

Aldol-Type Reactions over Basic Microporous Titanosilicate ETS-10 Type Catalysts

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The catalytic performance of the microporous titanosilicate ETS-10-type catalysts for the aldol condensation of acetone has been investigated and compared with that of zeolite-X-type materials. The reaction was carried out on as-prepared, potassium- and cesium-exchanged and cesium oxide-impregnated catalysts. It is shown that this reaction may be catalysed by both acidic and basic sites and the product distribution depends, to a great extent, on the acid–base properties of the catalyst. The strong basicity of ETS-10 materials is manifested in this reaction process by promoting the base-catalysed condensation mode yielding remarkably high selectivities for mesityl oxides. These experimental findings highlight the potential of ETS-10 in aldol-type reactions. © 2000 Academic Press

INTRODUCTION

There has been an increasing interest in basic catalysis (1) by inorganic porous materials and a large number of contributions have already been reported on reactions in this area. These include side-chain alkylation of toluene (2–5), dehydration of alcohols (6), dehydrocyclisation of *n*-alkanes (7–10), and aldol-type reactions (11–14). The catalysts used in these studies are predominately alkali-cation-exchanged zeolite-type materials. The basicity of these catalytic systems is defined by structure, aluminium content, and cation size and it is now widely accepted (1) that, for a given structure, basicity is enhanced with increasing cation size and aluminium content.

The aldol condensation reactions (11–14) are characteristic of aldehydes and ketones and may be catalysed by both acidic and basic active sites to form β -hydroxy aldehydes/ketones as primary products. The subsequent catalytic steps are dependent upon the nature of active sites. The aldol condensation of acetone produces diacetone alcohol as the primary product which over acidic sites decomposes readily to isobutene and acetic acid. Acetic acid decomposes further to methane and carbon dioxide while isobutene either desorbs as a final product or undergoes further oligomerisation/isomerisation/cracking reactions over

the acid sites. Over basic catalysts, the aldol condensation of acetone yields a completely different pattern of products. Primarily, diacetone alcohol forms, which dehydrates rapidly to a mixture of α - and β -mesityl oxides which either desorb as final products or undergo further reactions. The following catalytic steps entail either hydrogenation of mesityl oxides to 4-methyl-2-pentanone or further reactions of mesityl oxides with acetone to form trimeric intermediates which in turn undergo intramolecular rearrangements to form isophorone. Hence, the aldol condensation of acetone over basic catalysts leads to a mixture of mesityl oxides, 4-methyl-2-pentanone, and isophorone as the main final products. The selectivity for final products depends on a number of factors such as acid–base strength, catalyst structure, and reaction conditions. Both mesityl oxides and isophorone find application in the polymerisation industry, whereas mesityl oxides are also useful for extracting–separating metals such as platinum, palladium, and lead.

ETS-10 (Engelhard titanosilicate structure 10) is potentially a very important new microporous inorganic titanosilicate framework material. The structure, which was first synthesised by Engelhard (15, 16) and solved by Anderson *et al.* (17, 18), consists of corner-sharing octahedral titanium(IV) and tetrahedral silicon. ETS-10 is one of a small group of zeolite or zeotype materials which contain a three-dimensional 12-ring pore system. Additionally, isomorphous substitution to incorporate both aluminium (19) and gallium (20) into ETS-10, thus producing ETAS-10 and ETGS-10, respectively (21), has been reported. It is worth pointing out that these materials are prepared by template-free synthesis procedures which entail rather inexpensive chemicals and thus the cost of making these solids is remarkably low.

The increasing interest in these inorganic materials with regard to catalysis stems from their unique structural characteristics as well as their novel chemical composition, and a number of contributions have already been reported on the catalytic properties of ETS-10 materials (22–30). Of great interest is a number of recent reports (28–30) which highlight the strong basicity of these solids. In this contribution, the catalytic performance of basic ETS-10-type cata-

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lysts for the aldol condensation of acetone is described and compared with that of zeolite-X-type catalysts. The ETS-10-type catalysts used in these studies are as-synthesised ETS-10 and ETAS-10, Cs-exchanged ETS-10 (Cs-ETS-10), and Cs₂O-impregnated Cs-ETS-10 (Cs₂O/Cs-ETS-10). The zeolite X-type catalysts include as-synthesised Na-X and the ion-exchanged K-X, Cs-X, and Cs₂O/Cs-X.

