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Gallium oxide promoted zeolite catalysts for oxidehydrogenation of propane

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Abstract

Novel gallium-containing catalysts for oxidehydrogenation of propane, based on zeolite Beta, ZSM-5 and ferrierite, have been prepared and characterised by scanning electron microscopy, IR, MAS NMR and Raman spectroscopies. The catalytic properties of zeolitic matrixes with B, Al, and both ions at tetrahedral sites have been studied. Transformation of propane on pure zeolites and promoted with gallium (III) oxide depended on the structure of the matrix, its morphology and the type of cations occupying zeolite framework sites. Formation of new hydroxyl groups has been evidenced for some MFI zeolites promoted with Ga_2O_3.

Keywords: Oxidehydrogenation; Propane; Zeolites; Gallium(III) oxide

1. Introduction

Gallium-containing zeolites constitute a very interesting class of solids from catalytic standpoint. For example, the gallium analogue of ZSM-5 (MFI) is used for transformation of C_3–C_5 alkanes into aromatics [1]. Gallium ions can be substituted into zeolite tetrahedral framework sites either by direct hydrothermal synthesis or via postsynthesis treatment of silica polymorphs or high silica zeolites [2]. It is interesting to note that the mechanical mixtures of the [Si,Al]-ZSM-5 zeolite and Ga_2O_3 after reduction with hydrogen, are active catalysts for dehydrogenation of lower alkanes [3]. Most of the research has been focused on the Ga_2O_3-MFI [4,5] and Ga_2O_3-MEL [6,7] systems, but there is a dearth of information on the interaction of Ga_2O_3 with other zeolites and also little attention has been paid to the *oxidative* dehydrogenation of alkanes on these mixed systems. In a previous work [8], we have studied the Ga_2O_3-faujasite (FAU) system for the oxidehydrogenation of propane. We report here on the physico-chemical properties of gallium oxide promoted catalysts based on different zeolites structures and their application to the title reaction. We explored large- and medium-pore zeolites, i.e., beta (BEA), ZSM-5 (MFI) and ferrierite (FER).

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2. Experimental

2.1. Sample preparation

Zeolite [B,Al]-BEA was crystallised at 423K, calcined and ion-exchanged with NH_4Cl to give the sample with $Si/Al = 94$ and $Si/B = 80$. [B]-MFI sample was prepared with boric acid and ethylorthosilicate at 443K for 48h ($Si/B = 64$, $Si/Al > 2300$). Pentasil samples [B]- and [B,Al]-MFI (F) were synthesized by the "fluoride" route for 10 to 20 days at 433K [2], washed and calcined at 723K.

Ferrierite was synthesized at 473K, calcined, and ion-exchanged with NH_4Cl ($Si/Al = 6.5$). All the zeolitic matrixes were ground in an agate mortar with spectroscopically pure β-Ga_2O_3 (Bi, Cr, Zn, Sn, Al, Co and Fe — the content of each metal $< 10^{-4}$ wt%; In, Mg, Mn, Cu and Pb $< 5.10^{-5}$ wt%; $BET_{Ar} = 2.90\ m^2/g$). The hybrid catalysts containing various amounts of β-Ga_2O_3 were reduced in hydrogen at 773 to 873K. For brevity the samples were labelled as "x Ga/MFI", where x denotes the amount of Ga_2O_3 (wt%) used for the matrix MFI. The samples were heated at a rate of 3K/min in a nitrogen flow (30 cm^3/min). The reduction with hydrogen (20 cm^3/min) was performed for 2h followed by cooling the samples to ambient temperature in a dry N_2 flow.

2.2. Characterisation

High-resolution solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 6.3 T. ^{29}Si MAS NMR spectra were acquired with $\pi/2$ pulses and repetition time of 10 s. ^{27}Al MAS NMR spectra were obtained using very short (1 μs) with 25 kHz B_1 amplitude pulses to ensure that they are quantitatively reliable (recycle delay 0.5 s) [9,10]. The rotors were spun in air at 4 kHz. Chemical shifts for silicon and aluminium are quoted in ppm from external tetramethylsilane (TMS) and $Al(NO_3)_3$.

The IR spectra of the zeolite framework vibration region and in situ experiments were obtained with a Nicolet 800 FT spectrometer (resolution 2 cm^{-1}); the samples were evacuated at 873K and ca. 10^{-7} Torr. Laser Raman FT spectra of the hydrated samples were collected with a Raman module of the Nicolet 800 spectrometer. Sorption of argon was measured in a volumetric sorption unit of standard design; the samples were outgassed at 623K.

2.3. Catalytic tests

Catalyst particles (ca. 0.1 g, 0.25–0.42 mm) were loaded into a tubular, down-flow quartz reactor. SiC chips were placed above the catalyst to give a total bed volume of 1 cm^3. The catalyst was preheated in a flow of dry He (100 cm^3/min) at 773K for 1h. The propane (99.9%)–oxygen (99.99%) mixture diluted with He was fed into the reactor to give a total flow of 100 cm^3/min, $W/F = 4$ g cat. h/gmol C_3 with the propane:oxygen:helium ratio of 12:6:82 (by volume). The conversion of propane was studied at temperatures 673–873 K under the atmospheric pressure. Special precautions have been undertaken to suppress the homogeneous reaction of propane (construction of the microreactor). Reactants and products were analysed on-line with a Varian 3400 gas chromatograph equipped a TCD detector. Mass and carbon balances were within $\pm 5\%$ error.

