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Improved catalytic activity upon Ge incorporation into ZSM-5 zeolites

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Abstract

The catalytic stability of ZSM-5 can be greatly improved by the isomorphous substitution of some Si atoms by Ge. The catalytic properties of Ge-ZSM-5 zeolites have been compared to ZSM-5 in a series of acid-catalysed test reactions (the dehydration of 2-propanol and 2-butanol, the isomerisation of isobutyraldehyde to 2-butanone, and the Friedel–Crafts acylation of anisole). The propene yield in the 2-propanol dehydration reaction at 180 °C is as high as 98% for Ge-ZSM-5 and only 40% for ZSM-5. For the other investigated reactions similar differences are observed. The presence of a considerable amount of mesopores in Ge-ZSM-5 (compared to ZSM-5) is proposed to be the main explanation for the difference. These mesopores are formed upon synthesis and reduce the effect of pore blocking by coke residues that are formed at high reaction temperatures.

Keywords: ZSM-5; Germanium; Isomorphous substitution; Mesoporosity; Acid catalysis; Alcohol dehydration; Isomerisation

1. Introduction

Zeolites are extensively used as shape-selective solid acid catalysts in many industrial processes [1]. Factors such as framework type and Si/Al ratio determine the porous the acid-base and, hence, the catalytic properties, of the material. The framework acidity can be modified by variation of the Si/Al ratio of the zeolite, by variation of the framework type, or by substitution of Al by other trivalent elements. In the case of ZSM-5, the incorporation of trivalent elements such as B, Fe, and Ga has been reported [2–4]. The framework acidity is generally believed to decrease in the order Al-ZSM-5 > Ga-ZSM-5 > Fe-ZSM-5 > B-ZSM-5 [5,6]. Modification of the framework acidity may lead to materials with improved catalytic properties. For example, B-ZSM-5 has been reported to give higher yields in the isomerisation of aldehydes to ketones than ZSM-5 [7], as less deactivation occurs on B-ZSM-5 due to its lower acidity. Substitution of Al atoms is not the only type of isomorphous substitution that modifies the catalytic properties of a zeolite, as is illustrated by the effect of Si substitution by (tetravalent) Ge atoms. The introduction of 0.2 wt% Ge in the epoxidation catalyst TS-1 has been reported to result in a substantial increase in catalytic activity [8]. Na(Ge)-X has been used in base-catalysed reactions and showed increased catalytic activity compared to Na-X [9]. The catalytically active sites are in these cases influenced by the incorporation of T atoms that do not generate catalytic centres themselves.

Several papers on the isomorphous substitution of Si by Ge have appeared recently. For example, Ge has been used in zeolite syntheses to facilitate the formation of structures that cannot be obtained otherwise. Polymorph C of zeolite beta, which cannot be obtained with only Si and Al in the framework, was synthesised from reaction mixtures containing GeO_2 [10,11].

In this paper, investigations of the effect on the acidic catalytic properties of partial substitution of Si by Ge in (Al)-ZSM-5 are reported. The incorporation of Ge in the MFI framework was described for the first time by Gabelica and Guth [12]; however, as no Al atoms were present in these materials, no effects on catalytic properties could be studied. The synthesis and characterisation of a series of Ge-substituted ZSM-5 samples (with both Al and Ge in the framework) have been reported previously [13]. Ge incorpo-

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Table 1
Properties of zeolite samples (sample numbers correspond to numbers in the figures)

Sample number	Code	Ge/[Ge + Si] gel	Ge/[Ge + Si] product	[Si + Ge]/Al gel	[Si + Ge]/Al product	S_{BET}[a] (m^2/g)	V_{tot}[a] (cm^3/g)	V_{micro}[a] (cm^3/g)	S_{meso}[a] (m^2/g)	$(S_{meso}/S_{BET}) \times 100$
1	ZSM-5(47)	0	0	29.5	47	369	0.19	0.17	15	4.1
2	Ge(0.04)ZSM-5(49)	0.05	0.04	29.5	49	374	0.19	0.16	24	6.6
3	Ge(0.06)ZSM-5(58)	0.10	0.06	29.5	58	398	0.22	0.16	36	9.1
4	Ge(0.09)ZSM-5(36)	0.20	0.09	29.5	36	410	0.27	0.15	75	18.3
5	ZSM-5(55)	0	0	29.5	55	375	0.20	0.15	6	1.7
6	Ge(0.04)ZSM-5(63)	0.05	0.04	29.5	63	394	0.21	0.15	21	5.3
7	Ge(0.07)ZSM-5(61)	0.10	0.07	29.5	61	394	0.21	0.16	22	5.5
8	Ge(0.08)ZSM-5(47)	0.15	0.08	29.5	47	383	0.23	0.14	34	8.8
9	Ge(0.11)ZSM-5(41)	0.20	0.11	29.5	41	391	0.26	0.14	48	12.2
10	B-ZSM-5(53)	0	0	29.5[b]	53[b]	355	0.20	0.15	20	5.6
11	Silicalite-I	0	0	∞	∞	332	0.18	0.16	7	2.1
12	Ge(0.05)Silicalite-I	0.05	0.05	∞	∞	363	0.20	0.18	11	2.8
13	Ge(0.07)Silicalite-I	0.10	0.07	∞	∞	354	0.20	0.18	15	4.0

Molar atomic ratios of the products were determined by ICP-OES.

[a] Values are normalised for changes in density due to Ge incorporation.

[b] [Si + Ge]/B instead of [Si + Ge]/Al.

ration appears to increase the mesoporosity of the materials, as well as the number of defects and hydroxyl groups, while having only a very small effect on the strength of the acid sites. The combination of micropores and mesopores is very interesting from a catalytic point of view. Large molecules can easily enter the material via the mesopores to be converted into smaller molecules, which may react further in the micropores [14]. Here we report the effect of Ge incorporation on the catalytic properties of ZSM-5 in acid-catalysed reactions, the investigated reactions include the dehydration of 2-propanol and 2-butanol, the isomerisation of isobutyraldehyde to 2-butanone, and the Friedel–Crafts acylation of anisole.

