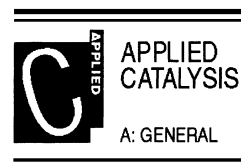APPLIED
CATALYSIS
A: GENERAL

A novel family of solid acid catalysts: substantially amorphous or partially crystalline zeolitic materials

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Abstract

Hydrogels, typically used for the synthesis of highly crystalline ZSM-5 samples at 150°C and under autogenous pressure, were subjected to lower hydrothermal synthesis temperatures, i.e., from 25°C to 130°C. XRD analysis of the samples obtained at the various temperatures showed that for synthesis temperatures of up to 70°C, X-ray amorphous aluminosilicates were obtained, whereas treatment at 90°C produced a material exhibiting a 2% XRD crystallinity. Higher synthesis temperatures resulted in higher levels of % crystallinity. Evaluation of the samples as catalysts for the skeletal isomerization of linear butenes was carried out in a flow reactor at 500°C, MHSV=3 and a butene:nitrogen dilution of 1:10. The results showed that the % conversion of the linear butenes increases and the % selectivity to isobutene decreases with increasing autoclave synthesis temperature, with the highest yield of isobutene (23.4%) being achieved with the 2% XRD crystallinity sample. Higher crystallinities produced considerably lower yields of the branched alkene. The catalytic properties of the 2% XRD crystallinity sample were further evaluated as a function of reaction temperature, 350–500°C, at MHSV=1 and a dilution of 1:10. Highest yield of isobutene was obtained at 500°C and under these reaction conditions, the sample exhibited stable catalytic performance (31% yield) for up to 40 h on-stream. In contrast, under the same reaction conditions, an 86% crystalline ZSM-5 sample gave a 4.9% yield of isobutene. Work on partially crystalline ferrierite-based materials as catalysts for the same reaction was also carried out. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The use of zeolites as catalysts for acid- or base-catalysed organic reactions, and in industrial processes based on these reactions, is well documented in the literature [1–4]. The reactions vary from the simple double-bond shift reaction to the synthesis of fine chemicals [5]. In the utilization of zeolitic catalysts, improvements in product selectivities can be obtained by the judicious choice of zeolite pore size and shape, or by varying parameters such as crystallite size and morphology, Si/Al ratio, or by modifications such as extra-framework cation exchange, isomorphous substitution, pore blockage, elimination of external sites, etc. [1].

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One of the reactions that has received considerable attention over the past 10 years is the skeletal isomerization of 1-butene to yield isobutene. The interest in this reaction arises from the fact that the branched alkene can subsequently be reacted with methanol over Amberlyst 15 catalysts for the synthesis of MTBE [6].

A large number of catalytic systems for this skeletal isomerization reaction has been described in the literature and these have recently been reviewed [7]. The catalysts studied varied from metal oxides (with or without halogen additives) to amorphous or crystalline aluminosilicates. Most of the aluminosilicate and halogenated alumina catalysts exhibited relatively fast deactivation rates due to coke formation (apart from the loss of catalytic activity due to the elution of the halogen, in the case of the halogenated catalysts) which results from the occurrence of the undesired side-reactions, such as dimerization, oligomerization, cracking (i.e., the olefin interconversion reactions) and the H-transfer reactions [1,8].

It has also been shown [7,9] that the skeletal isomerization reaction is more demanding than both the *cis–trans* and double bond shift isomerization reactions, and the alcohol dehydration reactions, and that it requires sites of high acid strength such as those found in halogenated alumina and zeolites.

A consequence, however, of all the above-indicated olefin interconversion reactions and H-transfer reactions taking place on ''open-surface'' catalysts or in medium-pore zeolites, such as HZSM-5 (pore sizes of 5.3×5.6 Å and 5.1×5.5 Å), is the lowering of the selectivity to the desired isobutene product. For example, with ZSM-5 at 377°C, the % selectivity to isobutene was 11.2% [10], whereas with the narrower-pore zeolite Theta-1 (4.4×5.5 Å), the selectivity increases to 35%. With both of these catalysts, the reactions were conducted under low olefin partial pressures.

