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Preparation of acidic or bifunctional catalysts by means of straightforward calcination of as-synthesized [Ga]-ZSM-5 zeolites obtained from alkali-free media. Propane aromatization

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Propane aromatization (530°C, 1 atm) was used as a reaction model to evaluate the effect of the calcination temperature on the catalytic properties of an as-synthesized $[Ga_{1.3}]$-ZSM-5 zeolite obtained from alkali-free media and calcined at two different temperatures: 530°C (C-530) and 750°C (C-750). Results show that in spite of its lower acidity, C-750 is more active and selective toward aromatics than C-530. This is probably due to the fact that at higher temperature the decomposition of organic compounds used during the zeolite synthesis is accompanied by a partial degalliation of the zeolitic support leading to the production of a bifunctional x"Ga_2O_3"/H-$[Ga_y]$-ZSM-5 ($2x + y = 1.3$) catalyst.

Keywords: Alkali-free synthesis zeolite; [Ga]-ZSM-5; degalliation; acidic and bifunctional catalysts; propane aromatization

1. Introduction

Gallium exchange and/or impregnation of H-[Al]-ZSM-5 zeolite leads to Ga/H-[Al]-ZSM-5 catalysts which are more active and selective in aromatization of

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light paraffins C_3–C_4 than the purely acidic support [1,2]. This is due to the fact that gallium extraframework species catalyze the dehydrogenation reactions of alkane reactants to alkenes and of naphthenic intermediates to aromatics [3–10]. Nevertheless, the conventional preparation of these catalysts involves (i) calcination of TPA-Na-zeolite to obtain H-Na-zeolite, (ii) ammonium exchange to produce the NH_4-zeolite, (iii) calcination to form the H-[Al]-ZSM-5 and (iv) exchange and/or impregnation of the protonic zeolite with Ga^{3+} ions to obtain the bifunctional Ga/H-[Al]-ZSM-5 catalyst. This catalyst can also be produced by degalliation of NH_4-[Ga]-ZSM-5 [9–14], but, here again, steps (i) and (ii) are necessary for its preparation. In this paper, we show that pure acidic H-[$Ga_{1.3}$]-ZSM-5 catalyst or bifunctional Ga-acidic-MFI-type catalyst could be directly prepared through straightforward calcination of as-synthesized [Ga]-ZSM-5 obtained from alkali-free media [15]. The bifunctional catalyst obtained behaves as a conventional bifunctional catalyst for propane aromatization.

2. Experimental

Two samples of as-synthesized alkali-free [$Ga_{1.3}$]-ZSM-5 (Si/Ga = 72.8) zeolite [15] were calcined under dry air at 530°C (C-530) and 750°C (C-750). Additionally, 1% Ga/C-530 catalyst was prepared by conventional impregnation of the zeolite calcined at 530°C. Samples were characterized by XRD, FT-IR, N_2 adsorption, flame-atomic absorption spectroscopy, and XPS (table 1).

n-heptane cracking ($T = 350°C$; $p = 1$ atm; N_2/hydrocarbon = 4) was used as a reaction model to characterize the acidity of catalysts. Propane aromatization (530°C; $p = 1$ atm) was used as a reaction model to evaluate the acidic or the bifunctional behavior of the solids. Catalytic tests were conducted in a fixed-bed microreactor, under dynamic flow conditions. Activities were calculated for conversion below 20%. Different degrees of propane conversion were obtained by changing space velocity.

Table 1
Characterization of the solids

Sample	C_{XRD} [a] (%)	$IR_{I_{550}/I_{450}}$ [b]	S [c] ($m^2 g^{-1}$)	(Si/Ga) bulk [d]	$(Si/Ga)_{XPS}$ [e]
as-synthesized ($Ga_{1.3}$)-ZSM-5	100	0.82	–	72.8	75
C-530	99	0.82	400	73.3	72
C-750	85	0.80	382	72.0	90
1% Ga/C-530	105	0.80	390	–	7

[a] Relative crystallinity determined by XRD [16].
[b] Optical density ratio (I_{550}/I_{450}) [17].
[c] BET surface determination (N_2, −196°C).
[d] Flame-atomic absorption spectroscopy [18].
[e] Surface chemical composition by XPS.