2. Experimental

2.1. Zeolite synthesis

The synthesis and characterisation of Ge-ZSM-5 with different Ge/[Ge + Si] ratios have been reported previously [13]. The main characteristics of the Ge-ZSM-5 samples are summarised in Table 1. Ge-Silicalite-I was prepared according to Kosslick et al. [15].

B-ZSM-5 was prepared according to Shibata and Gabelica [16]. The amount of 7.41 g LUDOX HS 40 (Aldrich) (49.33 mmol SiO_2) was mixed with 3.28 g (21.33 mmol) tetrapropylammonium bromide (TPABr, obtained from CFZ Zaltbommel), 11.49 g methylamine solution (40 wt% in water (Aldrich), 148 mmol methylamine), 0.102 g H_3BO_3 (Aldrich, 1.63 mmol) and 5 g water. The mixture was stirred for 1 h at room temperature and was then transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C. After 42 h, the autoclave was cooled and the product was isolated by filtration and thoroughly washed with water. The product was calcined under a constant flow of ammonia (600 °C, 1 h), according to the optimised calcination procedure for B-ZSM-5 by De Ruiter [17]. After cooling to room temperature, the light brown sample was ion-exchanged with a 0.1 M $NaNO_3$ solution (three times) and then calcined in air at 550 °C (6 h). The NH_4^+ form was obtained after ion exchange with 0.1 M NH_4Cl (three times). ^{11}B NMR confirmed the presence of the B atoms in framework positions. The main characteristics of the B-ZSM-5 sample (after calcination) are reported in Table 1.

2.2. Catalyst preparation

Catalyst particles in the range from 180 to 250 µm were used for all gas-flow reactions. To this end, the zeolites (in NH_4^+ form) were pressed in to pellets and subsequently crushed and sieved. 25 mg of these catalyst particles was then mixed with SiC particles (50 mg) of similar size. The samples were calcined at 500 °C (6 h) prior to reaction. For the regeneration experiments, catalyst particles were regenerated between cycles by calcination in air at 500 °C (6 h). For the acylation reaction of anisole, zeolite crystals (H^+ form) were ground for different lengths of time and were activated at 500 °C (6 h) prior to reaction.

2.3. Catalytic reactions

Dehydration of 2-propanol and 2-butanol and isomerisation of isobutyraldehyde were performed in a reactor block containing 16 miniaturised gas-flow reactors (internal diameter of 5 mm), which required only small amounts (25 mg) of catalyst. In order to test the reproducibility of the reactions, all experiments were performed in triplicate (thereby randomly distributing the different catalysts over the 16 reactors and applying different gas-flow rates for the feed). These multiple experiments revealed a very high degree of reproducibility of the reactions. The reactor block was coupled to an on-line gas chromatograph (TRACE 2000, equipped with a FID detector) which analysed each of the gas flows at regular intervals and at variable, regulated temperatures. GC samples were taken in the gas phase by means of a bypass loop leading to the GC. All lines involved were properly insulated to avoid undesired condensation of the sample in the lines. Conversion, yield, and selectivity data of the reactions are all relative data. The gas feed for the alcohol dehydration reactions consisted of a N_2/2-propanol or N_2/2-butanol mixture generated by leading a N_2 flow through a 2-propanol- or 2-butanol-containing saturation vessel, respectively. Similarly, an Ar/isobutyraldehyde mixture was used for the isomerisation reaction. Acetylation of anisole with acetic anhydride was performed under an inert nitrogen atmosphere in the liquid phase by mixing dry anisole (0.995 g, 9.20 mmol) and dry acetic anhydride (0.940 g, 9.20 mmol) with 200 mg of calcined (500 °C) ground zeolite and 200 mg of 1,3,5-tri-*tert*-butylbenzene (internal standard for GC analysis). The mixture was heated in an oil bath at 120 °C and samples for GC analysis were taken at regular intervals.

3. Results

3.1. Dehydration of 2-propanol

Dehydration of 2-propanol was investigated in the temperature range from 90 to 180 °C. The conversion and propene selectivity data for a series of (Ge)-ZSM-5 samples are shown in Figs. 1a and b (WHSV $= 3.5\ h^{-1}$). The Ge and Al contents of each sample are given in parentheses: Ge(0.04)ZSM-5(49) indicates a $Ge/(Ge + Si)$ ratio of 0.04 and a $(Si + Ge)/Al$ ratio of 49. In the temperature range up to 150 °C no significant differences in conversion and selectivity are observed between different samples: conversion values rapidly increase with T, and the propene selectivity increases from around 60% (at 90 °C) to almost 100% (at 150 °C) for all catalysts. The small differences in conversion values of the four catalysts can be explained by the slightly different $(Si + Ge)/Al$ ratios: 36 for Ge(0.09)ZSM-5(36) and 58 for Ge(0.06)ZSM-5(58). Diisopropyl ether is the only side product for all catalysts.

Differences in catalytic behaviour are observed above 150 °C, where the conversion values of all catalysts initially decrease. This is probably due to deactivation of some of the catalytically active sites by coke residues. Ge(0.09)ZSM-5(36), however, shows only a small drop in conversion at 160 °C (compared to that at 150 °C), and at higher temperatures the conversion increases further to a value of 99% at 180 °C. The increase of the activity over all catalysts at temperatures of 170 °C and higher is probably due to the higher activity of the remaining sites at these temperatures, compared to their activity at 150 °C. In other words, the loss in catalytic activity is (partly) compensated by an increased activity of the remaining sites. The reaction was monitored for 3 h at 180 °C and no deactivation was observed for this catalyst. In contrast, ZSM-5(47) appears to be seriously deactivated at temperatures above 150 °C, the conversion at 180 °C being only 41%. Ge(0.06)ZSM-5(58) shows intermediate behaviour: some deactivation at 160 °C and a final conversion of 61% at 180 °C. Ge(0.04)ZSM-5(49) behaves in a similar way to ZSM-5(47). The selectivity of all catalysts remains between 98 and 100% above 150 °C. The colour of the zeolites after reaction varies from off white [ZSM-5(47)] to yellow [Ge(0.09)ZSM-5(36)].