3. Results and Discussion

The as-prepared samples of zeolite Beta, ferrierite and ZSM-5 were, according to XRD, highly crystalline. ^{29}Si MAS NMR spectra of the samples were typical for BEA, MFI (not shown) and FER (cf. Fig. 4a) structures.

The absorption bands related to the internal vibration of TO_4 tetrahedra (1095, 796, 469 cm^{-1}) and to the external linkage between tetrahedra (1218, 626, 578, 532 and 426 cm^{-1}) in the zeolitic matrixes were found [11]. After calcination followed by ion exchange a part of framework boron in [B,Al]-BEA, seen in IR at

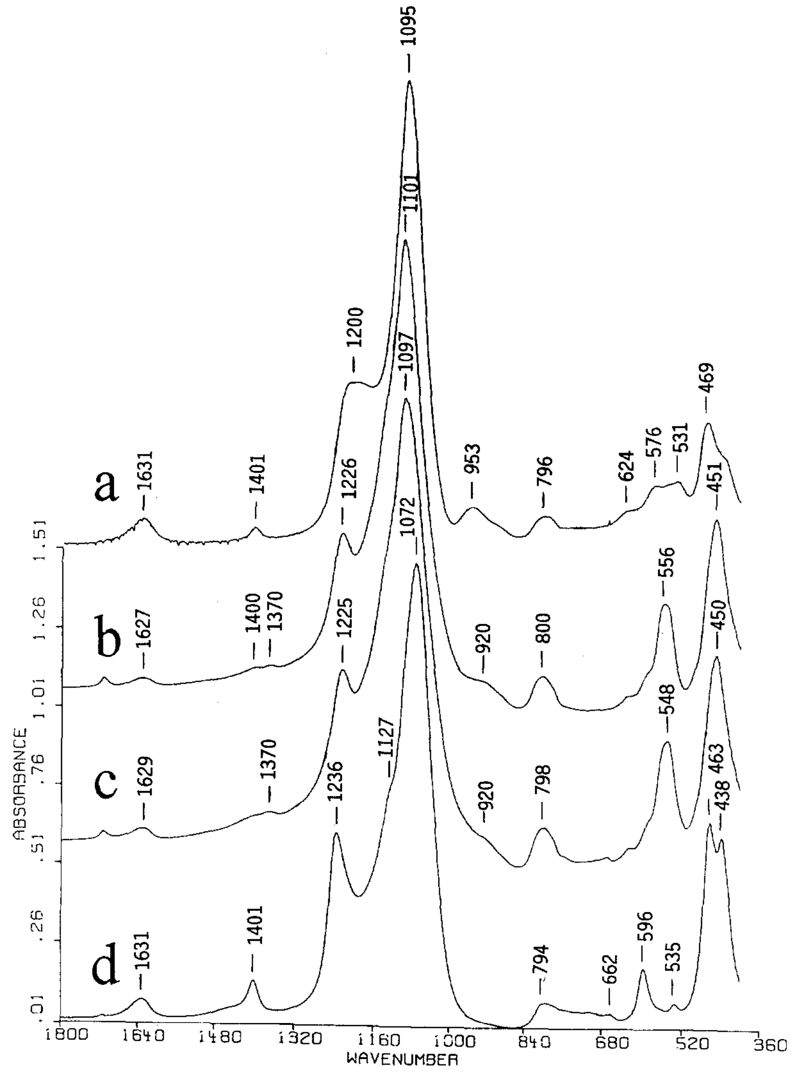

Fig. 1. IR spectra in the framework vibration of: (a) H-[B,Al]-BEA; (b) H-[B]-MFI; (c) H-[B,Al]-MFI (F); and (d) NH_4-FER.

899 cm^{-1}, was removed with the formation of the lattice defects — silanol nests [12] (a new signal at 953 cm^{-1}Fig. 1a). The bands at 1226, 1110, 800, 556 and 451 were found for H-[B]-MFI (Fig. 1b). Three weak signals at 1400, 920 and 700 cm^{-1} are due to B–O vibrations. The stretching B–O vibrations are seen in Fig. 1b, 1c as the shoulders. A spectrum of H-[B,Al]-MFI (F) sample reveals the framework vibration bands at 1225, 1097, 799, 548 and 450 cm^{-1} (Fig. 1c). The spectrum is a very similar to that of [B]-MFI, and substitution of the second heteroatom (Al) is not reflected in the framework vibration region. Finally, the signals of ferrierite were found at 1236, 1072, 794, 596, 536, 463 and 439 cm^{-1} (Fig. 1d), in accord with published data [13]. Note that all the samples investigated display narrow IR bands, due to a highly crystalline material.

