Role of substrate's electrophilicity in base catalysis by zeolites: alkylation of acetonitrile with methanol

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Abstract

The role of substrate's electrophilicity in base catalysis was studied by competitive adsorption and catalytic alkylation of acetonitrile over basic zeolite catalysts. Methanol was used as alkylating agent, comparing with the side-chain alkylation of toluene. Solid base zeolite catalysts including CsNaX, CsNaY and CsNaEMT were prepared and modified by simple ion exchange and impregnating parent zeolites with caesium salt. Their physical and chemical characteristics were then determined by XRD, SEM and elemental analysis. Adsorption was studied by FTIR using a special in situ adsorption cell. The gas-phase catalytic reaction was carried in a down-flow microreactor and products from the reaction were analysed by on-line TCD–GC. Adsorption strength of the substrates was found to depend largely on their electrophilicity and basicity of the zeolite framework. The strong adsorption of acetonitrile on basic zeolite catalysts also leads to an increased alkylation activity, but reduces the decomposition of methanol to carbon monoxide and hydrogen. In addition to the reaction temperature, the competitive adsorption of acetonitrile and methanol predominantly effects on product selectivity, particularly the unsaturation/saturation ratio. Moreover, the excess caesium "clusters" present in the zeolite framework plays important role in both adsorption and alkylation of the substrates. Further investigation was made on stability of the catalysts and it was found that coke formation is small in base catalysis, as compared to those found in acid zeolites. FTIR reveals that the carbon deposits are composed mainly of high polar products and the catalysts can be readily regenerated without significant loss of catalytic activity.
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1. Introduction

A report on the mechanism of the side-chain alkylation of toluene with methanol suggested that the formation of a "benzyl carbanion" determined the rate of the reaction [1]. This intermediate was believed to be generated by the basic sites of the catalysts. The "benzyl carbanion" could only be stabilised within the restricted micropores of high aluminium-content zeolites, where the high polar environment facilitates the formation and the reaction of the carbanion intermediates. Accordingly, it seems reasonable that the electrophilicity of the substrate which leads to the stability of the carbanions, presumably plays an important role in the reaction promoted by basic zeolites.

The depolymerisation of polystyrene over base catalysts was also claimed to proceed via benzyl carbanion intermediate [2]. It was suggested that the species that actually interact with the active basic sites would determine the final products' selectivity. In addition, different catalytic activities have been reported when different reactants were tested over other base catalysts, such as alumina-supported KF [3], zirconium oxide and magnesium oxide [4]. The results reveal that complexity of the active sites [3,5] and the distribution of acid–base sites on the catalyst surfaces [6] strongly effect the catalytic activity, particularly for the bimolecular reaction. Although, these observations have already implied the significance of the substrate being used, most of the investigations were focussed on nature and activity of the catalysts. Whilst, in base catalysis, an example for the influence of substrate's electrophilicity have not yet been highlighted.

In this work, the role of substrate's electrophilicity in base catalysis by zeolites is demonstrated by the alkylation of

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acetonitrile which is more electrophilic than toluene. Since the reaction proceeded via bimolecular intermediate, competitive sorption activity of the substrate over the catalyst is suggested to be significant for its reactivity. This can be shown by probe analysis using FTIR technique from which the sorption strength of toluene, acetonitrile and methanol over basic zeolite catalysts can be evaluated. In addition, it was suggested earlier [1] that site proximity also influences the stability of the substrate. Therefore, CsNaY and CsNaX are used as catalysts in order to demonstrate the trend of this effect when electrophilicity of the substrates is modified.

