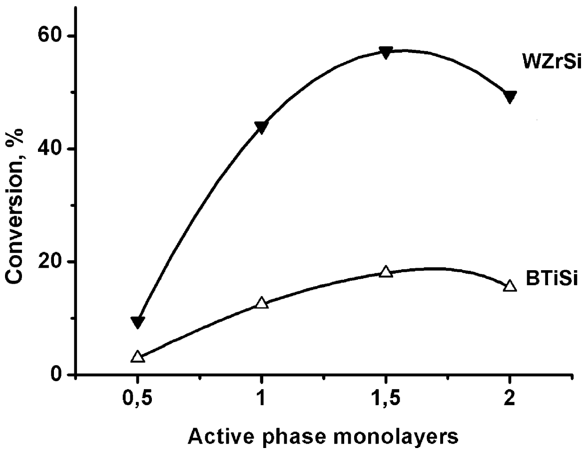

Fig. 5. Activity in the *cis*-butene reaction as a function of the content of active phase. (▼) WZrSi$^{1.5}$ calcined at 750 °C and (△) BTiSi$^{1.5}$ calcined at 500 °C.

The conversion of the bulk WZr catalyst is included in Fig. 4 for comparison. It can be seen that the level of activity is similar to that of WZrSi but the range of activation is different. The second peak in WZrSi is shifted to higher temperatures with respect to WZr, indicating that the formation of active sites by crystallization of ZrO_2 and stabilization of WO_x surface species is delayed by the influence of the support.

BTiSi was moderately active in *cis*-butene isomerization and seemingly also had a bimodal activity pattern. Local optima were located at 400 and 800 °C though the exact location of the low temperature point was not refined by additional tests. All catalysts had activity in *cis–trans* and bond-shift isomerization but only the reaction over WZrSi$^{1.5}$ calcined at high temperatures (higher than 700 °C) produced isobutene indicating that the other catalysts lacked acid sites strong enough to produce the skeletal branching of the adsorbed carbenium ion.

Fig. 5 contains the plots of the initial activity values of the WZrSi and BTiSi catalysts in the *cis*-butene pulse reaction as a function of the amount of active phase. A blank experiment indicated that the activity of the silica support was negligible. The activity of the catalysts with half a monolayer of active phase was very low. The activity increased non-linearly from the value at 0.5 monolayers to the value at 1.0 monolayers, i.e. the activity of ZrWSi$^{1.0}$ was not double the value of ZrWSi$^{0.5}$. The same happened in the case of BTiSi but the effect was less pronounced. An additional increase of 0.5 monolayers (from 1.0 to 1.5) produced an important increase in activity of the BTiSi and WZrSi catalysts but this trend did not continue further. Both WZrSi$^{2.0}$ and BTiSi$^{2.0}$ had smaller conversion values than their counterparts with 1.5 monolayers of active phase. In the case of the BTiSi catalysts, the activity of the samples with 1.5 and 2.0 monolayers was fairly similar. Pyridine TPD traces corresponding to these BTiSi catalysts are included in Fig. 6. It can be seen that when the amount of active phase is increased, the area of the TPD trace is increased and the fraction of sites of higher acid strength is

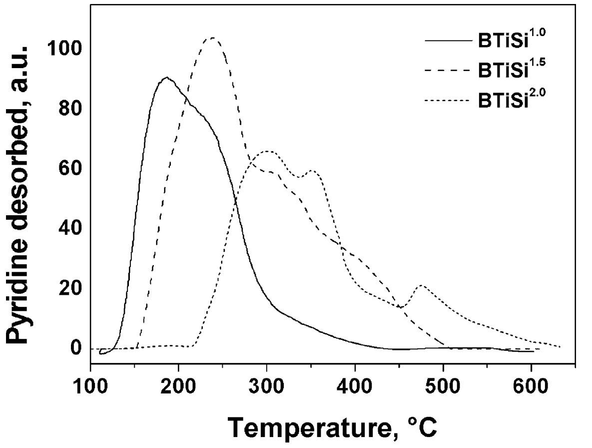

Fig. 6. Temperature programmed desorption of pyridine. BTiSi catalysts calcined at 500 °C.

also increased. On a relative basis, the amount of acid was 1.0, 1.96, 2.89 and 2.14 for the $BTiSi^{0.5}$, $BTiSi^{1.0}$, $BTiSi^{1.5}$ and $BTiSi^{2.0}$ catalysts, respectively (taking the acidity of $BTiSi^{0.5}$ as unity). Again, the activity pattern approximately follows the variation of the total amount of acid sites. This seems natural, because butene isomerization can proceed both on weak and strong sites and therefore the activity is related the concentration of all acid sites.

This activity pattern was rationalized by recalling that there is a competition between many opposing phenomena that depend on the amount of loading of the transition metal oxide. At low loadings, there is a high interaction between the support and the particles, which tend to be highly dispersed. As the content of Ti and Zr grows, the interaction with the support becomes weaker and bigger particles are produced upon sintering, thus producing after calcination a lower surface area accessible to the reactants. It can be supposed that high loadings (2.0 monolayers or higher) do not produce a higher amount of active sites because the accessible surface area decreases too much. The ZrO_2 and TiO_2 crystals formed would also be too big and would have a low surface/bulk atom ratio.

The samples with only half a monolayer of active phase may have had only poorly crystallized WZr and BTi particles because of their interaction with the support. Greater crystals of more adequate size must have grown in the case of the samples with 1.0–1.5 monolayers.

It must be recalled that boron-titania and tungsten-zirconia are catalysts that develop their highest acid activity in the crystalline state. The active phase in our supported samples must therefore sinter in order to display activity. The choice of a catalytically optimum formulation thus involves a careful balance of the loading of the active phase and the temperature of calcination. A minimum amount of active phase must be present and must sinter to an important degree, though not to a great extent, in order to keep a sizable amount of active sites exposed.

4. Conclusions

Silica supported tungsten-zirconia, tungsten-titania, boron-zirconia and boron-titania catalysts can be synthesized in a process involving the following successive steps: (i) deposition of ZrO_2 and TiO_2 on the surface by controlled hydrolysis with surface silanols; (ii) promotion with W and B salts and calcination at a sufficiently high temperature (500–800 °C).

At the conditions of preparation of this work, two combinations of support and promoter produced the most active catalysts, boron-titania and tungsten-zirconia. Tungsten-zirconia had the highest activity.

The catalytic activity for *cis*-butene isomerization in a same catalyst type as a function of the temperature of calcination or the amount of active phase is correlated to the total acidity generated. Increasing amounts of active phase augment the amount of acid sites and the fraction of sites of high acid strength.

The best supported catalysts have a content of about 1.5 monolayers of active phase. Higher and lower contents produce a decrease of the activity of the acid function. This seems to be the result of a balance between the increase in the amount of active phase and the decrease of the surface area by sintering and pore plugging.

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