EXPERIMENTAL

Materials

ETS-10 and ETAS-10 were prepared using the procedures described in the literature (15, 16). Zeolite Na-X was obtained from a commercially available source (13X, with Si/Al: 1.3). The ETS-10 and Na-X samples were partially exchanged to produce Cs-ETS-10 and Cs-X using 0.5 M aqueous solution of CsOH at 60°C (30 ml of solution/1 g of solid). The Cs-exchanged samples were impregnated with cesium acetate using the procedure reported (31) by Hathaway *et al.* and then calcined at 450°C to produce the Cs₂O/Cs-ETS-10 and Cs₂O/Cs-X catalysts. Zeolite K-X was prepared by ion exchange of Na-X with 0.5 M aqueous solution of KOH and the conditions described above. All these materials were characterised by powder X-ray diffraction, ²⁹Si MAS NMR, N₂ adsorption experiments, and wet chemical analysis techniques. Furthermore, the acid-base properties of all catalysts were assessed by means of the isopropanol conversion as a probe reaction (1, 31).

Catalysis

These experiments were performed in a fixed-bed stainless steel reactor at atmospheric pressure. The reactor's length and internal diameter are 16.0 and 0.5 cm, respectively, and the reactor bed measures 1.0-cm long and exhibits an internal diameter of 0.5 cm. The catalyst (50 mg) was activated at 450°C in a hydrogen-containing carrier gas (H₂ 20% in Ar) with a flow rate of 10.0 ml min⁻¹ and a heating rate of 3.0°C min⁻¹ for 3.0 h. The reaction temperature was 400°C and the reactant was fed and controlled by a syringe pump while the H₂/acetone molar ratio was kept constant at 5. Residence times were adjusted by keeping the catalyst weight constant and altering the volumetric flow rate of the reactant. Products were analysed *in situ* using gas chromatography with a 30-m long capillary column (DP1 fused silica phase) and an FID (flame ionisation detector). The isopropanol conversion (probe reaction) was carried out on the same system at 350°C.

RESULTS AND DISCUSSION

Characterisation of ETS-10-Type Catalysts

The X-ray diffraction patterns and the ²⁹Si MAS NMR spectra of the as-synthesised ETS-10 and ETAS-10

materials match very closely with those published earlier (17–19). A small loss of crystallinity was observed in both the X-ray diffractograms and the ²⁹Si MAS NMR spectra of the ion-exchanged and impregnated ETS-10 materials. Figure 1 illustrates the ²⁹Si MAS NMR spectra of the as-synthesised ETS-10, cesium-exchanged (Cs-ETS-10), and cesium oxide-impregnated (Cs₂O/Cs-ETS-10) catalysts. These spectra are the fingerprints of ETS-10-type materials with resonances in the chemical shift range of –94 to –97 ppm assigned to Si (3Si, 1Ti) while the peaks at ca. –103 ppm are ascribed to a Si (4Si) chemical environment. The small loss of crystallinity is evident in the spectra of the chemically treated materials by the broadening of all resonances while these chemical treatments have an additional effect on the chemical shifts of these peaks. All lines in the spectrum of Cs-ETS-10 are shifted by ca. 1 ppm low field relative to that of ETS-10 while the lines of the Cs₂O/Cs-ETS-10 spectrum are shifted by ca. 1.7 ppm low field relative to that of ETS-10. These shifts must result from the alterations in the basicity and the oxygen charge of these framework materials.

N₂ adsorption experiments on ETS-10-type materials yield isotherms of type I, characteristic of microporosity with maximum uptakes of ca. 12–14% (w/w). The catalyst chemical compositions (mol%) were obtained by wet chemical analysis techniques and are illustrated in Table 1.

Acid-Base Properties of ETS-10- and Zeolite-X-type Materials

The acid-base properties of all catalysts were assessed by means of a probe reaction, the conversion of isopropanol. The selectivity for acetone is a measure of the catalyst basicity as it results from base-catalysed dehydrogenation whereas propene is the product of acid-catalysed dehydration (1, 31). The strong basicity of ETS-10 materials has been recently reported (30) in the literature and must relate to both chemistry and structure of these novel inorganic solids. Figure 2 depicts the selectivity for acetone for all materials used in these studies. Of great interest is a comparison between the basicity of ETS-10 and that of zeolite Na-X, both materials in the as-synthesised form before any chemical treatments. ETS-10 is considerably more

TABLE 1

The Catalyst Chemical Compositions (Unit Cell mol%)