2. Experimental procedure

Acetonitrile (99%, Fluka®) was used without further purification. Toluene (99.5%, Jensen®) and methanol (99.5%, BDH®) were dried and kept over predried Molecular sieve 3A. Caesium exchanged zeolites X, Y, EMT and Na-silicalites were used as catalysts. Molecular sieve 13X (BDH®), NaY and NaEMT (ELF®) were ion-exchanged three times with 0.5 M CsCl at 50 °C and once with 0.5 M CsOH at room temperature. The solid materials were washed several times with 0.5 M CsOH and left to dry overnight at room temperature. These materials believed to contain clusters of CsOH (possibly $CsHCO_3/Cs_2CO_3$), were defined as "CsNaX–CsOH", "CsNaY–CsOH" and "CsNaEMT–CsOH". For Molecular Sieve 13X, another portion of the exchanged material was washed with deionised water until no basicity was detected. The caesium cations in this material, designated as "CsNaX", were presumably exchangeable cations. Na-silicalite was synthesised using tetrapropylammonium bromide (($C_3H_7)_4$NBr) as an organic template. A synthesis gel with molar composition of $12Na_2O \cdot 100SiO_2 \cdot 20TPABr \cdot 4000H_2O$ was prepared. The gel mixture (100 ml) was then autogeneously pressurised and crystallised in a Teflon-lined stainless steel autoclave for 84 h at 175 °C. The solid precipitate was filtered using a Büchner funnel and left to dry at room temperature. This catalyst was believed to contain an excess of NaOH solution in the channels prior to calcination. The organic template was removed by heating the catalyst to 500 °C under nitrogen flow. Calcination was continued at this temperature for 10 h under an air stream.

Adsorption study was performed using an in situ adsorption cell. Zeolites (10–15 mg) were pelletted and placed in a cell where vacuum ($\sim10^{-6}$ Torr) was applied overnight at 350 °C. Adsorbates (acetonitrile, methanol or toluene) were loaded (0.2, 0.5, 1.0 and 2.0 μl) into the cell at room temperature, respectively. The samples were then evacuated at room temperature and at 100 °C. Infrared spectra of the adsorbed molecules were recorded before and after evacuation. A resolution of $2 cm^{-1}$ was used with 100 scans in the spectral range of $4000–1250 cm^{-1}$.

The alkylation with methanol was carried out at 350 °C in a fixed bed down-flow reactor. Helium was used as carrier gas at a flowrate of 25 ml/min. The mixture of acetonitrile/methanol or toluene/methanol were fed using syringe pump. Liquid products from the reaction were collected every 30 min using an acetone/dry-ice bath and analysed by TCD–GC using a 6 ft × 1/8 in. Porapack Q column. Gas products were periodically detected by on-line GC. Helium was again used as carrier gas for both analyses. 2-Propanol was employed as internal standard for analysis of the liquid products whilst an external standard method was used for gas analysis. The structures of the products were confirmed using GC–MS.

3. Results and discussion

3.1. Adsorption studies

From a catalytic point of view, the adsorption of the substrates would influence the catalytic activity and also determine the reaction pathway. Inhibition of the reactant(s) by strong adsorption of the products or side-products would simply result in a reduced catalytic activity. Especially in the case of bimolecular reactions, the relative adsorption strength of two substrates becomes significant when the adsorption of the more weakly sorbed substrate is involved in the rate determining step. It has been suggested that proton abstraction of toluene is the rate determining step in its side-chain alkylation with methanol. Therefore, a strong adsorption of toluene over the basic sites would facilitate the reaction. However, it appears that adsorption of methanol on basic sites is favoured over that of toluene according to the competitive adsorption between toluene and methanol as shown in Fig. 1.

The results showed that when methanol (0.5–1.0 μl) is gradually loaded to the sample, where toluene was first adsorbed at room temperature, a reduction of toluene (1596 and $1489 cm^{-1}$) sorbed on the CsNaX–CsOH was observed. It was evident that methanol was strongly adsorbed on CsNaX–CsOH, as compared to toluene. Consequently, under the catalytic condition, decomposition of methanol to carbon monoxide and hydrogen is largely promoted by basic catalysts [7]. This was also observed in the side-chain alkylation of toluene with methanol, where selectivity of toluene conversion is suppressed when highly active basic catalysts are used [8–10].

