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CONVERSION OF *n*-BUTANE TO *iso*-BUTENE ON GALLIUM/HZSM-5 CATALYSTS

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Abstract - The conversion of n-butane to iso-butene on gallium/HZSM-5 catalysts at 350°C and WHSV=$2.5h8^{-1}$ was studied. The catalysts were prepared by ion exchange from a $Ga(NO3)_2$ solution and further submitted to calcination in air at 530°C. TEM analysis with an EDAX detector and TPR-H_2 data showed that after calcination the Ga species were present mainly as Ga_2O_3, which are reduced to Ga_2O at temperatures near 610°C. The specific acid activity (SAA) of the catalysts increased with the increase in aluminum content in the zeolite, and for a fixed Si/Al ratio, the SAA increased with Ga content. Values for specific hydro/dehydrogenation activity (SH/DHA) were significantly higher than those for SAA, indicating that the catalytic process is controlled by the kinetics on acid sites. Moreover, the production of iso-butene with a selectivity higher than 25% was a evidence that in gallium/HZSM-5-based catalysts the rate of the hydrogenation reaction is lower than that of the dehydrogenation reaction; this behavior confirmed the dehydrogenation nature of gallium species, thereby showing great promise for iso-butene production.

Keywords: n-butane, iso-butene, MTBE, gallium/ZSM-5, dehydrogenation, isomerization.

INTRODUCTION

Since 1970, the petroleum industry has introduced several modifications into the composition of gasoline (Seddon, 1992). The objective has been to enhance the octane number and the minimize emissions of pollutants in the exhaust gases of automotive vehicles. One of the most important changes has been the addition of oxygenated organic compounds, such as methyl tert-buthyl ether (MTBE), tert-amil-methyl ether (TAME), ethanol, methanol, etc. Of these additives, MTBE has been the most commonly used; therefore, great efforts have been made to maximize its production. The most frequently utilized process for the commercial production of MTBE is the conversion of iso-butene and methanol on acid catalysts (Naber, 1994).Thus, the manufacture of MTBE is strongly dependent on iso-butene production, which is possible by the following processes:

(a) typical n-butene isomerization using acid catalysts and mainly acid zeolites (Butler and Nicolaides, 1993; Cheng and Ponec, 1994; Seo et al., 1997);

(b) conversion of n-butane to iso-butene, involving dehydrogenation/isomerization steps on bifunctional catalysts (Giannetto et al., 1994), with a strongly dehydrogenation metallic function associated with strong acid sites such as those found in H/zeolites. This process, though not sufficiently studied, is the most attractive as it allows production of iso-butene in only one step.

In this work, the conversion of n-butane to iso-butene on gallium/HZSM-5 catalysts based on alternative (b) was studied. The study was focused to verify the effect of the ratio of silicon to aluminum in the zeolite on the activity and the selectivity for iso-butene. The nature of active species and the ratio of metallic to acid sites on the catalysts was also studied.

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EXPERIMENTAL

Preparation of the Catalysts

Na-ZSM-5 zeolites with Si/Al ratios of 18, 28 and 38 were synthesized under hydrothermal conditions using the procedure utilized by Batista (1997). The acid forms of the zeolites (H-ZSM-5) were obtained at room temperature by ion exchange in a HCl diluted solution (0.1 mol/L). The gallium-based H-ZSM-5 catalysts were obtained by ion exchange at 90°C using a $Ga(NO_3)_3$ solution (0.05 mol/L; Aldrich). After the ion exchange the catalysts were filtered, washed with deionized water, dried at 105°C during 4 hours and calcined during 10 hours at 530°C under air flow ($20cm^3$/min.g). The catalysts are referred to as Ga(x)/HZ(y), where x is the gallium content in the catalyst (% w/w) and y the Si/Al ratio of the zeolite. The bulk chemical composition obtained by atomic absorption spectroscopy and the unit cell composition of the zeolites are show in Table 1.