Scanning electron microscopy has confirmed all the zeolites are well developed and contain no amorphous phase. Zeolite Beta (Fig. 2a) was prepared as small crystals with the diameter below 0.5 μm. [B]-MFI prepared via an alkaline route consists of aggregates up to 50 μm of tiny 1 μm crystals (Fig. 2b). All the samples of

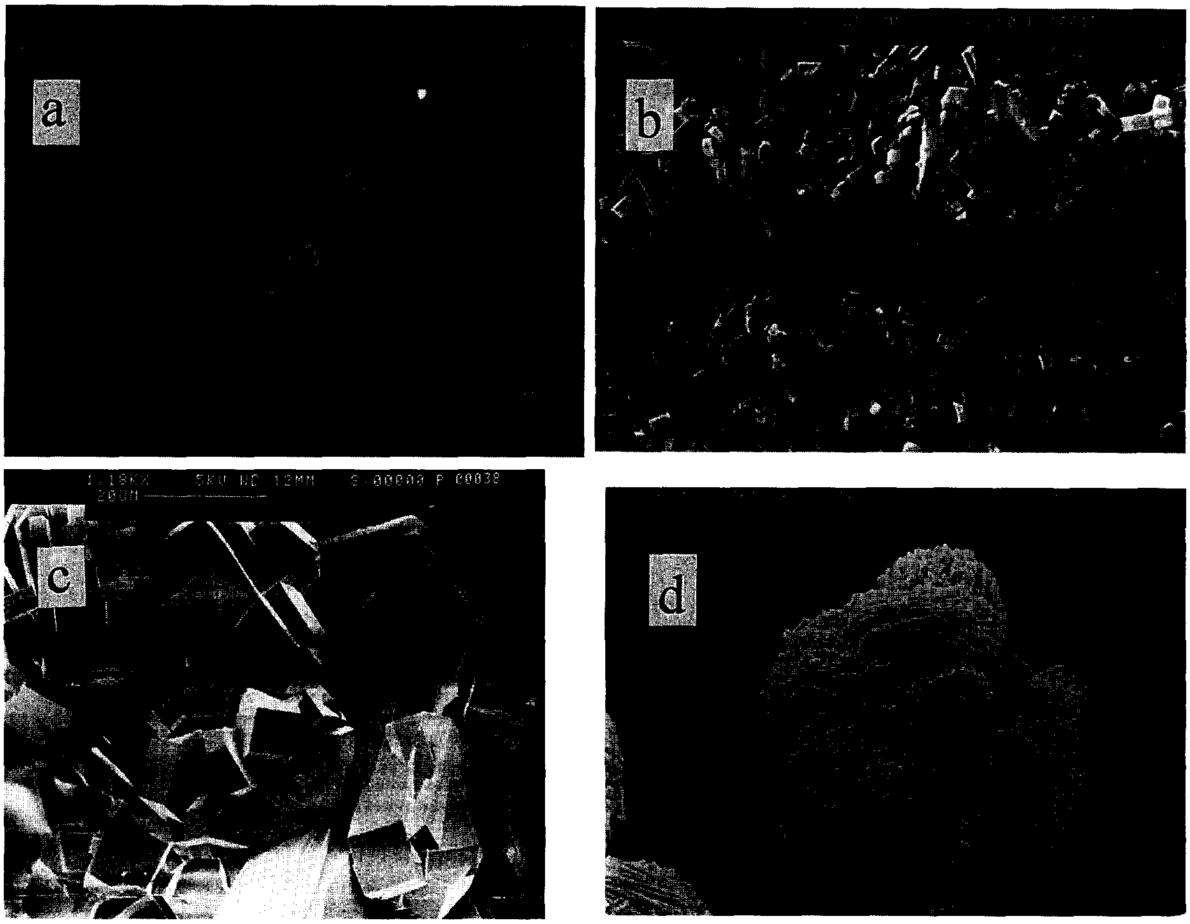

Fig. 2. Scanning electron micrographs of the: (a) [B,Al]-BEA; (b) [B]-MFI; (c) [B,Al]-MFI (F); and (d) FER.

differently substituted MFI (F) display similar morphology (Fig. 2c). The sample consists of elongated, very well developed prism-like crystals (30–40 μm). The morphology of ferrierite is quite different. A very small rod-like, elongated crystals form spheres with the diameter of

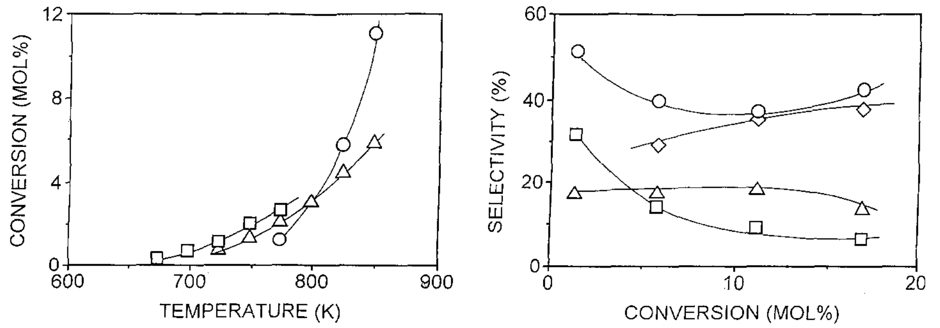

Fig. 3. (a) Conversion of propane on: H-FER (○); and H-FER loaded with 5% Ga_2O_3 (△) and 10.8% Ga_2O_3 (□). W/F = 3.7 g.h./mol C_3 for H-FER and 5 Ga/FER and 9.3 g.h./mol C_3 for 10.8 Ga/FER; (b) Product distribution on H-FER: (◇) C_3H_6; (□) CO_2; (△) CO; (○) cracking.