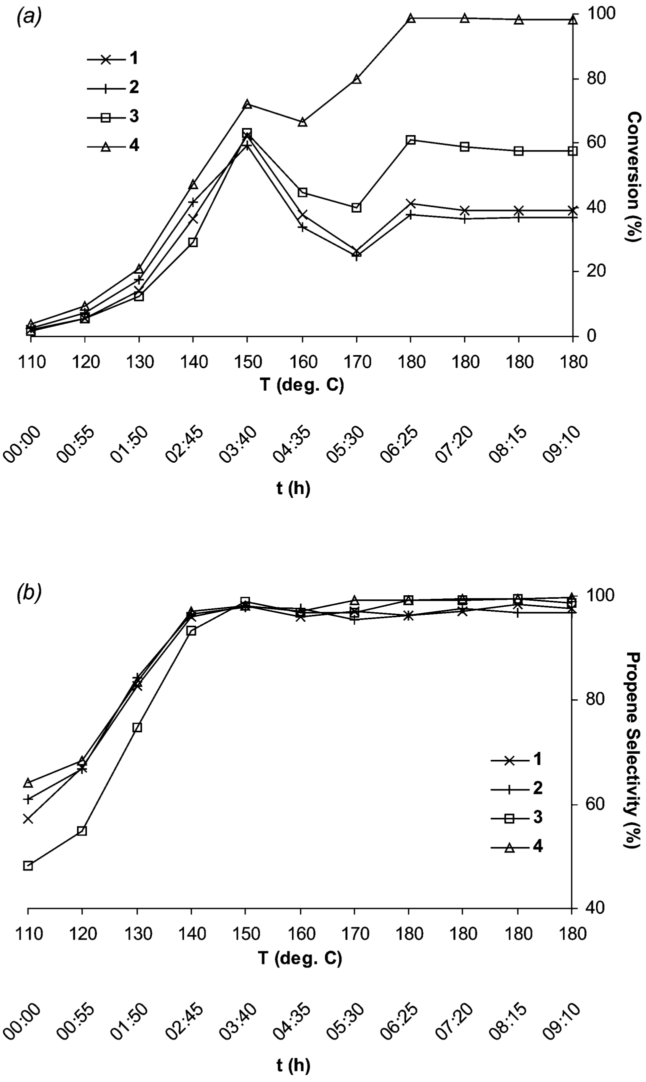

Fig. 1. Conversion (a) and propene selectivity (b) of the dehydration reaction of 2-propanol by (1) ZSM-5(47), (2) Ge(0.04)ZSM-5(49), (3) Ge(0.06)ZSM-5(58), and (4) Ge(0.09)ZSM-5(36) as a function of temperature and total time on stream. WHSV $= 3.5\ h^{-1}$.

After the reaction, catalysts were regenerated by calcination in air at 500 °C (6 h) and were reused in the same reaction. The results after regeneration for Ge(0.04)ZSM-5(49), Ge(0.06)ZSM-5(58), and Ge(0.09)ZSM-5(36) (three runs in each case) are depicted in Fig. 2. It appears that the high activity of the catalysts with high Ge contents is not retained after the first run, instead a drop of the conversion over Ge(0.09)ZSM-5(36) at 180 °C from 95% in the first run to 79% in the third run is observed. In contrast, the conversion over Ge(0.04)ZSM-5(49) remains constant (at a level of 37%

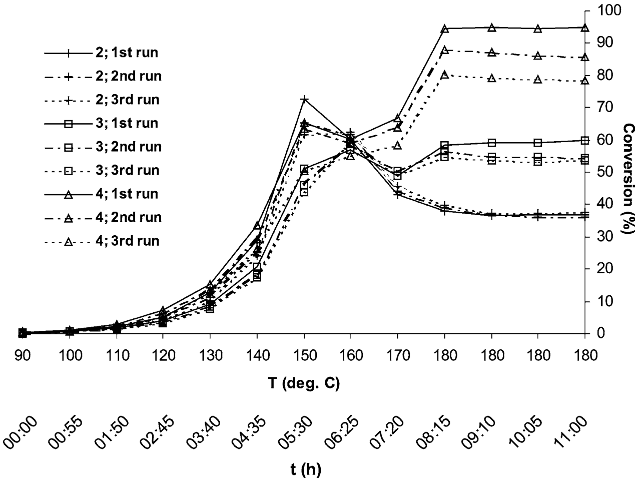

Fig. 2. Conversions in the 2-propanol dehydration reaction by (2) Ge(0.04)ZSM-5(49), (3) Ge(0.06)ZSM-5(58), and (4) Ge(0.09)ZSM-5(36) as a function of temperature and total time on stream. Samples were calcined at 500 °C after each run. WHSV = 10.8 h^{-1}.

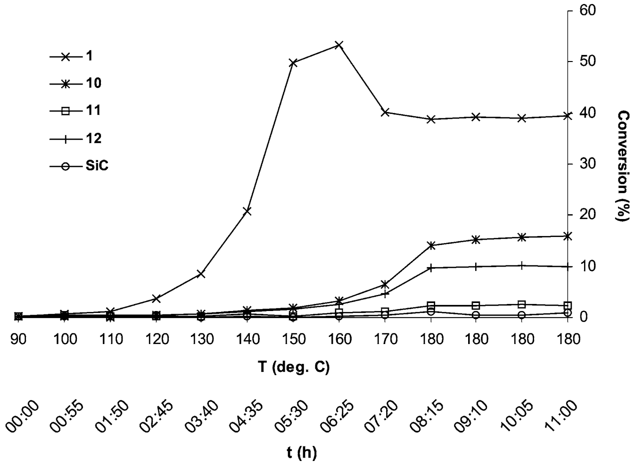

Fig. 3. Conversions in the 2-propanol dehydration reaction by (10) B-ZSM-5(53), (11) Silicalite-I, (12) Ge(0.05)Silicalite-I, and SiC as compared to (1) ZSM-5(47). WHSV = 10.8 h^{-1}.