ETS-10	[Si ₇₈ Ti ₁₆ O ₂₀₈]Na ₂₃ K ₉
ETAS-10	[Si ₇₃ Al ₄ Ti ₁₆ O ₂₀₈]Na ₁₉ K ₁₃
Cs-ETS-10	[Si ₇₈ Ti ₁₆ O ₂₀₈]Na ₁₇ K ₄ Cs ₁₁
Cs ₂ O/Cs-ETS-10	[Si ₇₈ Ti ₁₆ O ₂₀₈]Na ₁₅ K ₄ Cs ₁₃ (Cs ₂ O)
Na-X	[Al ₈₄ Si ₁₀₈ O ₃₈₄]Na ₈₄
K-X	[Al ₈₄ Si ₁₀₈ O ₃₈₄]Na ₄ K ₈₀
Cs-X	[Al ₈₄ Si ₁₀₈ O ₃₈₄]Na ₄₀ Cs ₄₄
Cs ₂ O/Cs-X	[Al ₈₄ Si ₁₀₈ O ₃₈₄]Na ₃₅ Cs ₄₉ (Cs ₂ O)

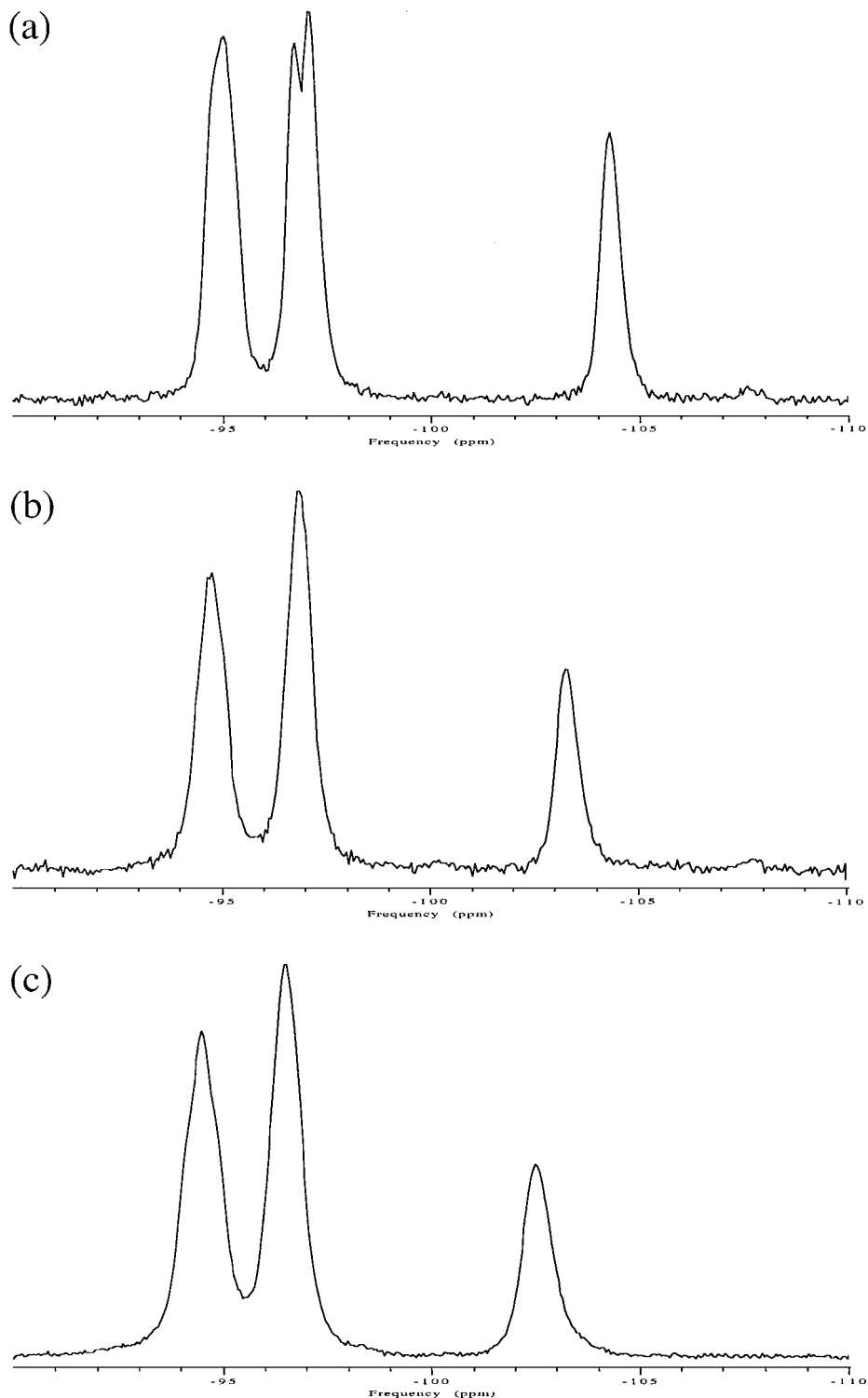


FIG. 1. ^{29}Si MAS NMR spectra of (a) as-synthesised ETS-10, (b) Cs-ETS-10, and (c) $\text{Cs}_2\text{O}/\text{Cs-ETS-10}$.