In a recent patent granted to Shell [11] it was shown that with the small-pore zeolite ferrierite (4.2×5.4 Å and 3.5×4.8 Å) the conversion of the linear butenes to isobutene can be carried out at relatively low temperatures (350°C), in the absence of any diluent, with high activity, selectivity and stability with time-on-stream.

In our present publication, we wish to report on another parameter in zeolite synthesis and catalysis, which, according to our review of the literature, has not received any attention in previous publications, viz. the percentage XRD crystallinity of the zeolite materials and its effect on their catalytic behaviour. The importance of this parameter will be discussed with particular reference to the skeletal isomerization reaction of the linear butenes.

2. Experimental

The batches of ZSM-5 zeolites ($SiO_2/Al_2O_3 \approx 80$) were prepared from a literature method [12] and the detailed experimental procedure is given below.

A sodium aluminate solution was prepared from 17.9 g of NaOH and 2.7 g of $Al(OH)_3$ to which 75 ml of distilled water was added. The mixture was heated and stirred until a clear solution was obtained (solution A).

Another solution (solution B) was prepared by mixing 29.7 g of tetrapropylammonium bromide (Fluka) with 75 ml of water and stirring it (without heating) until the solids dissolved.

A silica slurry (mixture C) was prepared from 80.4 g of fumed silica (Degussa, Aerosil 200) to which 650 ml of water was added, under vigorous stirring, until a smooth slurry was obtained.

To this slurry, solutions A and then B were added, again under vigorous stirring. An additional 440 ml of water was added to this final mixture which was then transferred to an autoclave (Parr) where it was allowed to react for 72 h with stirring, under autogenous pressure, at the temperatures indicated in the text. The post-synthesis treatment, to produce the H^+-form of the zeolite, has been described previously [12].

The % XRD crystallinity of the samples obtained was determined according to our previously published method [12] which is based on the ratio of the major peak intensities between 22° 2θ and 25° 2θ of the sample relative to those of a highly crystalline reference material, i.e.,

% XRD crystallinity

$$= \frac{\text{sum of peak intensities of sample}}{\text{sum of peak intensities of reference}} \times 100.$$

As reference material we used a highly crystalline silicalite sample previously prepared in our laboratories [12].

The catalytic experiments were performed in a fixed-bed flow microreactor (stainless steel, i.d. 20 mm) whose detailed construction has been given elsewhere [13]. In all the catalytic evaluations, 3 g of catalyst of particle size 45–160 microns were employed and the experiments were performed at the MHSVs, temperatures and nitrogen dilutions indicated in the text. On-line analysis of the product stream was carried out using gas chromatography (FID, and using both a 50 m PLOT fused silica KCl/Al$_2$O$_3$ column (Chrompack) and a DB-1 capillary column).

3. Results and discussion

Based on our previously published procedure [12], batches of highly crystalline ZSM-5 zeolites were prepared by subjecting the aluminosilicate hydrogel described in Section 2 to hydrothermal treatment, in the presence of the template tetrapropylammonium bromide, in a stirred autoclave at 150°C for 72 h under autogenous pressure. The XRD spectrum of such a sample (86% XRD crystallinity) is shown in Fig. 1(a).