According to the presence of hydroxylic hydrogen in methanol, hydrogen bonding to the active basic site is readily formed. In contrast, the nucleophilic nature, arising from delocalised electrons in the ring of toluene, would repulse to such basic sites. Increase in Lewis acidity of the framework by addition of different charge-balancing cations shows an increase in catalytic activity of toluene in the side-chain alkylation [6]. Therefore, it can be hypothesised that, over basic catalysts, toluene is relatively less adsorptive than methanol and the side-chain alkylation can be optimised by acidity–basicity variation of framework.
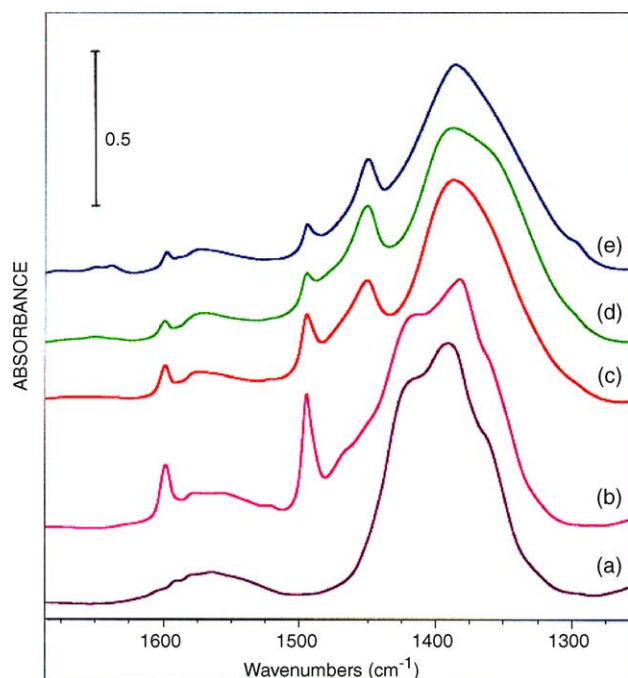
Fig. 1. Competitive adsorption between toluene and methanol (a) CsNaX–CsOH calcined in vacuum at 350 °C, (b) with 1.0 μl of toluene at room temperature, (c) with 0.5 μl of methanol after contact with toluene, (d) with 1.0 μl of methanol after contact with toluene and (e) evacuated at room temperature after contact with toluene and methanol.

Fig. 2. Competitive adsorption between methanol and acetonitrile (a) CsNaX–CsOH with 1.0 μl of methanol at room temperature, (b) with 0.2 μl of acetonitrile after contact with methanol, (c) with 0.5 μl of acetonitrile after contact with methanol, (d) with 1.0 μl of acetonitrile after contact with methanol, (e) with 2.0 μl of acetonitrile after contact with methanol, (f) evacuated at room temperature after contact with acetonitrile and methanol, (g) evacuated at 100 °C after contact with acetonitrile and methanol.

On competitive adsorption between acetonitrile ($\nu_{CN} \sim$ 2245 cm^{-1}) and methanol ($\nu_{CN} \sim$ 2816 cm^{-1}), Fig. 2 shows that methanol, which is first sorbed on CsNaX–CsOH, was driven out of the pores on loading of acetonitrile (0.2–2 μl). Although high vacuum was applied to the system at 100 °C, acetonitrile still remained on sites whilst methanol was no longer detected. The strong interaction of acetonitrile on the active basic site can be referred to the greater electron withdrawal by the –CN group. As opposed to the –OH group, the –CN group increases the polarity and α-hydrogen acidity of acetonitrile. Moreover, the –CN group can provide an electron-donor interaction (either from π electrons or lone-pair electrons) for possible bonding to the surface cations particularly the charge-balancing cations in the zeolite framework. The localised electrons of the –CN group would interact with the exchangeable cation and the acidic α-hydrogen would interact with the oxygen bridge, which can subsequently lead to the proton abstraction.