basic than zeolite X and the basicity of ETS-10 appears to be comparable to that of $\text{Cs}_2\text{O}/\text{Cs-X}$, a material which has undergone a number of chemical treatments to reach that basicity level. Ion exchange with larger cation sizes followed

by Cs_2O impregnation leads to a striking increase in the basicity of zeolite Na-X whereas these chemical treatments have a less pronounced effect on the already strongly basic ETS-10.

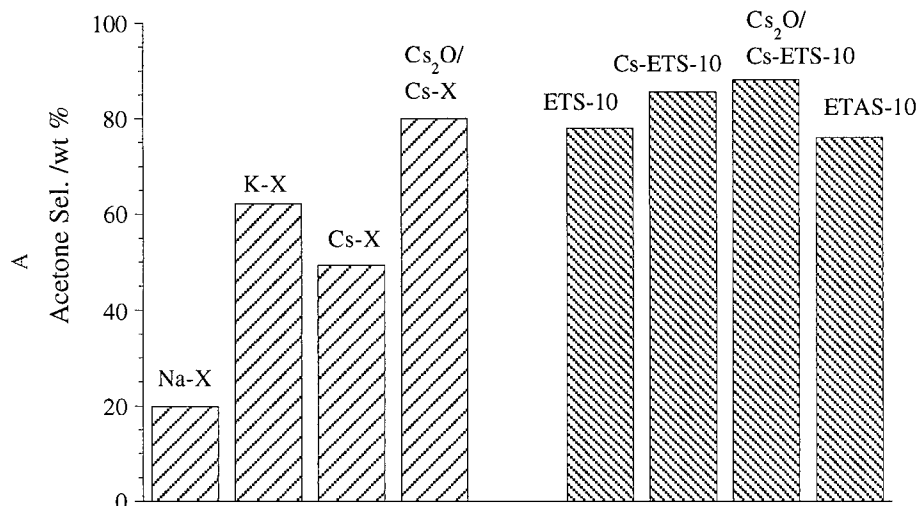


FIG. 2. The selectivity for acetone (wt%) in the isopropanol reaction over both zeolite X and ETS-10-type catalysts at 350°C and isopropanol conversion levels of ca. 25 wt% for all catalysts.

Aldol Condensation of Acetone over Zeolite X Catalysts

Figure 3a illustrates the reaction rates for all zeolite-X-type catalysts versus time on stream (TOS). The acetone conversion levels at these conditions are ca. 5.0–15.0 wt% and the reaction temperature is 400°C. Ostensibly, the most active catalyst is Na-X while the activity of K-X is considerably lower than that of Na-X. Both Cs-X and Cs₂O/Cs-X, exhibiting similar activities, are the least active. While the chemical treatments of the as-synthesised Na-X have enhanced the basicity of this material markedly, the overall catalytic activity of the chemically treated materials is considerably lower than that of the as-prepared Na-X. The two different modes of aldol-condensation reactions, acid- and base-catalysed, complicate the comparison among the catalytic activities of these materials. That is to say that the high catalytic activity of Na-X results from the acidity of this catalyst and this is clearly shown in the product distribution of this material. Thus, the catalyst acid-base properties as well as other factors such as steric constraints and accessibility to active sites must define the catalytic activity of these materials. The deactivation patterns of these materials are very similar, with the exception of that of Cs₂O/Cs-X which deactivates extremely fast in the first hour of the reaction. Such a fast deactivation must relate to extra-framework Cs₂O basic sites.