3. Results and discussion

Table 1 clearly shows that direct calcination of as-synthesized alkali-free $[Ga_{1.3}]$-ZSM-5 does not produce important changes in the crystallinity of C-530 and C-750. As a matter of fact, the relative crystallinity determined by XRD [16], C_{XRD}, the optical density ratios of the IR bands occurring at 550 and 450 cm^{-1} [17], I_{550}/I_{450}, and the specific surface area, S, are very similar for all the solids. Moreover, bulk Si/Ga ratios, obtained by flame-atomic absorption spectroscopy [18], are practically the same for the three samples (table 1). This indicates that no loss of gallium has occurred from the sieve. Nevertheless, XPS shows that whereas C-530 presents almost the same surface chemical composition as as-synthesized zeolite, the sample calcined at higher temperature, C-750, shows changes in its surface chemical composition, which is richer in silicon than the pattern sample. This change in surface chemical composition without any change in the bulk Si/Ga ratio, suggests that a partial degalliation of the zeolite was produced. Unlike the dealumination process occurring on [Al]-zeolites, in which extraframework aluminum species migrate to the outer surface of the zeolite crystallites [19,20], extraframework gallium species, EFGS, apparently migrate into the zeolite channels. This particular migration of EFGS was recently reported for catalysts prepared by mixture of H-[Al]-ZSM-5 and α-Ga_2O_3 and activated under reducing conditions [21].

1% Ga/C-530 also shows a similar degree of crystallinity as the pattern zeolite, but in this case, almost all of the impregnated gallium is deposited in the outer surface of the zeolite crystallites, as its low Si/Ga surface ratio indicates (table 1).

The acidities of the catalysts, determined using the *n*-heptane cracking as a reaction model (table 2) show that C-750 is less active than C-530, and 1% Ga/C-530 (table 2), both solids presenting almost the same activity for *n*-heptane cracking as it has been previously reported by other authors [1,3,22]. The lower activity of C-750 in *n*-heptane cracking can be related to the reduction of the number of acidic sites in this catalyst, produced by partial degalliation of the zeolite structure, as the chemical surface composition determined by XPS suggests (table 1).

However, fig. 1 shows that despite its lower acidity, C-750 is almost three times more active in propane aromatization than C-530, a more acidic catalyst. Only the above mentioned partial degalliation – produced by calcination at 750°C – and the subsequent formation of a bifunctional x"Ga_2O_3"/H-$[Ga_y]$-ZSM-5

Table 2
Initial activities of catalysts, A_0 (10^{-3} mol g^{-1} h^{-1}) in *n*-heptane cracking ($T = 350°C$; $p = 1$ atm; N_2/*n*-heptane = 4)

Catalyst	A_0 [a] (10^{-3} mol g^{-1} h^{-1})
C-530	7.3
C-750	4.5
1% Ga/C-530	7.1

[a] Obtained by extrapolation at $t = 0$.

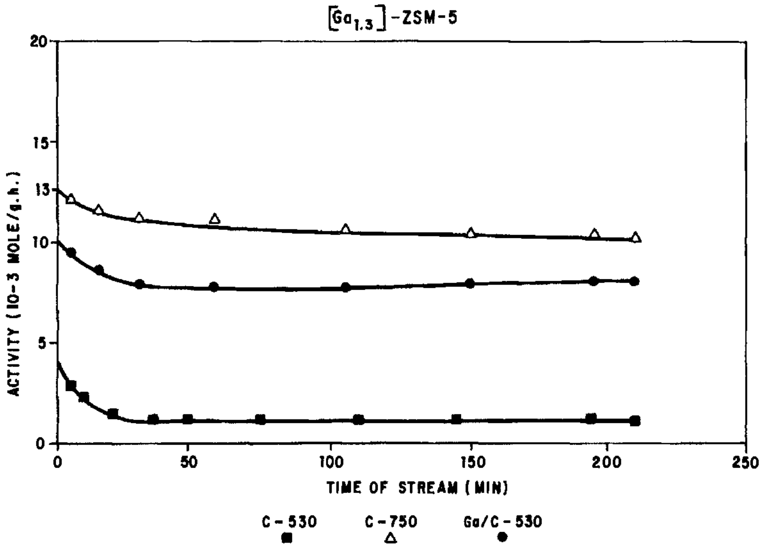

Fig. 1. Activities of catalysts, A (10^{-3} mol g^{-1} h^{-1}) on propane aromatization as a function of the time on stream, t (min) ($T = 530°C$; $p = 1$ atm; WWH $= 2\,h^{-1}$).