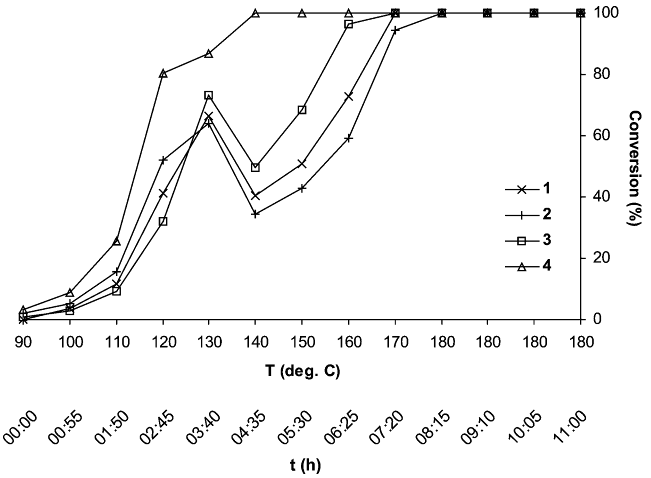

Fig. 4. Conversions in the 2-butanol dehydration reaction by (1) ZSM-5(47), (2) Ge(0.04)ZSM-5(49), (3) Ge(0.06)ZSM-5(58), and (4) Ge(0.09)ZSM-5(36) (Ge)-ZSM-5 as a function of temperature and total time on stream. WHSV = 1.5 h^{-1}.

at 180 °C) over three runs, as is the case for ZSM-5(47) (not shown). These multiple-cycle experiments were performed with a WHSV of 10.8 h^{-1}, which is much higher than in the experiments presented in Fig. 1 (WHSV of 3.5 h^{-1}). The effect of this difference on the catalytic activity is relatively small, as can be deduced from the small difference between Fig. 1a and Fig. 2 (first run results).

After the third run, XRD diffractograms were recorded (at room temperature) in order to detect differences in zeolite crystallinity and composition upon the catalytic reaction. (The introduction of Ge changes the crystal symmetry of the MFI framework at room temperature from monoclinic (ZSM-5) to orthorhombic (Ge-ZSM-5 with $\mathrm{Ge}/(\mathrm{Ge}+\mathrm{Si}) > 0.07$) [13]. This phase transition is expressed in a splitting of the orthorhombic 1 3 3 peak ($d = 3.6391$) into 3 1 3 and 3 1 3 peaks for the monoclinic form. The extent of Ge incorporation in the framework can therefore be deduced from the shape of this/these peak(s) [13].) Comparison of the XRD patterns of catalyst samples before reaction (H^+ form) with calcined samples after the third catalytic run (also in the H^+ form, recorded at room temperature) indicates no loss of Ge from the framework, as no changes indicative of different crystal symmetry are observed.

For the sake of comparison, B-ZSM-5(53), Silicalite-I, Ge(0.05)Silicalite-I, and SiC (as a nonreactive reference material) samples were tested in the dehydration reaction of 2-propanol; see Fig. 3. As expected, the absence of strong acid sites in these samples results in very low conversions compared to the (Ge-)ZSM-5 samples. All zeolite samples were white after the reaction.

3.2. Dehydration of 2-butanol

The dehydration of 2-butanol was investigated in the same temperature range as the 2-propanol dehydration (90–180 °C). The conversions for a range of (Ge)-ZSM-5 samples are depicted in Fig. 4. The selectivity toward butenes (1-butene, *cis*-2-butene and *trans*-2-butene) is 100% for all catalysts and at all investigated temperatures. The distribution of butene products is very similar for these four zeolites and is not a function of the temperature, the 1-butene:*trans*-2-butene:*cis*-2-butene ratio being around 11:55:34. This isomer distribution is similar to the equilibrium composition of 8:63:29, but different from the distribution found by others in ZSM-5 catalysed 2-butanol dehydration reactions [18]. No dibutyl ether could be detected, although it cannot be excluded that some ether product was formed, as desorption of such species may be hindered for steric reasons. Dibutyl ether formation is known to be a considerable side reaction in the dehydration of n-butyl alcohol [19]. The situation for the 2-butanol dehydration reaction is somewhat different, however, due to the higher reactivity of di-2-butyl ether compared to di-n-butyl ether [18]. The 2-butanol conversion

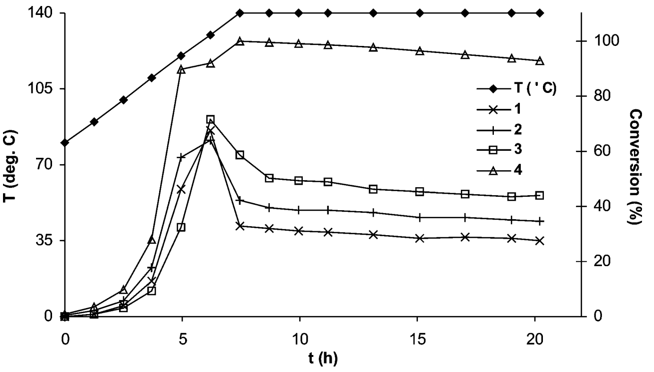

Fig. 5. Conversions in the 2-butanol dehydration reaction by (1) ZSM-5(47), (2) Ge(0.04)ZSM-5(49), (3) Ge(0.06)ZSM-5(58), and (4) Ge(0.09)ZSM-5(36) at prolonged reaction time at 140 °C. WHSV = 1.5 h^{-1}.

values (Fig. 4) are much higher than those for 2-propanol dehydration (Fig. 1a), which is due to the higher WHSV in that case (3.5 h^{-1} in the 2-propanol dehydration versus 1.5 h^{-1} in the 2-butanol dehydration). At 180 °C, complete conversion of 2-butanol is observed for all tested catalysts, albeit that Ge(0.09)ZSM-5(36) reaches this conversion level at a much lower temperature (140 °C) than ZSM-5(47), Ge(0.04)ZSM-5(49), and Ge(0.06)ZSM-5(58). The conversion at 140 °C was further investigated by monitoring the reaction at this temperature for 14 h (Fig. 5). Upon heating from 80 to 130 °C the conversion increases in all cases, following a common pattern. Again, the small differences in conversion values originate from the slightly different Al contents of the zeolites. Above 130 °C, deactivation of ZSM-5(47), Ge(0.04)ZSM-5(49), and Ge(0.06)ZSM-5(58) clearly occurs, as the conversion drops from 63% [ZSM-5(47)] and 71% [Ge(0.06)ZSM-5(58)] at 130 °C to 33% [ZSM-5(47)] and 59% [Ge(0.06)ZSM-5(58)] at 140 °C, respectively. In contrast, by increasing the temperature from 130 to 140 °C the conversion by Ge(0.09)ZSM-5(36) increases from 92 to 100%. Upon reaction at 140 °C for 14 h, a slight decrease in activity was observed for all catalysts: from 100 to 93% for Ge(0.09)ZSM-5(36), from 59 to 44% for Ge(0.06)ZSM-5(58), from 42 to 34% for Ge(0.04)ZSM-5(49), and from 33 to 27% for ZSM-5(47), respectively.