Table 2 shows the product distribution of acetone aldol condensation over zeolite-X-type catalysts. The acid-base properties of these catalysts seem to dictate the selectivity for the final products. Over the most acidic Na-X, isobutene dominates in the product stream, whereas small amounts of mesityl oxides and 4-methyl-2-pentanone are also detected. Trimethylbenzenes, and to a lesser extent isophorone, are also observed as trimeric products, whereas diacetone alcohol and phorone were not observed. Mesitylene accounts

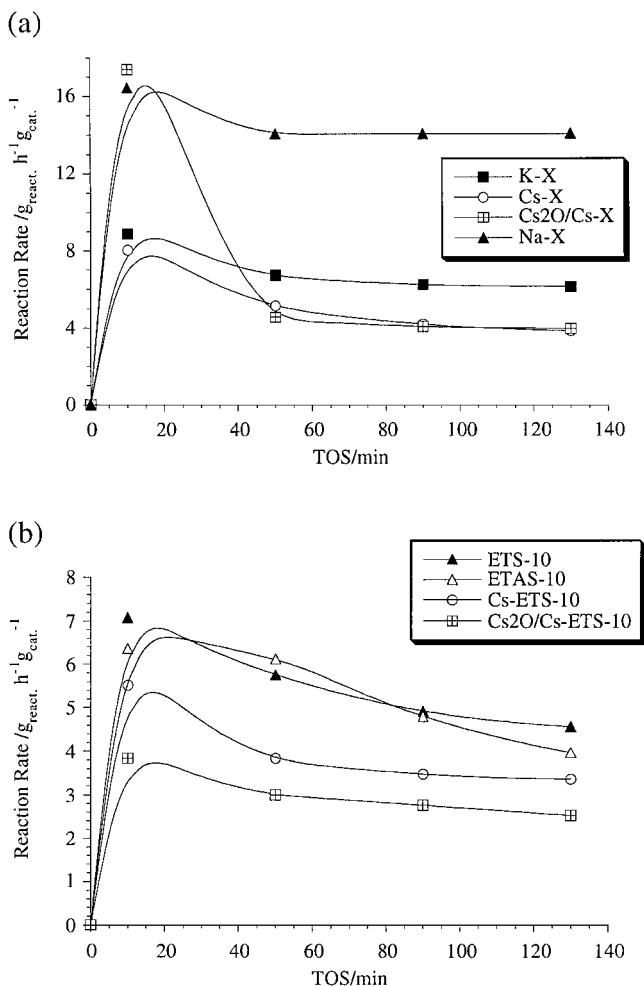


FIG. 3. The reaction rates versus TOS for (a) zeolite-X- and (b) ETS-10-type catalysts. Reaction temperature = 400°C; WHSV 1.2 h⁻¹; Ar/reactant = 26 (mol); H₂/reactant = 5 (mol).

TABLE 2
Product Distribution (wt%) of Acetone Condensation
over Zeolite-X-type Catalysts

	Na-X	K-X	Cs-X	Cs ₂ O/Cs-X
C ₁ -C ₃	5.1	14.2	11.6	10.5
isobutene	80.5	5.3	6.7	5.3
4-methyl-2-pentanone	1.7	7.1	4.6	7.9
α -mesityl oxide	2.5	25.3	28.2	34.2
β -mesityl oxide	0.8	7.1	9.3	10.5
trimethylbenzenes	6.8	16.0	20.9	10.5
phorone	0.0	0.0	0.0	2.6
isophorone	0.8	8.9	11.6	10.5
tetramethylbenzenes	1.7	16.0	7.0	7.9

Note. Reaction temperature = 400°C; WHSV = 1.2 h⁻¹; TOS = 50 min.

for about 70 wt% of trimethylbenzenes and its formation has been suggested (32) to be related to acid-catalysed 1,6-aldol condensation of 2,4-dimethyl-2,4-heptadiene, a trimeric intermediate. The products in the C₁-C₃ range must result from secondary reactions of isobutene while decomposition of acetic acid to methane (11) also contributes to this product range. Fragmentation of the more complex organic species may also produce some products in the C₁-C₃ range. The formation of tetramethylbenzenes is not clearly understood and may relate to secondary reactions of isobutene. The product distributions of the other three zeolite-X-type catalysts are markedly different to that of Na-X. The base-catalysed aldol reactions dominate in these catalytic processes, leading to mesityl oxides and isophorone as the main products. Furthermore, a noticeable increase in the amount of trimethylbenzenes is observed which must relate to further reactions of the abundant mesityl oxides with acetone. The dramatic decrease of isobutene indicates that the acid-catalysed decomposition of diacetone alcohol to isobutene and acetic acid is not favoured over these basic systems, whereas the notable increase of the C₁-C₃ products suggests that the secondary reactions of isobutene are less hindered. Hydrogenation of mesityl oxides to 4-methyl-2-pentanone is also noticed in small amounts while diacetone alcohol is not detected because it either dehydrates rapidly to mesityl oxides or decomposes, to a lesser extent, to isobutene and acetic acid.