12 μm (Fig. 2d). As shown by XRD, loading of zeolitic matrixes with gallium oxide (III) followed with reduction by hydrogen, do not affect their crystallinity. After the treatment of precursors with hydrogen, SEM and XRD revealed neither the presence of Ga_2O_3 nor new phases.

3.1. Ferrierite

Conversion and selectivity of the propane transformation over the hydrogen form of ferrierite (H-FER) is shown in Fig. 3. The ferrierite catalysts did not deactivate with time-on-stream. On the contrary, a slight activation was observed: for example, conversion at 823K (5.8 mol%) raised to 7.1 mol% when measured after the first series of tests carried out at 873K. Product distribution was different at the lowest temperature studied (773K) than at the higher one (Fig. 3b). Cracking to methane and ethene and combustion to CO_X were the only reactions observed. However, propene was formed at 823K, with the selectivity increasing with temperature. Selectivity to cracking did not change in this higher temperature range, while that of combustion decreased to 20% at 873K. The modification of ferrierite with gallium oxide led to the two significant effects. First, the overall activity was decreased, especially for 10.8 Ga/FER, for which a higher catalyst charge was needed to obtain a comparable conversion (Fig. 3a). The apparent energies of activation were similar for both samples (86.7 ± 5.9 and 89.6 ± 14.6 kJ/mol versus 146.5 ± 20.9 kJ/mol observed for H-FER). Second, the product distribution was changed: a significant increase of combustion was observed on both catalysts (ca. 60–70% selectivity), while the pathway to propene was completely blocked. Only at 873K a 14% selectivity to propene on 5 Ga/FER was observed. Selectivity of cracking revealed a similar tendency as that observed for H-FER. The BET_{Ar} areas of 5 Ga/FER (243 m^2/g) and 10.8 Ga/FER (213 m^2/g) were lower than that of the parent H-FER (307 m^2/g). This may decrease the activity, but the observed activities at the same temperature on both Ga-containing catalysts were not proportional to their BET areas. As the pore system of ferrierite is smaller than that of the MFI and BEA samples, such a behaviour may be rationalised by assuming more difficult diffusion of gallium species into the internal pore system, and/or blocking of the pore mouth by Ga_xO_y. The access of reactants to these samples is thus restricted.

Three well developed signals at −115.5, −111 and −105 ppm were found in ^{29}Si MAS NMR spectrum of ferrierite (Fig. 4). Silicon spectra of ferrierite often give not well resolved lines, but a broad hump [13,14]. This is due to overlapping of a number of lines, coming from non-equivalent silicon sites (ferrierite was thought to contain 4 such sites). However, a recent study [15] has shown that symmetry is even lower than previously accepted Immm, and five silicon sites were discerned in the structure with the Pmnn symmetry. The line centred around −116 ppm (Fig. 4a) is due to Si(1), Si(3) and Si(5) signals, with no aluminium present in the first co-ordination sphere. The peak at −111 ppm has contributions from Si(2) − and Si(4)-0Al, as well as from Si(1)-, Si(5)-1Al groupings. Finally, the signal at −105 ppm is first of all due to Si(2)- and Si(4)-1Al, with minor contribution arising from Si(1)-, Si(3)- and Si(5)-2Al. As seen, the spectrum of ferrierite is complex, and hence more detailed analysis would be premature. However, the spectrum of gallium-doped sample is strikingly different (Fig. 4c). It is seen that the fraction of the Si(0Al) line of Si(1), Si(3) and Si(5) sites is now higher, and this points out to some decrease of the population of Si(1Al) sites. This means that some aluminium must be expelled from the framework into extra lattice positions, and during such a process Si(1Al) sites are transformed into Si(0Al) ones [16]. Simultaneously, it can be assumed that signals from Si(1Ga) groupings contribute to the peak at −105 ~ −107 ppm. In this way some gallium ions would be accommodated by the ferrierite