Characterization

(a) X-ray Diffraction (XRD)

The X-ray powder diffraction patterns of the zeolites in the angular range of 3 to 40°(2θ) were recorded in a Rigaku diffractometer using monochromated $Cu\kappa_\alpha$ radiation generated at 30kV and 10mA. The scanning speed used was 2°(2θ)/min.

(b) Scanning Electronic Microscopy (SEM)

The Na-ZSM-5 micrographs were obtained in a Zeiss – DSM 960 scanning electron microscope operated at 30 kV and 75 mA.

(c) Transmission Electron Microscopy (TEM)

The micrographs of the Ga(1.0)/HZ(28) sample were obtained on a Phillips CM-120 transmission electron microscopy with a EDAX CM-120 detection unit. A mechanism with a high cryogenic vacuum and a beryllium window with a thickness of 7 μm was utilized. The incident beam in the sample area analyzed was 20 – 30 nm in diameter and the contact time, 100 s.

(d) Temperature-Programmed Reduction of Hydrogen (TPR-H_2)

The TPR analysis of 100 mg of each calcined Ga-ZSM-5 catalyst was carried out in a Micromeritics pulse chemisorb 2705 from room temperature to 1000 °C (heating rate of 10 °C/min), using a gas flow of 40 cm^3/min.g with 5% H_2 (v/v in N_2). The reduced Ga species were calculated from hydrogen consumption in accordance with the following reaction:

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O$$

Catalytic Activity

The n-butane conversion was carried out in a fixed bed reactor operated under steady state conditions at 350°C and atmospheric pressure. The feed stream was a mixture of nitrogen and n-butane at a molar ratio of 9, which results for n-butane in a WHSV= 2.5 h^{-1}. Concerning with the results of scanning electron microscopy (see Figure 2), the metal exchanged zeolites have particle size lower than 100 μm, resulting in relations of high bed to particle size much higher than 10 and of diameter of the reactor to particle size higher than 16. The values pointed are considered the minimal necessary to minimize the external and internal diffusion effects, the dispersion and the axial and radial temperature gradients in porous catalysts (Zotin, J. L., 2001). Another condition adopted to minimize these transport phenomena effects was the dilution of n-butane in nitrogen flow as commented above (Smith, J. S., 1981).

The products were analyzed by gas chromatography using a VARIAN 3400 chromatograph with an FID detector and a capillary column with an internal diameter of 0.25 mm and a length of 50 m. Before the reaction the catalysts were activated in situ at 530°C under H_2 flow (160 cm^3/min) during 8 h. After reduction of the gallium species, the reactor was cooled to the reaction temperature.

RESULTS AND DISCUSSION

Characterization

The XRD patterns (Figure 1) and SEM micrographs (Figure 2) of the synthesized Na-ZSM-5 zeolites indicate that the solids have an MFI structure with high crystallinity and without the presence of another crystalline phase. The SEM micrographs also show that the zeolites are composed of crystal aggregates with diameters between 30 to 60 μm. The tendency of the aggregates to increase in crystal size with a decrease in aluminum content can be observed.

The TEM micrographs of the calcined Ga(1.0)/HZ(28) sample, which is 1.06% gallium and has a ratio of Ga/Al=0.268 (Table 1), are shown in Figure 3. Particles can be seen on the catalyst surface, these are visible in both micrographs, the clear field image (Figure 3a) and the dark field image (Figure 3b). *In situ* chemical analysis of the particles by EDAX and X-ray diffraction confirmed that they are composed of Ga_2O_3, which is seen as little aggregates or thin sheets, located principally on the external surface of the zeolite crystals.