($2x + y = 1.3$) catalyst can explain the later observation. The presence of these dehydrogenating EFGS when catalyzing the rate limiting step of the aromatization reaction – dehydrogenation of propane [3–5,9,10] – can explain the increase in the reaction rate of C-750 with respect to C-530. On the other hand, C-750 is 1.3 times more active than 1% Ga/C-530, a bifunctional, and conventionally prepared, catalyst, which is more acidic than C-750 (table 2). This seems to indicate that EFGS produced by direct calcination of the as-synthesized alkali-free zeolite are more disperse than those of 1% Ga/C-530, which generate a bifunctional catalyst with a better "balance" between their dehydrogenating and their acidic functions and hence a more active catalyst [10].

This partial degalliation can also explain the higher selectivity of C-750 toward BTX in relation with C-530 (fig. 2). Because of their dehydrogenating activity, EFGS also catalyze the aromatization of naphthene intermediates toward BTX thus reducing their cracking [3–10]. This causes C-750 to present a BTX/light product (methane, ethane, ethene) molar ratio similar to that of 1% Ga/C-530, and higher than that of C-530 (fig. 3). Moreover, whereas C-750 and 1% Ga/C-530 at high conversion level (>20 mol% of aromatic production) exhibit a H_2/BTX molar ratio higher than 4, typical value for bifunctional catalysts [5,9,10,14], C-530 has a H_2/BTX molar ratio of about 2 at the same conversion level. This value of 2 is typical for pure acidic catalysts [5,9,10,14] and indicates that almost no degalliation, if any, is produced for a calcination temperature of 530°C.

The effect of the calcination temperature on the catalytic properties of [Ga, Al]-

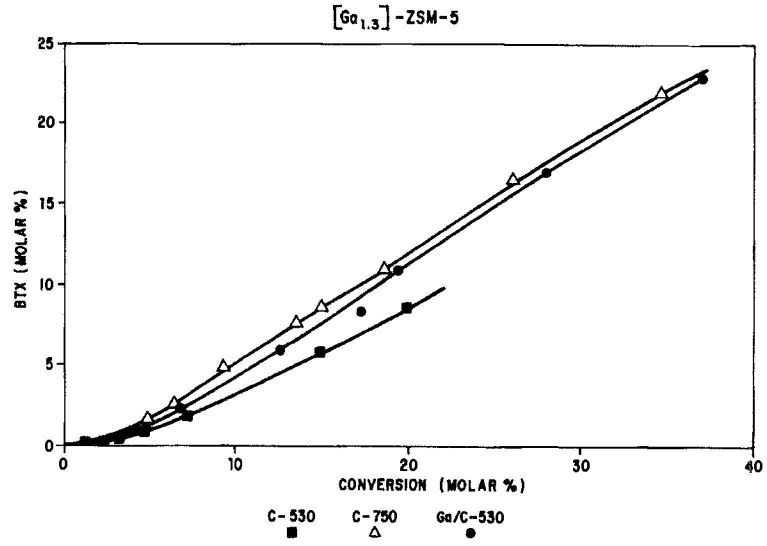

Fig. 2. Evolution of BTX (mol%) as a function of the total conversion (mol%) ($T = 530°C$; $p = 1$ atm).

ZSM-5 zeolites synthesized in alkali-free media is very similar [23] to the one observed with [Ga]-ZSM-5 zeolites shown in this work.

4. Conclusions

The straightforward calcination of as-synthesized alkali-free [Ga]-ZSM-5 zeo-

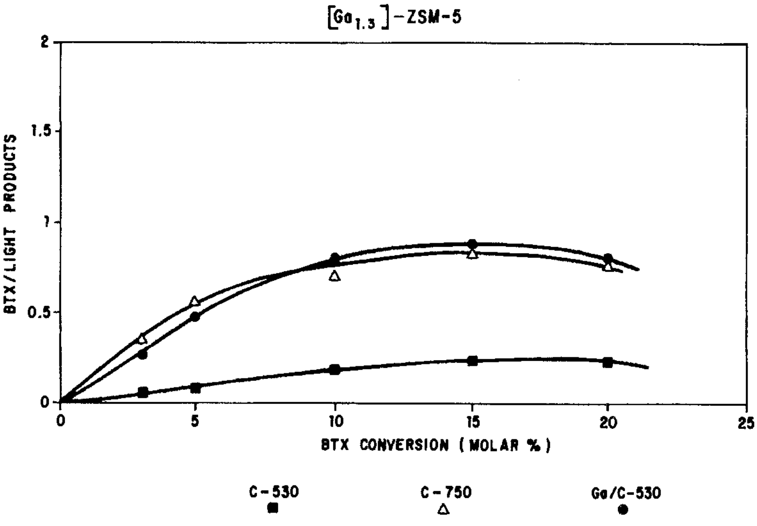

Fig. 3. Evolution of BTX/light products (methane, ethane, ethene) molar ratio as a function of BTX-conversion (mol%) ($T = 530°C$; $p = 1$ atm).

lites leads to the formation of pure acidic H-[Ga]-ZSM-5 or bifunctional x"Ga_2O_3"/H-[Ga_y]-ZSM-5 catalysts, depending on the calcination temperature. The latter catalyst produced by partial degalliation of zeolite structure at 750°C, shows similar catalytic properties for propane aromatization as a catalyst prepared by conventional impregnation methods, but avoiding the relatively expensive steps involved in conventional preparation.