Aldol Condensation of Acetone over ETS-10 type Catalysts

Figure 3b illustrates the reaction rates for all ETS-10-type catalysts versus TOS. The acetone conversion levels at these reaction conditions are 3.0–6.0 wt% and the reaction temperature is 400°C. The catalytic activities of the as-synthesised ETS-10 and ETAS-10 catalysts are very similar to those of K-X and Cs-X while the chemically treated Cs-ETS-10 and Cs₂O/Cs-ETS-10 are less active. As observed above, the various activities of these materials may be explained on the grounds of the acid–base proper-

ties, steric constraints, and crystallinity losses as there is not a direct correlation between basicity and catalytic activity. In addition, the deactivation rates of all four catalysts are very similar, with a tendency to stabilise at about 90 min TOS.

Table 3 shows the product distribution of acetone aldol condensation over ETS-10-type catalysts. As stated above, the product distribution of this reaction is defined by the acid–base character of these solid catalysts. The strong basicity of these materials is clearly manifested in this reaction process, yielding product patterns which are indicative of base catalysis. As shown in Fig. 2, these materials exhibit a similar basic strength and one would therefore anticipate similar product distributions for all ETS-10-type catalysts. As expected, the formation of mesityl oxides dominate in the product distributions of all ETS-10-type catalysts (ca. 65–70 wt%) while various amounts of 4-methyl-2-pentanone, isophorone, and trimethylbenzenes are also detected. The strikingly low amounts of isobutene and C₁-C₃ products indicate that the acid-catalysed decomposition of diacetone alcohol is considerably suppressed. Of great interest is the detection of a small amount of *n*-nonane which is not observed in zeolite-X-type catalysts and is suggested to relate to trimeric intermediates. Furthermore, it is worth noting that ETS-10-type materials yield relatively lower amounts of trimethylbenzenes, compared with those of zeolite-X-type catalysts. This observation relates to the fact that trimethylbenzenes may result from acid-catalysed reactions of trimeric intermediates (32) which are not favoured over ETS-10-type catalysts. Isophorone is observed in considerable amounts in ETS-10 and ETAS-10 and its formation is associated (32) with strong basic sites. The decrease in isophorone in the product stream of Cs-ETS-10 and Cs₂O/Cs-ETS-10 may be due to steric hindrance of the bulky trimeric intermediates which limits their accessibility to the active sites of these catalysts.

TABLE 3
Product Distribution of Acetone Condensation over
ETS-10-type Catalysts

	ETS-10	ETAS-10	Cs-ETS-10	Cs ₂ O/ Cs-ETS-10
C ₁ -C ₃	4.2	3.9	3.1	4.0
isobutene	4.2	7.8	3.1	4.0
4-methyl-2-pentanone	8.3	7.8	6.2	8.0
α -mesityl oxide	49.9	49.0	56.4	51.9
β -mesityl oxide	14.6	13.7	15.6	16.0
<i>n</i> -nonane	2.1	2.0	6.2	4.0
trimethylbenzenes	6.2	5.9	3.1	4.0
phorone	0.0	0.0	0.0	0.0
isophorone	8.3	7.8	3.1	4.0
tetramethylbenzenes	2.1	2.0	3.1	4.0

Note. Reaction temperature = 400°C; WHSV = 1.2 h⁻¹; TOS = 50 min.

CONCLUSIONS

Aldol condensation of acetone may be catalysed by both acidic and basic sites and the selectivity for final products relates to the acid–base character of the solid catalyst. The lack of correlation between catalytic activity and basicity must relate to factors such as steric constraints and accessibility to active sites. For zeolite-X-type catalysts, the base-catalysed mode of acetone condensation is clearly evident in the more basic, chemically treated materials, whereas the as-synthesised Na–X promotes acid-catalysed condensation reactions, leading to isobutene as a main product. Conversely, both as-synthesised and chemically treated ETS-10-type materials favour base-catalysed condensation of acetone, resulting in uncommonly high selectivities for mesityl oxides as the main products. This interesting catalytic behaviour of ETS-10-type materials must relate to the strong basicity of these microporous solids. That is to say that ETS-10 constitutes a unique microporous-type catalyst for base-catalysed aldol reactions where chemical modifications for basicity enhancement are not necessary.

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