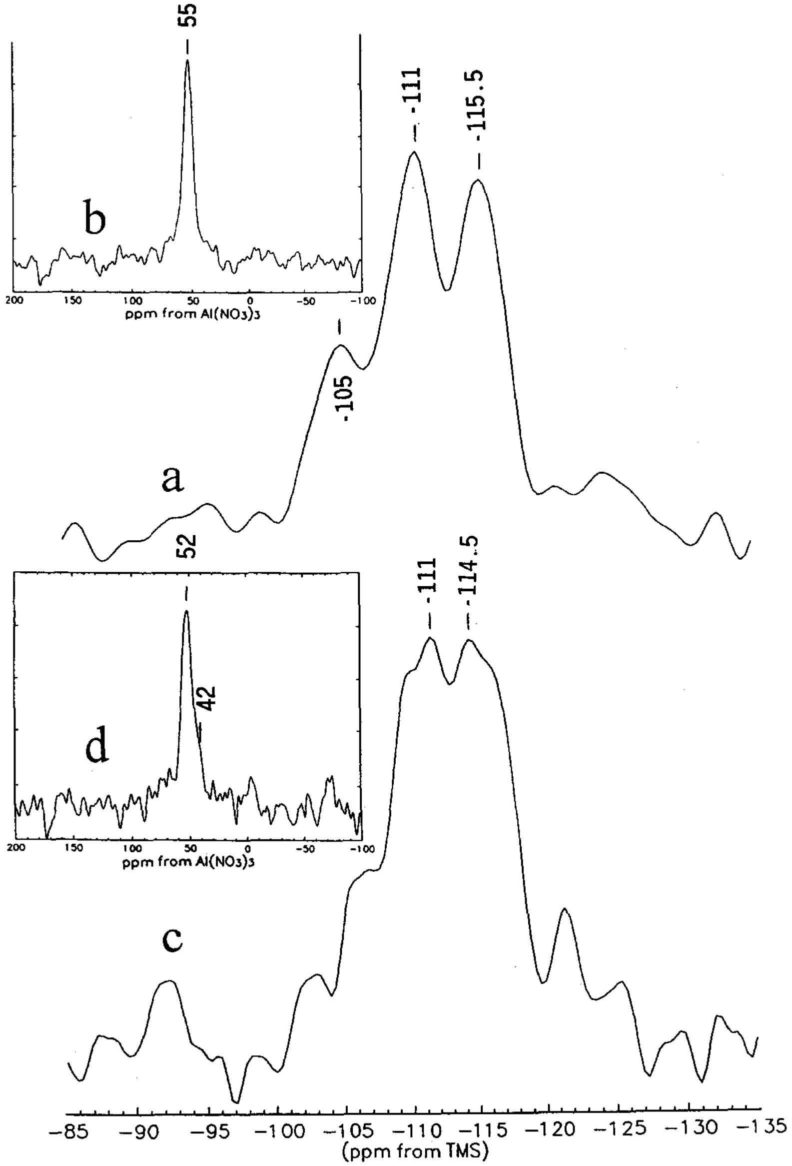

Fig. 4. ^{29}Si and ^{27}Al MAS NMR spectra of ammonium form of ferrierite (a), (b) and the catalyst 10.8% Ga/FER, reduced at 773K for 2h, (c) and (d).

framework sites, as found previously for faujasite [8]. In the ^{27}Al MAS NMR of H-FER only one symmetric signal of the tetrahedrally coordinated framework aluminium was found at 55 ppm (Fig. 4b). In the 5 Ga and 10.8 Ga/FER (Fig. 4d) the line of aluminium has a shoulder at -42 ppm, which we ascribe to non-framework tetrahedrally coordinated aluminium. Its intensity is ca. 15% of the total aluminium signal. The presence of such aluminium species may be responsible for high Brønsted acidity of the sample, evidenced by preponderance of the cracking and combustion products of propane. Finally, no octahedral Al was found in the sample. Most of the Ga species are siting at the pore mouths and, thus, restrict the accessibility of propane to zeolite pore system. Propane interacts mainly with the outer surface of Ga-modified crystals and this is a reason of selectivity pattern found for the ferrierite catalysts.

3.2. ZSM-5

Combustion of propane to CO_2 was the only reaction observed on fresh [B]-MFI below 800K (Table 1). After increasing the temperature to 823K combustion was accompanied by dehydrogenation to propene (54%) and cracking. Then dehydrogenation selectivity was lowered at the expense of cracking and combustion. After the first series of tests, further experiments on the same sample revealed: (i) increase of activity in the range 823–900K; (ii) novel selectivity pattern of propane transformation; and (iii) formation of propene at 773–800K, in addition to CO_2. As the yield to CO_2 was the same on the fresh and used catalyst, it is clear that transformation of the catalyst took place during the tests and a new parallel route for C_3H_8 conversion has been opened. Novel centres were formed by deboronation of the framework and deposition of boron species in the channels took place (^{11}B MAS NMR spectrum — not shown). Cracking of propane on this catalyst is low due to the absence of strong Brønsted acid sites (TPD and IR spectra after adsorption of pyridine showed no acidity).

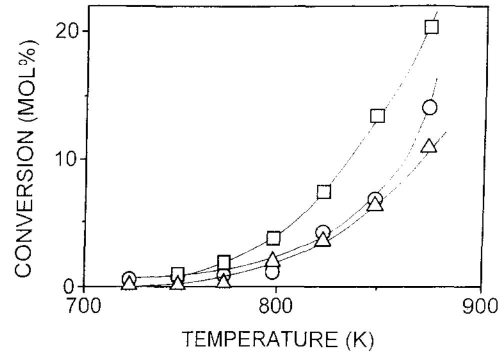

Fig. 5. Conversion of propane on [B]-MFI (○), 5 Ga/[B]-MFI (□) and 5 Ga/[B]-MFI (F) (△).

A promoted 5 Ga/[B]-MFI catalyst ($BET_{Ar} = 428\ m^2/g$) displays higher overall activity (Fig. 5). Contrary to pure [B]-MFI, repeating the test after the high temperature one, affects neither activity nor the product distribution. Obviously, dispersion of gallium oxide in the channels and substitution of gallium in the framework sites must be responsible for such a behaviour. In situ IR experiments revealed that pure [B]-MFI does not contain any Brønsted sites (Fig. 6a). However, the 5Ga/[B]-MFI sample do show hydroxyl groups at about 3617 cm^{-1} which interact with NH_3 (Fig. 6b–6d). We assign these hydroxyls to Si(OH)Ga structural groupings, and this constitutes a direct

Table 1
Conversion X_T and selectivity of propane transformation over [B]-MFI prepared via a conventional synthesis

Temperature T (K)	Conversion X_T (mol%)	Selectivity (%)			
		C_3H_6	CO_2	CO	Cracking
723	0.59		100		
748	0.82		100		
773	0.95		100		
798	1.16		100		
823	4.20	53.6	34.3	6.2	6.0
848	6.82	33.6	29.8	23.5	13.1
873	14.13	28.7	25.7	29.2	16.4
773 [a]	1.56	42.9	52.9	4.3	
798 [a]	2.37	49.1	47.6		3.3
823 [a]	4.73	37.9	34.0	20.8	7.3
848 [a]	7.39	32.5	28.1	23.2	16.2
798 [b]	2.63	44.0	40.9	11.7	3.3

[a] Measured after test at 873K.
[b] Measured after the second series of experiments.