The TPR-H_2 curves of Ga(1.0)/HZ(18), (28) and (38) catalysts (Figure 4) showed that all the samples had one reduction peak near 610°C, which has been attributed to the reduction of Ga_2O_3 to Ga_2O (Brabec et al., 1998). The Ga(1.0)/HZ(18) sample, the catalyst with the highest aluminum content, showed an additional reduction peak at around 350°C, which was attributed in the case of this sample, having the highest number of exchangeable sites, to the reduction of the reminiscent not oxidized Ga^{3+} cations compensating the negative charge of the zeolite. This peak was also observed by Brabec et al. (1998) in the TPR profile of a modified boralite by gallium solid state ion exchange. The Ga(1.0)/HZ(18) sample also showed the highest H_2 consumption, indicating greater ability to reduce Ga_2O_3 in catalysts with higher numbers of protonic sites. This result was also evidenced by Joly (1991), Kanazirev et al. (1992) and Guisnet et al. (1992), who suggested that the presence of acid sites promotes Ga_2O_3 reduction.

Table 1: Characteristics of the prepared Ga-HZSM-5 catalysts after ion exchange.

Sample	Si/Al	$g_{Ga}/g_{zeolite}$	Exchange (%)	Ga/Al	Unit cell
Ga(1.0)/HZ(18)	18	0.0109	50.0	0.183	$H_{2.53}Ga_{0.84}Al_{5.02}Si_{90.91}O_{192}$
Ga(1.0)/HZ(28)	28	0.0106	75.0	0.268	$H_{0.83}Ga_{0.83}Al_{3.31}Si_{92.70}O_{192}$
Ga(1.0)/HZ(38)	38	0.0108	98.0	0.376	$H_{0.05}Ga_{0.80}Al_{2.46}Si_{93.54}O_{192}$
Ga(0.5)/HZ(18)	18	0.0048	25.0	0.092	$H_{3.76}Ga_{0.42}Al_{5.02}Si_{90.91}O_{192}$
Ga(0.5)/HZ(28)	28	0.0054	38.0	0.135	$H_{2.05}Ga_{0.42}Al_{3.31}Si_{92.70}O_{192}$
Ga(0.5)/HZ(38)	38	0.0052	52.0	0.189	$H_{1.18}Ga_{0.43}Al_{2.46}Si_{93.54}O_{192}$
Ga(0.1)/HZ(18)	18	0.0007	3.5	0.018	$H_{4.84}Ga_{0.06}Al_{5.02}Si_{90.91}O_{192}$
Ga(0.1)/HZ(28)	28	0.0010	7.0	0.027	$H_{3.08}Ga_{0.08}Al_{3.31}Si_{92.70}O_{192}$
Ga(0.1)/HZ(38)	38	0.0009	9.0	0.038	$H_{2.24}Ga_{0.07}Al_{2.46}Si_{93.54}O_{192}$