In order to obtain samples of lower % XRD crystallinity, hydrogels of exactly the same composition as
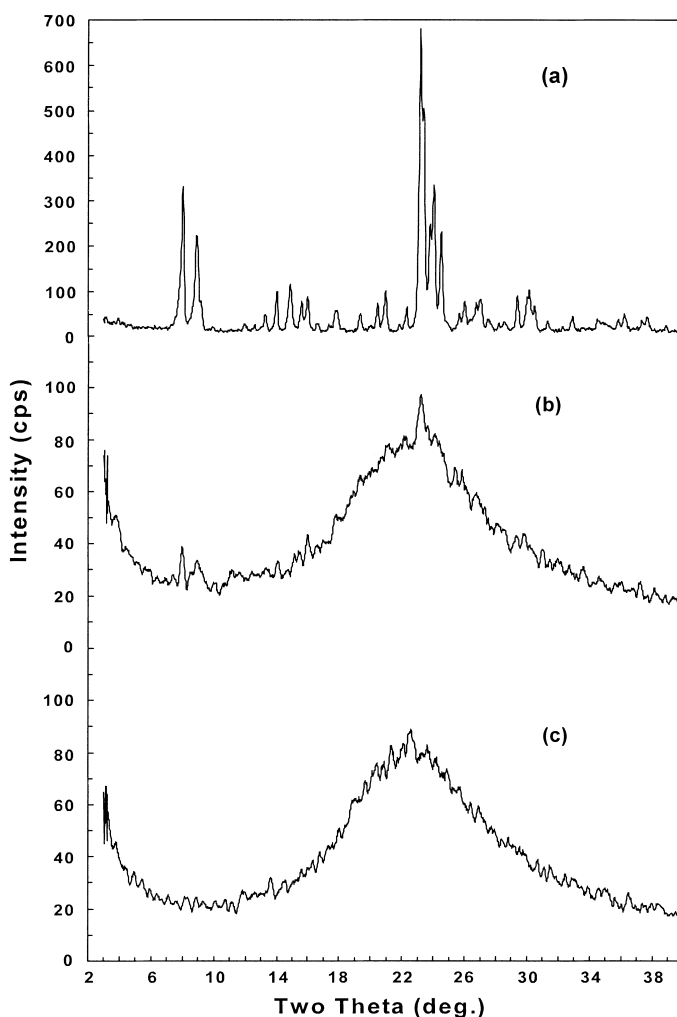

Fig. 1. X-ray diffractograms of (a) ZSM-5 sample prepared at 150°C, (b) low crystallinity sample prepared at 90°C, and (c) X-ray amorphous sample prepared at 70°C.

Table 1
XRD analysis of aluminosilicates obtained at different hydrothermal synthesis temperatures

Catalyst batch	Hydrothermal synthesis temperature (°C)	% XRD crystallinity
NAS-21	25	Amorphous
NAS-26	50	Amorphous
NAS-4	70	Amorphous
NAS-27	90	2
NAS-39	100	6
NAS-28	110	32
NAS-29	130	72
ZSM-5	150	86

Table 2
Effect of hydrothermal synthesis temperature on catalytic properties of aluminosilicate samples[a]

Catalyst batch	% Conversion	% Selectivity	% Yield
NAS-21	3.9	87.9	3.4
NAS-26	13.0	78.5	10.2
NAS-4	24.8	69.6	17.3
NAS-27	35.4	66.2	23.4
NAS-28	95.7	2.6	2.5

[a] Experiments conducted at 500°C, atmospheric pressure, MHSV=3 (based on the alkene), and butene:nitrogen=1:10.

described above, including template, were treated at *lower* hydrothermal synthesis temperatures, from below 150°C down to 25°C. The XRD analysis of the materials obtained at the various temperatures is given in Table 1 and in Fig. 1(b) and (c). It can be observed that at synthesis temperatures of up to 70°C, only X-ray amorphous materials are obtained which display the characteristic hump at around 22° 2θ (see Fig. 1(c)). For the sample synthesized at 90°C, the appearance of small peaks on top of the hump is observed, which are at the same degrees 2θ as the major peaks for ZSM-5 (compare Fig. 1(a) and (b)).

As the synthesis temperature is increased beyond 90°C, a rapid increase in the % XRD crystallinity of the samples is observed (see Table 1), which ultimately reaches a constant plateau value (see [12]).

The aluminosilicate samples thus prepared were then tested as catalysts in a fixed-bed flow reactor for the conversion of 1-butene in order to evaluate the influence of autoclave synthesis temperature (25–110°C) and of the resultant % XRD crystallinity on the catalytic activity, selectivity and yield for the skeletal isomerization reaction. The catalytic reaction was carried out at 500°C, atmospheric pressure, MHSV=3, based on the alkene, and a butene:nitrogen dilution of 1:10. The catalytic data obtained are listed in Table 2. It can be observed that for all samples the % conversion of the 1-butene increases with increasing hydrothermal synthesis temperature. The % selectivity to isobutene, however, decreases from 87.9% for NAS-21 (sample prepared at 25°C) to 2.6% for NAS-28 (sample prepared at 110°C). Maximum yield of isobutene, under these reaction conditions, is therefore

obtained with the sample designated as NAS-27 (sample prepared at 90°C), i.e., the sample with 2% XRD crystallinity.