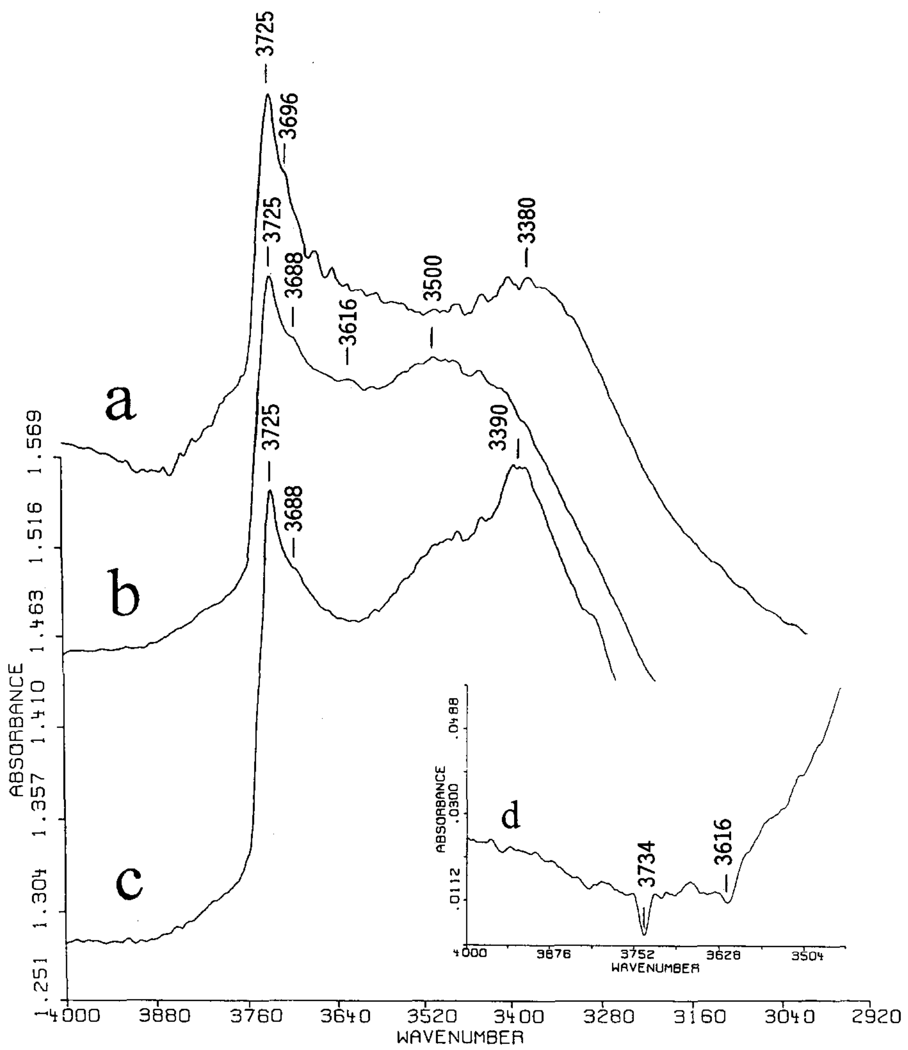

Fig. 6. In situ IR spectra of: (a) [B]-MFI; (b) 5 Ga/[B]-MFI after reduction and (c) after 0.001 T NH_3 adsorption, (d) difference spectrum (c)–(b).

evidence for incorporation of some Ga ions into the framework sites. The presence of ethene and methane in the reaction product already at 848K (1.2% conversion, Fig. 7) is an indirect proof of the strong Brønsted acidity of the catalyst. Much higher temperatures are required to obtain cracking products on the parent [B]-MFI, and only in a minor amounts (below 5%). Second, we observe the formation of CO at 723–873K, instead of CO_2 found for borosilicate. The combustion on 5Ga/[B]-MFI decreases with temperature, with 50% less CO formation. Third, we conclude that strong Brønsted acidity of the zeolitic matrix is not a prerequisite to facilitate the dispersion of gallium oxide on it, because our pure [B]-MFI did not contain such sites. Fourth, the selectivity to propene (ca. 51%) does not change significantly with temperature (Fig. 7). Therefore, doping [B]-MFI with gallium oxide leads, in contrast to ferrierite, to the stabilisation of selectivity to propene and to lowering the combustion to CO_X.