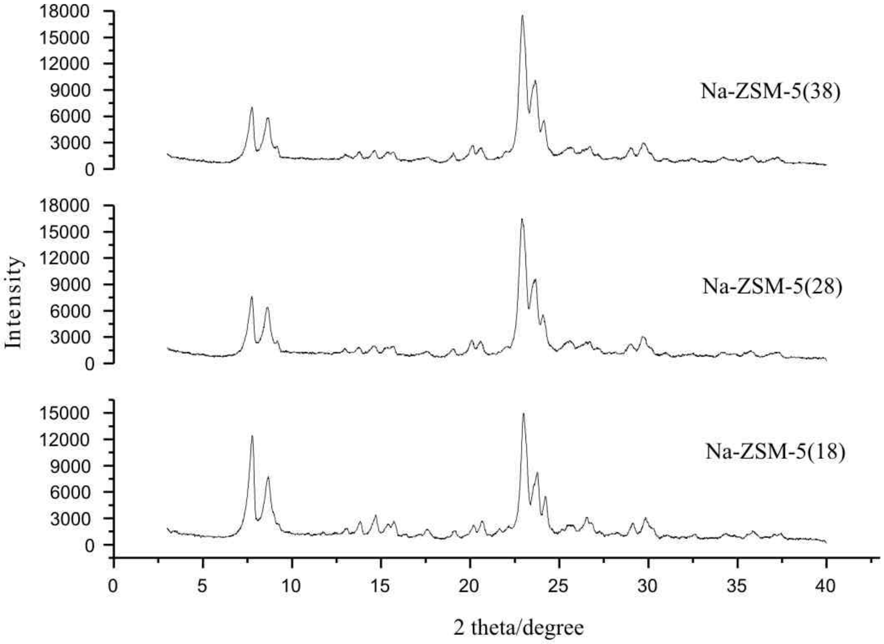
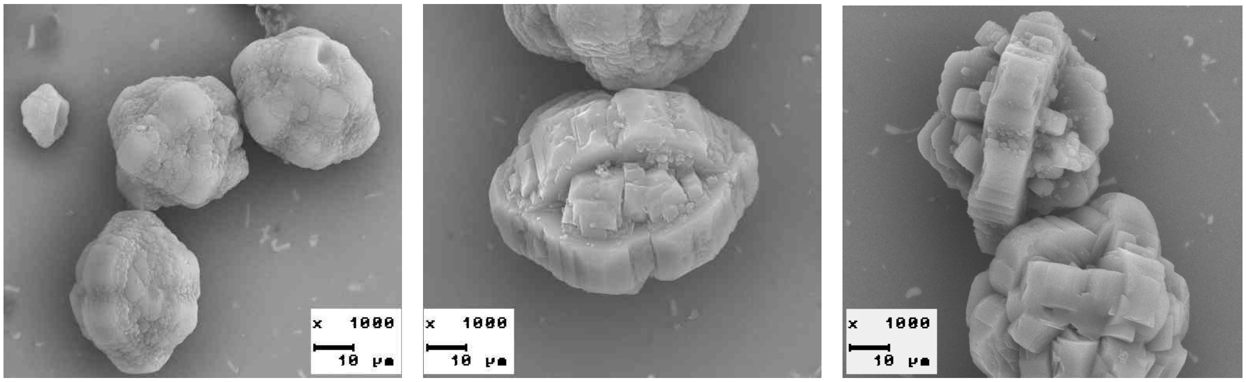
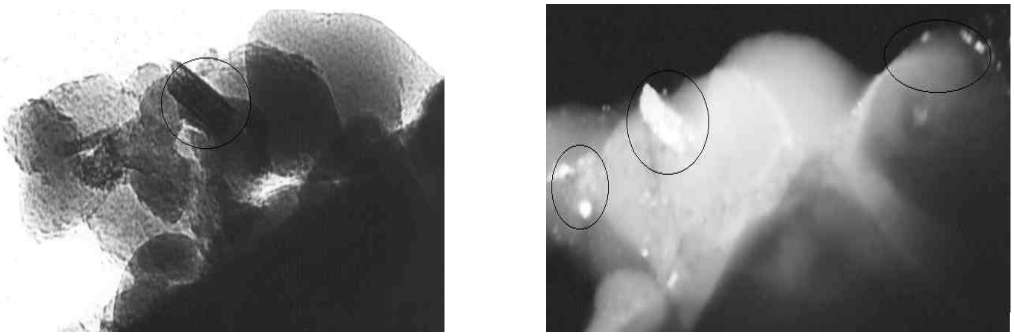


Figure 1: XRD patterns of the synthesized Na-ZSM-5 zeolites.



(a) (b) (c)

Figure 2: SEM micrographs of the synthesized zeolites: (a) Na-ZSM-5(18); (b) Na-ZSM-5(28); (c) Na-ZSM-5(38).



(a) (b)

Figure 3: TEM micrographs of the calcined Ga(1.0)/HZ(28) sample: (a) clear field image and (b) obscure field image.