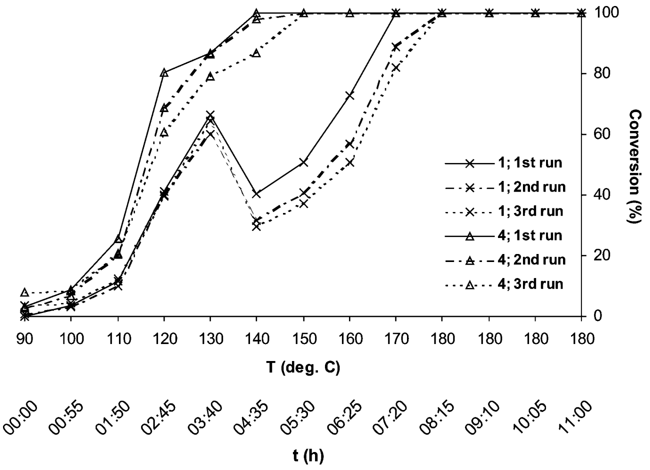

Fig. 6. Conversions in the 2-butanol dehydration reaction by (1) ZSM-5(47) and (4) Ge(0.09)ZSM-5(36) as a function of temperature and total time on stream. Samples were calcined at 500 °C after each run. WHSV = 1.5 h^{-1}.

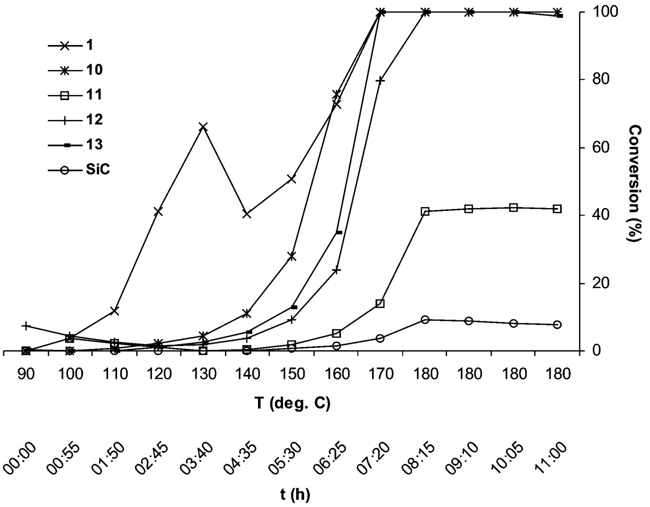

Fig. 7. Conversions in the 2-butanol dehydration reaction by (10) B-ZSM-5(53), (11) Silicalite-I, (12) Ge(0.05)Silicalite-I, (13) Ge(0.07)Silicalite-I, and SiC as compared to (1) ZSM-5(47). WHSV = 1.5 h^{-1}.

The regeneration characteristics of ZSM-5(47) and Ge(0.09)ZSM-5(36) have been investigated by using the same catalyst particles in three consecutive runs; see Fig. 6. Both catalysts lose some activity upon regeneration, but this is to a much smaller extent compared to that of Ge(0.09)ZSM-5(36) in the 2-propanol dehydration. XRD analysis of samples after the third run revealed no change in crystal symmetry (and thus no loss of Ge from the framework). The conversion data for B-ZSM-5(53), Silicalite-I, Ge(0.05)Silicalite-I, Ge(0.07)Silicalite-I, and SiC are depicted in Fig. 7. When the results are compared with those in Fig. 3, it becomes immediately clear that the activity of B-ZSM-5, Ge-Silicalite-I, Silicalite-I, and even SiC is much higher in the 2-butanol dehydration than in the 2-propanol dehydration, probably due to the difference in WHSV.

3.3. *Isomerisation of isobutyraldehyde to 2-butanone (MEK)*

Isobutyraldehyde isomerisation was investigated in the temperature range from 250 to 395 °C. Conversion, selectivity toward MEK, and yield over a range of (Ge)-ZSM-5 catalysts are depicted in Fig. 8. The conversion values rapidly increase with temperature to values higher than 90% at 300 °C (Fig. 8a). Upon increasing the temperature to 395 °C, conversion levels initially reach a value of almost 100%, but after some time deactivation occurs and decreasing conversion values are observed. The conversion of ZSM-5(55) starts to drop after 30 min at 395 °C, in contrast to