Boron expelled from the lattice of [B]-MFI forms extra framework boron oxide species as a finely dispersed phase. Framework defects which are formed in this way can catalyse trans-

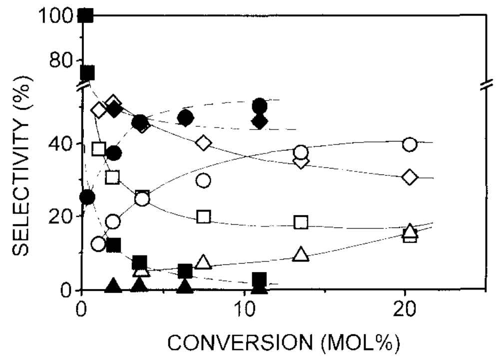

Fig. 7. Product distribution on 5 Ga/[B]-MFI: (◇) C_3H_6; (□) CO_2; (△) CO; (○) cracking; and on 5 Ga/[B]-MFI (F): (◆) C_3H_6; (■) CO_2; (▲) CO; (●) cracking.

formation of alkyl aromatic hydrocarbons [17]. Cracking observed on pure borosilicate is therefore due to extra framework boron oxide species and/or lattice defects. The defects are healed progressively with the reaction time (water facilitates this process). The change of boron framework/boron extra framework ratio with time is slow enough to be detected during the catalytic runs and it affects the overall conversion of propane. We presently investigate this in more details.

Aluminium-free borosilicate prepared by a "fluoride" route formed large crystals. The 5Ga/[B]-MFI(F) sample ($BET_{Ar} = 353$ m^2/g) was inactive up to 773K; only traces of CO_2 were present (Fig. 5). Dehydrogenation and cracking of propane commences at 798K (Fig. 7). We observed a slight activation of the catalyst after repeating the test cycle. Selectivity to propene was high (44–50%) and stable in the temperature range studied (Fig. 7). Total combustion on this sample was suppressed and decreased with temperature. Cracking of propane was significant over this catalyst, higher than over Ga/[B]-MFI (small crystals), and points to the presence of strong Brønsted acidity. Such centres can be formed by insertion of gallium ions into framework positions and generating thereby sites Si(OH)Ga, as discussed above. Total conversion on a large crystals sample is lower than on the catalyst prepared conventionally, possibly due to longer paths of reactants in the former. Nevertheless, the activation energies were similar for both samples: 133.1 ± 2.9 kJ/mol for small crystals (conventional synthesis) and 130.2 ± 8.4 kJ/mol for large crystals ("fluoride" route), indicating that the reaction probably proceeds on the same centres in both catalysts.

The zeolitic matrix [B,Al]-MFI (F) displayed very strong Brønsted acidity due to the Si(OH)Al groupings. After loading with Ga_2O_3 formation of some Si(OH)Ga centres would increase the Brønsted acidity further. The reaction of propene commences at 723K, and products of cracking and combustion are present. Increasing the temperature gives rise to: (i) lowering the combustion (from 54% at 723K to 30% at 873K); (ii) decreasing the selectivity of propene formation (from 57 to 35%), and (iii) increasing the cracking of propane (23 to 36%). However, the catalyst deactivated very quickly at the higher temperature: conversion at 823 decreased from 3.2% to 1.8% after the test at 873K. The strong acidity of zeolite matrix itself is responsible for high combustion and cracking, and should be avoided. As the morphology of both samples prepared in the presence of F^- ions is similar, we can conclude that the ZSM-5 matrix with both Al and B in the framework is less effective in the dehydrogenation of propane that one containing boron only. The Ga/[B]-MFI system seems therefore to be the most promising one for oxyfunctionalisation of propane.

3.3. Beta

The initial conversion of propane on H-[B,Al]-BEA sample at W/F = 9.3gr.h./mol at 723K was 3.2%, with a selectivity to propene 80%, the rest being CO_X. However, the sample deactivated quickly and we observed ca. 25% lost of its initial conversion after already 1 hour on stream (carbonaceous deposits were formed on the sample). The deactivation affected mostly the path route to propene and its yield dropped

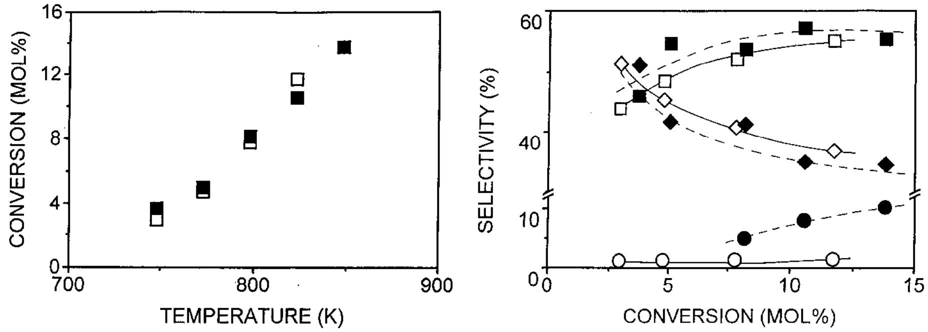

Fig. 8. Conversion (a) and selectivity (b) of propane transformation on H-[B,Al]-BEA (□) and 10.8 Ga/H-[B,Al]-BEA red. (■); (◇) C_3H_6; (□) CO_2; (○) cracking. Closed symbols denote product distribution for the second sample.

by one third during this period. Ethene was also formed at higher temperatures, but the cracking selectivity never exceeded 10%. The activity of 10.8 Ga/[B,Al]-BEA was stable with time-on-stream (TOS); further tests using revealed no changes in conversion and selectivity at various temperatures (Fig. 8a). The apparent activation energy was 92.9 ± 3.8 kJ/mol. The 50% initial selectivity to propene decreased with the conversion at the expense of combustion (Fig. 8b). A very low selectivity of cracking was observed on this sample (< 1.5%).