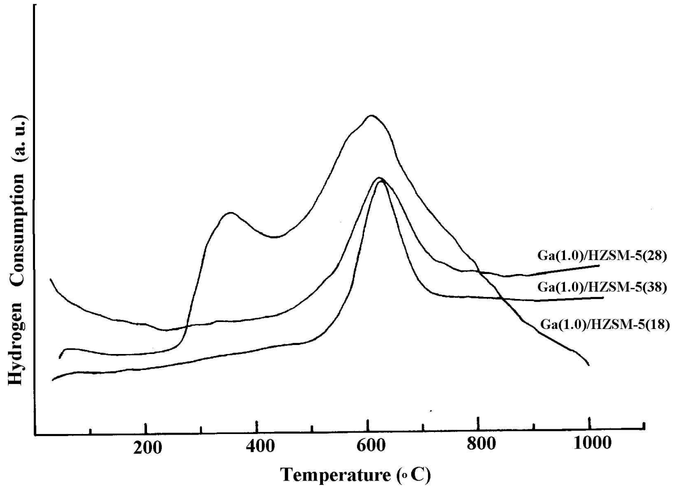


Figure 4: TPR-H_2 of Ga(1.0)/HY(y) catalysts.

n-Butane Conversion

At 350°C and WHSV=2.5h^{-1}, the conversion of n-butane on Ga(x)/HZ(y) generated principally iso-butane and iso-butene. For the most active samples, a low production level of the C_3 and C_5 fractions was also detected. On Ga/H-ZSM-5 catalysts, the occurrence of the classic bifunctional process can be expected. This process involves the participation of hydrogenation/dehydrogenation sites and acid sites (Giannetto, 1985; Giannetto et al., 1995) in the following steps: a) dehydrogenation of n-butane to butenes on gallium species; b) isomerization of n-butenes to iso-butene on acid sites and c) hydrogenation of the olefins formed on metallic sites. The isomerization of n-butenes can occur via monomolecular or bimolecular mechanisms (Mériaudeau et al., 1997; Guisnet et al., 1997); in the first one, n-butene is selectively transformed into iso-butene, involving the formation of a highly unstable primary carbenium ion and one protonated ciclopropane. Despite the fact that the monomolecular mechanism involves this unstable intermediate, on depending of the type of zeolite, it can not be always completely discarded; however, on HMFI and HFER zeolites this occurrence has not been important, therefore indicating that the most probable occurring mechanism is the bimolecular one, which elucidates the formation of iso-C_4, iso-$C_4^=$, and C_3 and C_5 fractions in the products (Mériaudeau et al., 1997; Guisnet et al., 1997). The bimolecular mechanism, which is more rapid than the monomolecular one, occurs by the sequence dimerization, isomerization and cracking, involving secondary and tertiary carbenium ions and the protonated ciclopropane (Mériaudeau et al., 1997).

The n-butane conversion (Figure 5) was strongly influenced by the presence of acid sites and hydro/dehydrogenation species:

a) independent of gallium content, higher levels of conversion were obtained on catalysts with higher aluminum contents:

Ga(x)/HZ(18)>>Ga(x)/HZ(28)>Ga(x)/HZ(38);

b) for a constant Si/Al ratio, propane conversion increased with an increase in gallium content:

Ga(1.0)/HZ(y)> Ga(0.5)/HZ(y)>Ga(0.1)/HZ(y).

For low Ga/Al ratios (Table 1), it can be expected that the number of dehydrogenation sites is not sufficient to supply intermediate olefins to all active acid sites responsible for the isomerization step. However, because the isomerization reaction is the rate-determining step (Runstraat, A. van de, 1997), an increase in the density of acid sites will favor the bifunctional catalytic process.

Specific Acid Activity (SAA)

The SAA (Figure 6), calculated as a ratio of the mol number of the converted propane to the mol number of aluminum in the catalyst, showed behavior similar to that in the conversion shown in Figure 5. In this manner, for a particular Si/Al ratio, the SAA increased with an increase in gallium content. This indicates that to obtain higher acid activity, a higher concentration of olefins, and therefore a higher number of dehydrogenation sites, is necessary.