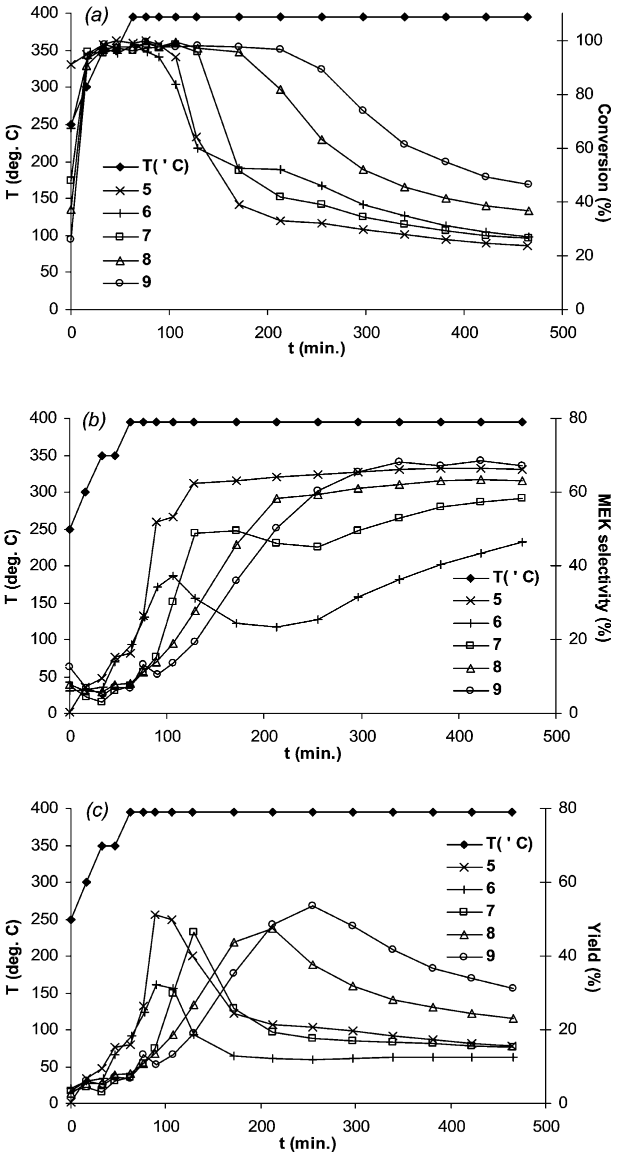

Fig. 8. Conversion (a), MEK selectivity (b), and yield (c) in the conversion of isobutyraldehyde to MEK by (5) ZSM-5(55), (6) Ge(0.04)ZSM-5(63), (7) Ge(0.07)ZSM-5(61), (8) Ge(0.08)ZSM-5(47), and (9) Ge(0.11)ZSM-5(41). WHSV = 3.5 h^{-1}.

Ge(0.11)ZSM-5(41), the conversion of which remains near 100% for 2 h at this temperature. The selectivity toward MEK (Fig. 8b) for most catalysts reaches a final level of around 60%, the difference being that this selectivity level is already reached after 1 h at 395 °C for ZSM-5(55) and only after 3.5 h for Ge(0.11)ZSM-5(41). The trends both in conversion and MEK selectivity are very similar for ZSM-5(55) and Ge(0.11)ZSM-5(41); however, the time scale on which they occur is remarkably different. This suggests that the deactivation process proceeds much faster on ZSM-5(55) than on Ge(0.11)ZSM-5(41).

The regeneration characteristics of samples ZSM-5(55) and Ge(0.11)ZSM-5(41) have been investigated by using the same batch of catalyst in three consecutive runs, the results are shown in Fig. 9. The MEK yield over ZSM-5(55) appears to decrease after the first run while the yield over Ge(0.11)ZSM-5(41) increases, which is in contrast to the trends observed for 2-propanol and 2-butanol dehydration, where a decreased activity of Ge-ZSM-5 was observed after the first run. This different behaviour was further analysed by comparing the XRD powder patterns before reaction and after the third run. As was the case in the alcohol dehydration reactions, no changes in the patterns (and thus no loss of Ge from the zeolite framework) could be observed. The increased conversion values after the first run by Ge(0.11)ZSM-5(41) may be due to “precoking” of the catalyst, which is known to have a positive effect on the catalytic performance for this reaction [7].

B-ZSM-5 has been claimed to be a more suitable catalyst than ZSM-5 for this isomerisation reaction [7]; therefore B-ZSM-5 was compared with (Ge-)ZSM-5 under our reaction conditions; see Fig. 10. The MEK yield is in all cases much lower than those in Fig. 8 due to the higher WHSV (10.8 h^{-1} vs 3.5 h^{-1}). B-ZSM-5(53) exhibits lower activity than both ZSM-5(55) and Ge(0.11)ZSM-5(41); the same trend as was observed for the dehydration reactions. It should be noted that the B-ZSM-5 sample of Ref. [7] was calcined in a different way (in air at 500 °C) than the B-ZSM-5 sample from this study, which was calcined in an ammonia atmosphere according to the optimised procedure by De Ruiter [17]. It

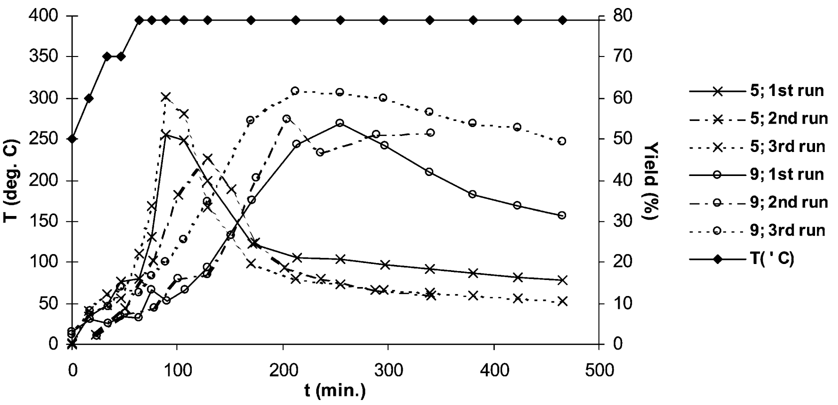

Fig. 9. Yield toward MEK in the isobutyraldehyde isomerisation reaction by (5) ZSM-5(55) and 9) Ge(0.11)ZSM-5(41). Samples were calcined at 500 °C after each run. WHSV = 3.5 h^{-1}.

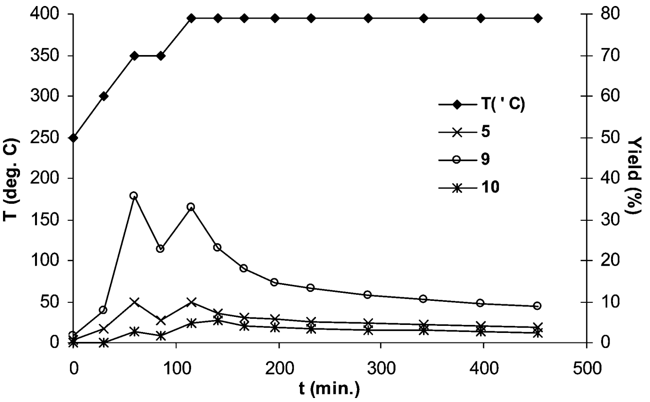

Fig. 10. Comparison of (10) B-ZSM-5(53) with (5) ZSM-5(55) and (9) Ge(0.11)ZSM-5(41) in the isomerisation reaction of isobutyraldehyde to MEK. WHSV = 10.8 h^{-1}.

may well be that the boron atoms do not stay in framework positions upon calcination in air, and therefore the catalytic results described in Ref. [7] may be due to (weakly acidic) extraframework boron oxide species. This issue was not further investigated as the activity of B-ZSM-5 as it was synthesised and calcined by us was significantly lower than the aluminum-containing zeolites.