Reduction of 10.8 Ga/[B,Al]-BEA with H_2 gave essentially the same product distribution (Fig. 8a), with more cracking products found at high temperature range. This means that reduction has not affected the nature of the active centres. The BET area of H-[B,Al]-BEA equal to 627 m^2/g was decreased to 360 m^2/g upon mixing with β-Ga_2O_3 and fully restored by reduction with hydrogen (614 m^2/g). Steric hindrance is thus removed by high dispersion of gallium oxide species. This is confirmed further by Raman studies. In FT Laser Raman spectrum of 10.8 Ga_2O_3/[B,Al]-BEA the bands characteristic for the gallium oxide are seen. After reduction features characteristic for the bulk oxide disappear and the lines resemble those found for Ga_2O_3 reduced with Ga metal (Fig. 9b).

Calcination of B-containing zeolites results in expelling of the framework boron into the extra framework positions [2]. Deboronation is accompanied by the formation of internal silanols (hydroxyl "nests") which can accommodate gallium ions. Such a process postulated in this work for Ga_2O_3/FER and Ga_2O_3/MFI has been already evidenced for faujasite [8], another zeolite with open structure. However, no band of the OH groups bound to the tetrahedrally coordinated framework Ga was found in the IR spectrum of 10.8 Ga/[B,Al]-BEA. The bridging hydroxyl groups Si(OH)Al are the only species responsible for the strong acidic properties in this sample. The observed decrease in the num-

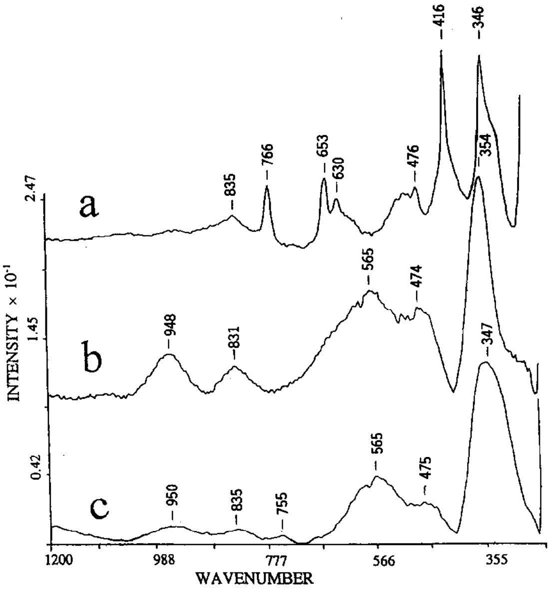

Fig. 9. Raman spectra of: (a) β-Ga_2O_3; (b) β-Ga_2O_3 reduced with stoichiometric amount of Ga under vacuum at 873K; (c) 10.8 Ga/H-[B,Al]-BEA reduced with H_2 at 873K for 2h.

ber of the internal silanols in the sample after hydrogen treatment can be explained by annealing of these sites. Formation of the framework gallium species in zeolite Beta, even if occurs, is below the limit of the IR experiment. The tests with Beta catalysts can be now compared with those on other wide-pore zeolitic matrix, i.e., faujasite (FAU). The undoped ultrastable zeolite US-Y is an active catalyst in the oxidative transformation of propane [8], with no deactivation with TOS. By comparing the present results for 10.8 Ga/[B,Al]-BEA with those for 5 Ga/FAU [8] one can immediately see that gallium oxide exerts a similar effect: it stabilizes the activity of the solid at the cost of lower selectivity to propene (due to combustion). Intrinsic activity of 5 Ga/FAU was higher (34 versus 23 mol/h.m^2 at 798K). However, the selectivity to propene at the isoconversion is about 10–15% higher on the 10.8 Ga/[B,Al]-BEA catalyst. The difference is due to the suppressed selectivity towards products of cracking on the Beta catalyst.

4. Conclusions

Transformation of propane on pure zeolites and promoted with gallium oxide depended on the structure of zeolite and, in the MFI series, also on the nature of cations siting at the framework positions. Dehydrogenation selectivity to propene (SD) was moderate on the as-prepared Ga_2O_3/Beta, and the activity of this sample was stable with time-on-stream (TOS). The reduction with hydrogen increased overall activity and cracking, but did not modify SD. Cracking and combustion to CO_X were the only reactions observed on H-ferrierite below 823K. Loading the sample with gallium oxide reduced activity of the solid and led to total combustion and cracking. This behaviour was explained as being due to rearrangement of the ferrierite framework and restricted access to the internal pore system. An unexpectedly changed product distribution observed on [B]-MFI above 800K, was related to a migration of boron out of the zeolite framework. We found spectroscopic evidence for, at least for some samples, formation of novel hydroxyl groupings of the type Si(OH)Ga. This was observed for boron containing MFI zeolites, and possibly ferrierite. On the other hand, the formation of such groups in zeolite [B]-BEA was not observed, or was below the detection limit of IR experiment. Finally, a detrimental influence of the aluminium on the propane transformation has been shown in the experiments with the [B,Al]-MFI type catalysts.

Acknowledgements

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