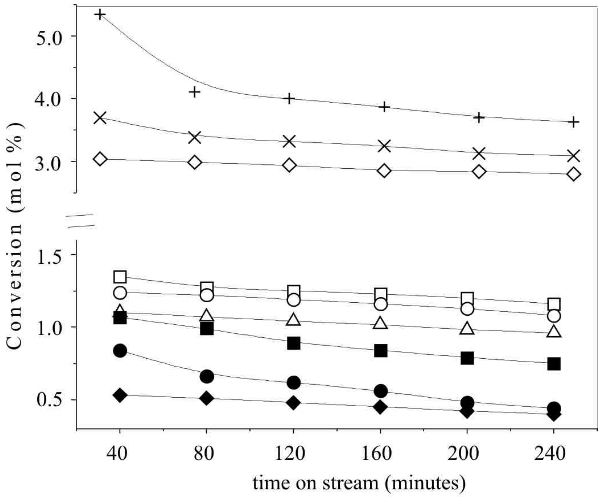


Figure 5: Conversion of n-Butane at 350 °C and WHSV= 2.5 h^{-1} on HZ(18)/Ga(%): (+) 1.0; (x) 0.5; (✧) 0.1. HZ(28)/Ga(%): (□) 1.0; (o) 0.5; (△) 0.1. HZ(38)/Ga(%): (■) 1.0; (●) 0.5; (◆) 0.1.

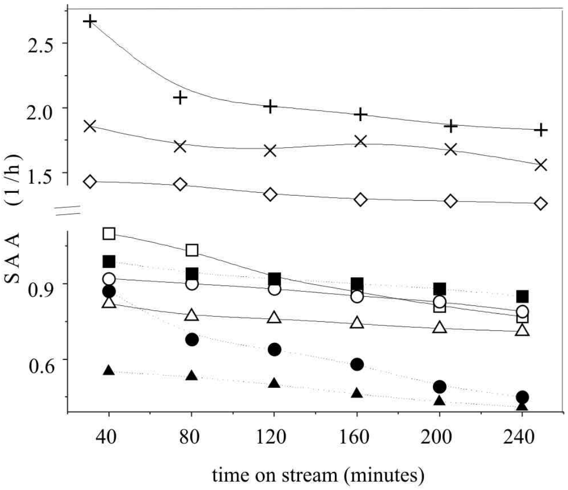


Figure 6: Specific acid activity (SAA) on HZ(18)/Ga(%): (+) 1.0; (x) 0.5; (✧) 0.1. HZ(28)/Ga(%): (□) 1.0; (o) 0.5; (∆) 0.1. HZ(38)/Ga(%): (■) 1.0; (●) 0.5; (◆) 0.1.

Table 2: Specific hydro/dehydrogenation activity (SH/DHA) on Ga(x)/HZ(y) catalysts in the conversion of n-butane at 350 °C and WHSV: 2.5 h^{-1}.

	AEH/HD								
Time	**Ga(x)/HZ(18)**			**Ga(x)/HZ(28)**			**Ga(x)/HZ(38)**		
(min)	**x=1.0**	**x=0.5**	**x=0.1**	**x=1.0**	**X=0.5**	**x=0.1**	**x=1.0**	**x=0.5**	**x=0.1**
40	5.51	7.81	31.96	1.40	3.05	14.2	1.35	2.18	6.83
80	4.63	7.27	26.22	1.26	3.00	13.1	1.26	1.69	6.55
120	4.60	7.15	24.86	1.24	2.95	12.8	1.21	1.52	6.01
160	4.49	7.10	24.04	1.13	2.84	12.6	1.18	1.47	6.01
200	4.38	6.94	23.22	1.07	2.73	12.0	1.15	1.20	5.46
240	4.16	6.83	22.67	0.99	2.62	11.7	1.10	1.14	5.19

Table 3: Selectivity (%) for iso-butane and for iso-butene in the conversion of n-butane at 350 °C and WHSV=2.5 h^{-1}.