References

[1] M.S. Scurrel, Appl. Catal. 32 (1987) 1.
[2] H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal. 101 (1986) 12.
[3] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Appl. Catal. 43 (1988) 155.
[4] N.S. Gnep, J.Y. Doyemet and M. Guisnet, J. Mol. Catal. 45 (1988) 281.
[5] N.S. Gnep, J.Y. Doyemet and M. Guisnet, in: *Zeolites as Catalysts, Sorbents and Detergent Builders*, Studies on Surface Science and Catalysis, Vol. 46, eds. H.G. Karge and J. Weitkamp (Elsevier, Amsterdam, 1989) p.153.
[6] P. Meriaudeau and C. Naccache, J. Mol. Catal. 50 (1989) L7.
[7] P. Meriaudeau and C. Naccache, in: *Zeolite Chemistry and Catalysis*, Studies in Surface Science and Catalysis, Vol. 69, eds. P.A. Jacobs, N.I. Jaeger, L. Kubelková and B. Wichterlová (Elsevier, Amsterdam, 1991) p.405.
[8] G. Giannetto, J.A. Pérez, R. Sciamanna, L. García, R. Galiasso and R. Monque, in: *Symp. Alkylation, Aromatization, Oligomerization, and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts*, New York City 1991, ACS Preprints 36 (4) p.659.
[9] G. Giannetto, in: *Proc. 6th Brazilian Seminar on Catalysis*, IBP Ed., Bahia, Sept. 1991, p.605.
[10] G. Giannetto, R. Monque and R. Galiasso, Catal. Rev., in press.
[11] L. Petit, J.P. Bournonville and F. Raatz, in: *Zeolites: Facts, Figures, Future*, Studies in Surface Science and Catalysis, Vol. 49B, eds. P.A. Jacobs and R.A. van Santen (Elsevier, Amsterdam, 1989) p.1163.
[12] J. Kanai and N. Kawata, Appl. Catal. 55 (1989) 115.
[13] J. Kanai and N. Kawata, Appl. Catal. 62 (1990) 141.
[14] G. Giannetto, A. Montes, N.S. Gnep and M. Guisnet, in: *Symp. Chemically Modified Molecular Sieves*, Chicago, 25–26 August 1993, ACS Preprints, in press.
[15] Z. Gabelica, G. Giannetto, F. Dos Santos, R. Monque and R. Galiasso, *9th Int. Zeolite Conf.*, Montreal, 5–10 July 1992, paper A-33, in press;
Z. Gabelica, R. Monque and G. Giannetto, US Patent, submitted.
[16] E.G. Derouane, S. Detremmerie, Z. Gabelica and N. Blom, Appl. Catal. 1 (1981) 201.
[17] C.J. Jansen, F.J. van der Gaag and H. van Bekkum, Zeolites 4 (1984) 369.
[18] R. Monque, A. Parisi, S. González and G. Giannetto, Zeolites 12 (1992) 806.
[19] T.H. Fleisch, B.L. Meyers, G.J. Ray, J.B. Hall and C.L. Marshall, J. Catal. 99 (1986) 117.
[20] Q.L. Wang, G. Giannetto, M. Torrealba, G. Perot, C. Kappenstein and M. Guisnet, J. Catal. 130 (1991) 459.
[21] V. Kanazirev, G.L. Price and G. Tyuliev, Zeolites 12 (1992) 846.
[22] T. Changyu, C. Changrui, Z. Lixin and P. Shaoryi, in: *Proc. 9th Int. Congr. on Catalysis*, eds. J.M. Phillips and M. Ternan (The Chemical Inst. of Canada, Ottawa, 1988) p.445.
[23] R. Monque, R. Galiasso, G. Giannetto, J. Papa and Z. Gabelica, in: *Symp. Chemically Modified Molecular Sieves*, Chicago, 25–26 August 1993, ACS Preprints, in press.