Since the adsorption strength of the preferred substrates on basic zeolite is put in the order: acetonitrile > methanol > toluene, acetonitrile was therefore selected as a probe molecule for basic strength evaluation of the catalysts. As the basic strength increases, it is expected that the stretching vibration frequency of C≡N group should decrease when compared with that of acetonitrile vapour. This is because an increase in basic strength of the active site would enhance α-proton perturbation and subsequently increase the electron density of the adsorbed acetonitrile.
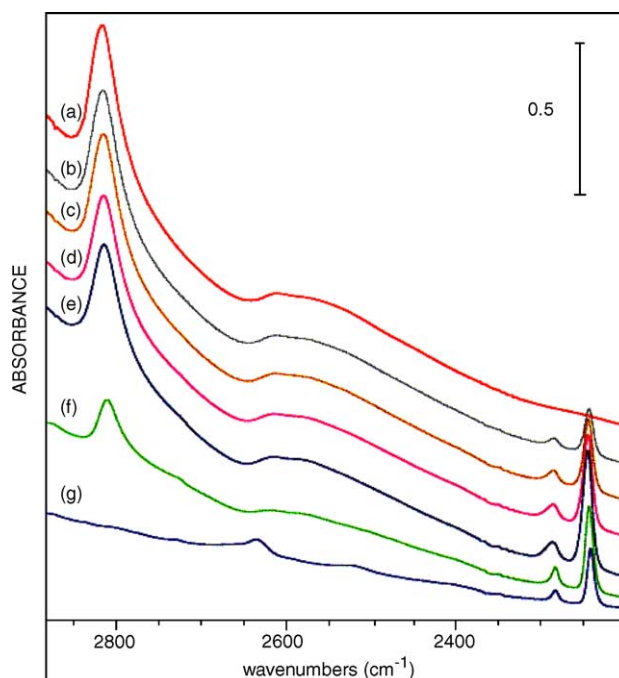
The C≡N bond of the perturbed species would presumably be lengthened as the electron density increases which consequently results in a reduction of stretching vibration frequency of such bond [11] The stronger the basic strength of the active sites, the longer the C≡N bond and the lower the vibration frequency. This was found from the measurement results that CsNaX–CsOH possess the highest basic strength among the catalysts used (Table 1).

The chemisorption of acetonitrile on basic zeolite has also revealed some evidences of α-hydrogen perturbation as shown in Fig. 3. The weakening of C–H bonding due to strong interaction with the basic sites was observed with corresponding reduction of C–H stretching vibration frequency. Such stronger interaction can be regarded as a result of the perturbation of acidic α-hydrogen by the basic sites.

Considering the vibration frequency of C≡N group, it appears that on Na-silicalite (2270 cm^{-1}) and NaX (2268 cm^{-1}), the major vibration frequency of C≡N is higher than that of acetonitrile with no interaction (2254 cm^{-1}) and it is found to decrease towards this value when the amount of acetonitrile loading is increased. In contrast, the C≡N stretching vibration frequency of acetonitrile adsorbed on catalysts containing caesium cations had a lower value compared to that of non-interacted acetonitrile, and when loading were increased, these values also increased as shown in Fig. 4. This change can be attributed

Table 1
Infrared spectroscopic data of acetonitrile adsorbed on basic zeolite catalysts

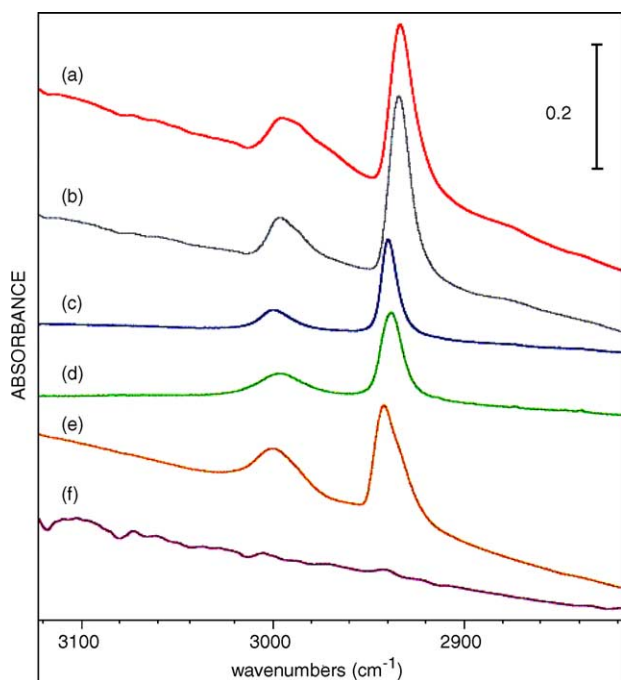| Catalyst	None	CsNaX–CsOH	CsNaX	CsNaY–CsOH	CsNaEMT–CsOH
C≡N stretching (cm^{-1})	2254	2243	2242	2250	2249

Fig. 3. Infrared spectra of the C–H stretching vibration frequency of acetonitrile (0.2 ml) adsorbed on various catalysts at room temperature (a) CsNaX–CsOH, (b) CsNaX, (c) CsNaEMT–CsOH, (d) CsNaY–CsOH, (e) NaX and (f) Na-silicalite.

to the multilayer adsorption of acetonitrile as loading were increased.