In another series of experiments, the effect of catalytic reaction temperature (350–550°C) on the activity and selectivity of the NAS-27 catalyst was evaluated under the reaction conditions of MHSV=1, atmospheric pressure and a butene:nitrogen dilution of 1:10. The results obtained at 20 h on-stream are listed in Table 3 and show that the yield of isobutene increases with increasing reaction temperature between 350°C and 500°C. Also, it can be noted here that for all the reaction temperatures studied, no significant decrease in the % yield was observed for up to 40 h on-stream. Fig. 2 shows the results obtained at 500°C, with the % yield remaining constant at 31%.

To demonstrate further the advantages that the extremely low crystallinity samples have over both the highly crystalline samples and the X-ray amorphous samples, all three types of catalysts were similarly evaluated at 500°C and MHSV=1, and the results are listed in Table 4. Our results therefore show that extremely low crystallinity samples (such as NAS-27,

Table 3
Effect of reaction temperature on catalytic properties of NAS-27[a]

Reaction temperature (°C)	% Conversion	% Selectivity	% Yield
350	69.8	17.1	11.9
400	43.7	41.0	17.9
450	39.8	63.2	25.2
500	42.4	74.1	31.4
550	36.1	83.3	30.1

[a] Experiments conducted at atmospheric pressure, MHSV=1 (based on the alkene), dilution of 1:10 and at 20 h on-stream.
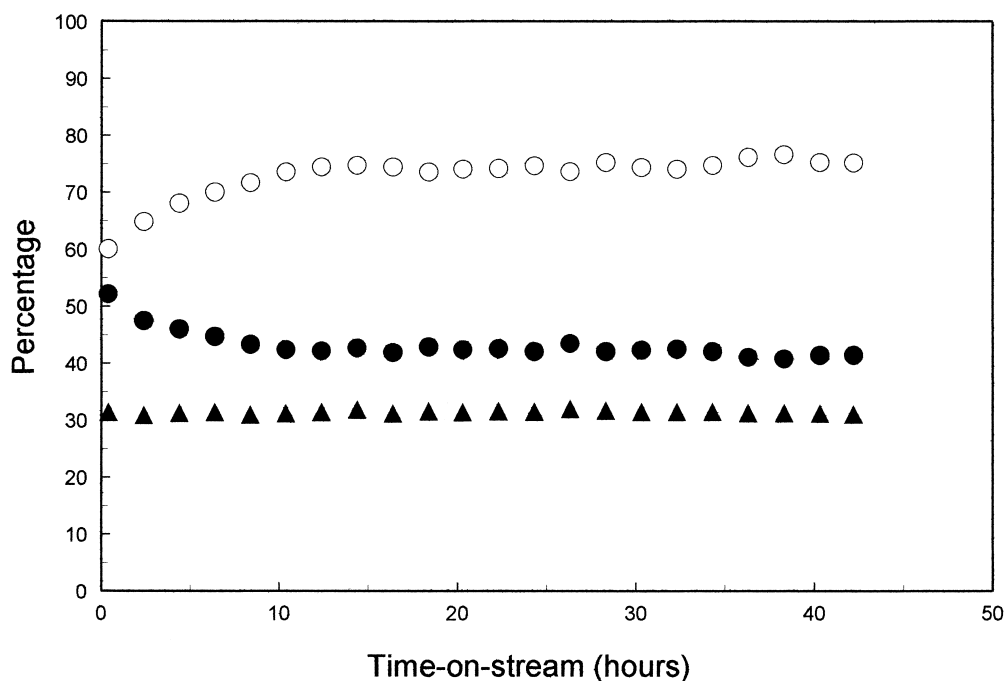
Fig. 2. Plots of % conversion (●), % selectivity (○) and % yield (▲) versus time-on-stream obtained with NAS-27 at 500°C, MHSV=1 and a dilution of 1:10.

2% XRD crystallinity) are highly active and exhibit higher selectivities for the skeletal isomerization reaction than the higher crystallinity samples, thus demonstrating the beneficial effect of lower levels of % XRD crystallinity. The product distribution obtained with the NAS-27 catalyst is listed in Table 5.