3.4. Acetylation of anisole

The zeolite-catalysed acylation of aryl compounds has been the subject of several papers [20–23]. Zeolite BEA shows the highest activity of all investigated zeolites [21], which is ascribed to the large size of its micropores (12-membered rings). Accumulation of the reaction products inside the micropores is the main cause of deactivation, and is therefore more pronounced for ZSM-5 (which contains 10-membered rings) than for BEA.

The results of the acetylation of anisole with acetic anhydride by (Ge)-ZSM-5 are depicted in Fig. 11. The reaction temperature was 120 °C in all cases and the zeolite samples were ground for either 5 or 20 min prior to reaction. As in the gas-flow reactions, Ge-ZSM-5 exhibits the highest activity, the conversion over Ge(0.09)ZSM-5(36) being 21–23% (depending on the grinding time). The conversion over ZSM-5(47) is markedly lower at a level of 3–6%, and Ge(0.06)ZSM-5(58) shows intermediate activity (18%). In all cases, the product selectivity toward the *para* product (*para*-methoxyacetophenone, PMAP) is $> 99\%$, which illustrates that the reaction predominantly takes place inside the zeolite micropores.

The effect of the grinding time on the catalytic activity is not the same for each sample: the conversion by ZSM-5(47) increases upon prolonged grinding, while the opposite is the case for Ge(0.09)ZSM-5(36); see Fig. 11. The decrease in activity in the case of Ge(0.09)ZSM-5(36) may be due to the destruction of some of the mesoporosity that is present in this sample (see Table 1). This is illustrated by the fact that the crystal intergrowths of Ge(0.09)ZSM-5(36) lose their spherical shape upon grinding (see Fig. 12, **4B** and **4C**) and thereby the mesoporosity between the crystallites. The decreased catalytic activity due to the loss of mesoporosity is partly compensated for by the increase of the outer-surface area due to the smaller particle size. In the case of ZSM-5(47), an increased grinding time results in an increased outer-surface area and hence an increased activity. As hardly any mesopores are present in ZSM-5(47) prior to grinding (see Table 1), the increase in activity is not balanced by a loss of mesoporosity.

Even after a grinding time of 20 min, the conversion by Ge(0.09)ZSM-5(36) is almost 4 times higher than in the case of ZSM-5(47). The particle size of these samples, however, is not very different (see Fig. 12 (**1C** and **4C**)). The reason for the different catalytic activity may be that there is still a large amount of mesopores in Ge(0.09)ZSM-5(36), compared to ZSM-5(47), even after 20 min of grinding.

4. Discussion and conclusion

The catalytic activities of a range of (Ge-)ZSM-5 samples in alcohol dehydration reactions and the isomerisation

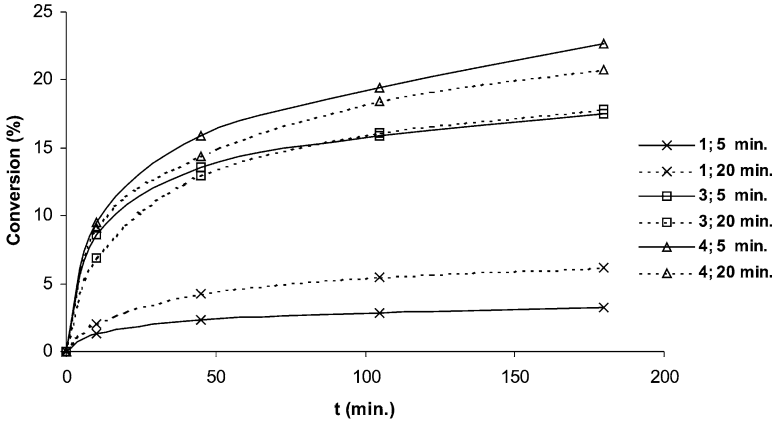

Fig. 11. Anisole conversions in the acylation reaction by (1) ZSM-5(47), (3) Ge(0.06)ZSM-5(58), and (4) Ge(0.09)ZSM-5(36). Zeolite samples were ground prior to reaction for the amount of time given.