	Sample		
	Ga(1.0)/HZ(18)	**Ga(1.0)/HZ(28)**	**Ga(1.0)/HZ(38)**
Conversion*	**5.3**	**1.3**	**1.1**
C_3	6.1	**	**
Iso-butane	66.5	57.2	54.7
Iso-butene	27.4	42.8	45.3
C_5	**	**	**
	Ga(0.5)/HZ(18)	**Ga(0,5)/HZ(28)**	**Ga(0,5)/HZ(38)**
Conversion*	**3.7**	**1.3**	**0.8**
C_3	5.3	**	**
Iso-butane	69.7	59.7	57.9
Iso-butene	25.5	40.3	42.1
C_5	**	**	**
	Ga(0.1)/HZ(18)	**Ga(0.1)/HZ(28)**	**Ga(0.1)/HZ(38)**
Conversion*	**3.04**	**1.1**	**0.6**
C_3	**	**	**
Iso-butane	76.5	63.8	61.3
Iso-butene	23.5	36.2	38.7
C_5	**	**	**

* Conversion (%) at 40 min on stream ** Not detected

Specific Hydro/Dehydrogenation Activity (SH/DHA)

The values of SH/DHA are shown in Table 2. These values were calculated as the ratio of the mol number of dehydrogenated n-butane + the mol number of hydrogenated olefins to the mol number of effectively reduced Ga_2O_3 species. For a constant Si/Al ratio, it can be seen in Table 2 that a decrease in the gallium content of the catalyst resulted in an increase in SH/DHA, where the SH/DHA values were significantly higher than those obtained for SAA (Figure 6), thereby providing evidence that the kinetics of the bifunctional process is controlled by the reaction occurring on acid sites (Runstraat, A. van de, 1997). In samples having the same gallium content, it was observed that the SH/DHA value was higher for those having lower Al/Si ratios. Taking into consideration that the reaction on acid sites occurs through a bimolecular mechanism involving dimerization/isomerization/cracking, a higher number of these sites will favor this process, resulting in a higher consumption of dehydrogenated compounds.

Selectivity for iso-Butane and for iso-Butene

Table 3 shows the selectivity for different products generated during the conversion of n-butane on Ga(x)/HZ(y) catalysts at 350 °C and WHSV=2.5 h^{-1}. As noted above, iso-butane and iso-butene were the principal products, providing evidence of the formation of a dimer intermediate C_8^+ with further isomerization and cracking to form iso-butene. Part of the iso-butene formed again reacted on metallic sites to form iso-butane, thus explaining its presence in the product stream. However, the presence of iso-butene in proportions between 23 and 45% indicates that in gallium/HZSM-5 catalysts the rate of the hydrogenation reaction is lower than that of the dehydrogenation reaction, thus confirming the dehydrogenation characteristics of the gallium species (Montes and Giannetto, 1995). It can also be observed in Table 3 that for a fixed Si/Al ratio the selectivity for iso-butane and for iso-butene are very similar, independent of gallium content, whereas an increase in the Si/Al ratio results in an enhancement of selectivity for iso-butene. This behavior can be explained by the decrease in the density of acid sites, which reduces the occurrence of the bimolecular mechanism and enhances the participation of the monomolecular mechanism, which is more selective for iso-butene formation (Mériaudeau et al., 1997).

CONCLUSION

After calcination at 530 °C the Ga/HZSM-5 catalysts obtained by ion exchange had the extra-structural Ga_2O_3 crystalline phase, which is reduced to Ga_2O near 610°C. The conversion of n-butane on these catalysts generated mainly iso-butane and iso-butene due to the bimolecular mechanism involving formation of a dimer intermediate, the C_8^+ tertiary carbenium ion and its isomerization and cracking.

An increase in the conversion and in the specific acid activity (SAA) occurred with the increase in aluminum content in the zeolite, and for a constant Si/Al ratio, both types of activity increased with the increase in gallium content in the catalyst. The specific hydro/dehydrogenant activities obtained (SH/DHA), with values significantly higher than the SAA, and the production of iso-butene with a selectivity higher than 25% were evidence that in the gallium/HZSM-5-based catalysts the rate of the hydrogenation reaction is lower than that of the dehydrogenation reaction. This behavior confirmed the dehydrogenation nature of gallium species, thereby showing great promise for iso-butene production.

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