The catalytic results obtained in this study therefore show that for the skeletal isomerization reaction conducted over zeolitic catalysts, the extent of the olefin interconversion and H-transfer reactions can be minimized by using low crystallinity samples where the

pore lengths will be shorter than in highly crystalline materials, i.e., the olefins (or other feeds) will have a lower residence time within a zeolite pore environment, in which they can be subjected to the sequential reactions.

It should be noted, however, that even though sample NAS-4 (see Table 1) has been shown to be X-ray amorphous, the presence of small zeolitic nuclei, which are not detected by X-ray techniques,

Table 4
Comparative studies of catalytic properties of X-ray amorphous, low crystallinity and high crystallinity samples[a]

Catalyst batch	% XRD crystallinity	% Yield of isobutene
ZSM-5	86	4.9
NAS-27	2	31.4
NAS-4	0	22.0

[a] Experiments conducted at 500°C, MHSV=1 (based on the alkene), dilution of 1:10 and at 5 h on-stream.

Table 5
Product distribution obtained with NAS-27 catalyst at 500°C, MHSV=1 and dilution of 1:10

	Mass %
Ethene	0.4
Propene	5.0
Isobutane	0.4
n-Butane	0.8
trans-2-Butene	19.6
1-Butene	21.4
Isobutene	31.4
cis-2-Butene	16.6
Pentenes and pentanes	4.4

Table 6
The conversion of linear butenes to isobutene over ferrierite-based catalysts[a]

Catalyst batch	% XRD crystallinity	% Yield of isobutene
NAS-112	24	44.0
NAS-113	56	38.9
NAS-114	63	33.0
NAS-115	67	31.7
Shell Patent [11]	*Essentially ferrierite*	40.1

[a] Experiments conducted at 350°C, atmospheric pressure, MHSV=2 and at 48 h on-stream.

Table 7
Comparative catalytic studies of as-synthesized materials versus physical mixtures[a]

Catalyst batch	% XRD crystallinity	% Yield of isobutene
NAS-112	24	42.7
NAS-114	63	22.8
Silica	0	0
66% NAS-114+34% silica	*42*	21.1
38% NAS-114+62% silica	*24*	14.6

[a] Experiments conducted at 350°C, atmospheric pressure, MHSV=2 and at 20 h on-stream.

cannot be excluded [14]. For such samples, use of a catalytic test reaction (CTR) which proceeds over strongly acidic zeolitic sites, rather than those found in amorphous silica–alumina, could be employed. Such a CTR is methanol conversion into dimethyl-lether and hydrocarbons, where formation of the latter requires strong acid sites [15].

The concept of lower crystallinity zeolite samples was also extended to the ferrierite zeolite. Using the synthetic procedure indicated in the Shell Patent [11], which involves usage of solid silica gel as the source of silica and pyridine as the template, ferrierite-based samples were obtained whose crystallinity varied from 24% to 67%. These samples were then tested for the conversion of linear butenes to isobutene at 350°C and MHSV=2. The results obtained at 48 h on-stream are listed in Table 6 and once again demonstrate the usefulness of lower levels of % XRD crystallinity on the catalytic reaction and yield of the branched alkene.

In order to confirm further that the results reported in this paper are due to the % XRD crystallinity of the as-synthesized materials, and not due to the dilution of higher crystallinity materials with an amorphous phase, comparative studies of the catalytic properties of as-synthesized materials and those of physical mixtures were carried out for the ferrierite-based catalysts (see Table 7). The results show that when a medium crystallinity material such as NAS-114 (XRD crystallinity of 63% and producing a yield of 22.8% isobutene) is diluted with a catalytically inactive and amorphous silica sample to give an effective 24% XRD crystallinity mixture, a yield of 14.6% of isobutene is obtained with this physical mixture as catalyst. This value is considerably lower than the

42.7% yield obtained with NAS-112 which has a 24% XRD crystallinity (as-synthesized).

4. Conclusions

Our results have shown that ZSM-5 zeolite-based aluminosilicate samples of low % XRD crystallinity can exhibit higher selectivities and yields than their corresponding highly crystalline analogues. This has been demonstrated for the skeletal isomerization of the linear butenes and further work on the application of these novel aluminosilicate catalysts or NAS-type catalysts, i.e., zeolite-based materials that are substantially amorphous or only partially crystalline, on other acid-catalysed organic reactions is continuing in our laboratories.

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