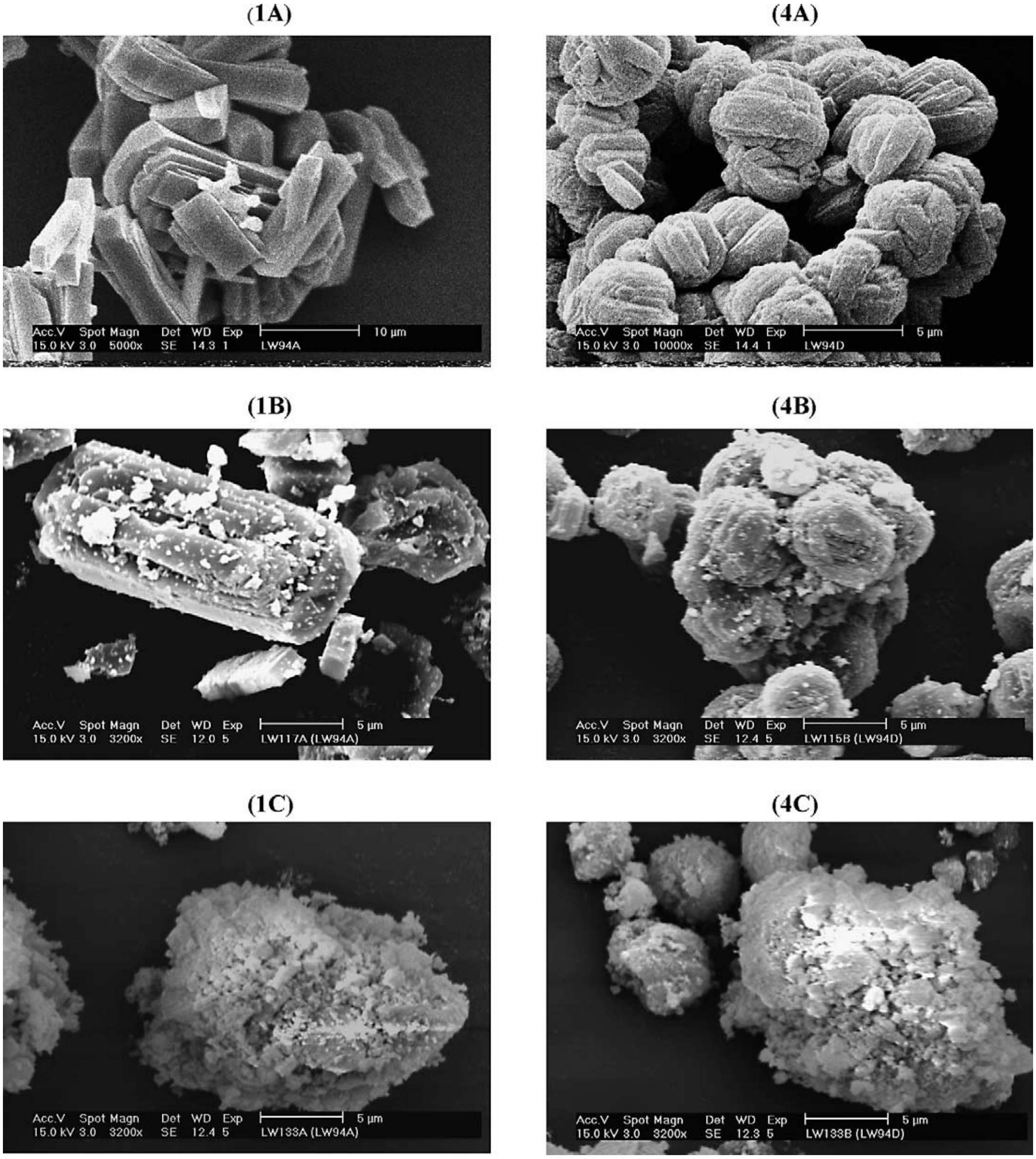

Fig. 12. SEM pictures of samples **(1)** ZSM-5(47) and **(4)** Ge(0.09)ZSM-5(36) before grinding **(A)**, after 5 minutes **(B)** and after 20 minutes grinding **(C)**.

reaction are very similar in the low-temperature range (90–150 °C in case of 2-propanol dehydration, 90–130 °C for 2-butanol dehydration, and 100–300 °C for the aldehyde to ketone isomerisation reaction). At these low temperatures, reaction is only expected to take place at the strongest Brønsted acid sites. As differences in catalytic activity at these low conversion levels are not observed, it can be concluded that the Brønsted acidity in Ge-ZSM-5 and in ZSM-5 is very similar. Indeed, the infrared hydroxyl stretch vibration band of Ge-ZSM-5 was found at a similar wavenumber to that of ZSM-5 (3614 cm^{-1}) [13], albeit that this band is broader in the case of Ge-ZSM-5. Furthermore, some additional infrared bands are present in the spectrum of Ge-ZSM-5, due to partially extraframework Al–OH groups and (weakly acidic) Ge–OH and Si–OH groups, which are the result of the higher number of local defects in Ge–ZSM-5 [13]. The low catalytic activity of Ge-Silicalite-I and Silicalite-I samples (which also contain Ge–OH and Si–OH groups) indicates that the catalytic relevance of these sites is very small. The presence of catalytically relevant additional weaker acid sites in Ge-ZSM-5 (in comparison with ZSM-5) is therefore unlikely. In conclusion, Ge incorporation has no significant effect on the framework acidity of ZSM-5.

At high reaction temperatures (above 150 °C in case of 2-propanol dehydration, above 130 °C for 2-butanol dehydration and at 350 °C for the aldehyde isomerisation reaction), the catalytic stability of Ge-ZSM-5 decreases to a much smaller extent than that of ZSM-5. Deactivation due to coke formation plays an important role at these temperatures. Apparently, coke residues are less likely to hinder the diffusion of substrate molecules into, and the diffusion of product molecules out of the zeolite pores of Ge-ZSM-5, compared to ZSM-5. This may be related to the fact that the amount of mesopores in Ge-ZSM-5 (S_{meso} values, which include the mesoporous and macroporous surface area, as well as the contribution of the external surface) is much higher than in ZSM-5 (see Table 1). The high S_{meso} values are due to the large amount of interfaces between the small crystallites of Ge-ZSM-5 aggregates. The micropore volumes (V_{micro} values, Table 1), on the other hand, are not a function of Ge content. The additional mesoporosity may change the catalytic properties in two ways: First, the accessibility of the micropores is improved and, second, the acid sites located inside the mesopores will still be available when the micropores are blocked. Consequently, the residual activity after blocking of (most of the) micropores is expected to be higher in the case of Ge-ZSM-5. The beneficial role of mesopores in zeolite catalysts has been reviewed recently [24].

Another difference between ZSM-5 and Ge-ZSM-5 is the size of the primary crystallites. The crystallites of which the spherical aggregates of Ge-ZSM-5 are built up (Fig. 12, **4A**) are much smaller than the ZSM-5 crystals (Fig. 12, **1A**). The average length of a zeolite channel is therefore expected to be shorter in Ge-ZSM-5, shortening the diffusion path for guest species to reach the active sites.

In conclusion, the catalytic stability of ZSM-5 can be significantly enhanced by substituting some of the Si atoms for Ge. Deactivation occurs to a much smaller extent on Ge-ZSM-5 than on ZSM-5 due to the increased mesoporosity of Ge-ZSM-5. The additional mesopores reduce the negative effects of coke formation on the diffusion of substrates and/or products. The effect of Ge incorporation on the framework acidity of ZSM-5 appears to be negligible. This phenomenon is the subject of further, current investigations [25].

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