The result is clear for Na-silicalite and NaX that interaction of acetonitrile with Lewis acid cations, for example sodium, would result in an increased vibration frequency of

C≡N. It is because the electron density in the triple bond will be decreased via electron donor through the nitrogen atom, thus shortening the bond length. This is also the case for the acetonitrile complex with protons [12–14] and some transition metal cations [15,16].

$$H_3C-C\equiv N \quad \overset{H^+}{\rightleftharpoons} \quad \left[H_3C-C\equiv N^{\cdots}H \right]^+$$
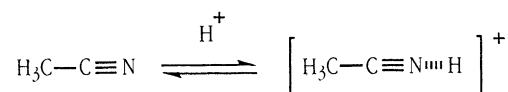
However, the phenomenon that C≡N stretching vibration frequency of the adsorbed acetonitrile is lower than that without interaction, as observed over caesium-containing zeolites, can possibly result from two causes. The first may be the fact that the catalyst is highly basic and perturbation of the α-hydrogen of acetonitrile by the basic framework of oxygen would result in an increased electron distribution into the triple bond.

$$H_3C-C\equiv N \quad \overset{\bar{B}}{\rightleftharpoons} \quad \left[\overset{\delta^-}{B}^{\cdots}H-\underset{H_2}{\overset{\delta^+}{C}}=C=N \right]^-$$
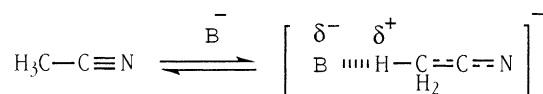
The second may be that interaction of the C≡N group with exchangeable cation, caesium in this case, may take place with the π electrons in the triple bond instead of the lone pair electrons of nitrogen. This hypothesis was raised due to the fact that caesium differs from the other group I alkali metals in its considerably larger size and lower polarising capacity, and its softness compared to other cations in this group. Therefore, there is a possibility that in the interaction with a soft ligand such as acetonitrile, the interaction may involve the π electrons of the –CN group in a similar
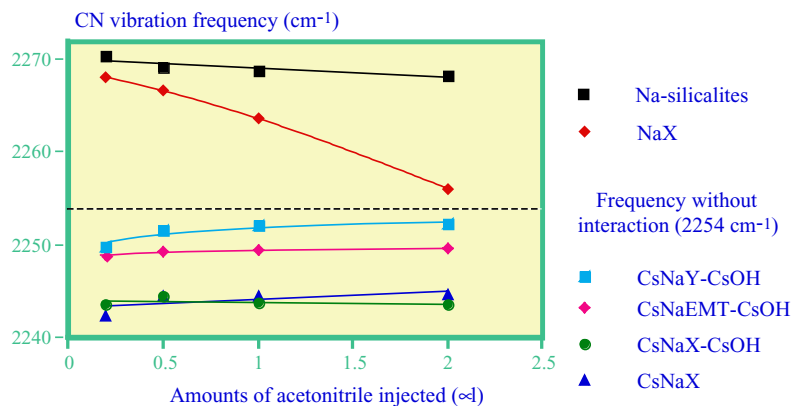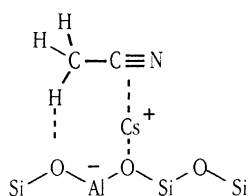

Fig. 4. The change in –CN stretching vibration frequency with increase acetonitrile loading.

manner observed with the interaction of caesium with π electrons of benzene [17,18].

Accordingly, the magnitude of reduction in the stretching vibration frequency of the adsorbed acetonitrile would directly reflect the strength of adsorption, and subsequently, the basicity of the catalysts. Therefore, it can be said that the basicity of the catalysts used in this experiment is in the order of CsNaX–CsOH > CsNaX > CsNaY–CsOH ∼ CsNaEMT–CsOH. A ready perturbation of the α-hydrogen is expected for the acetonitrile adsorbed on these basic catalysts because the acidity of the α-hydrogen can be facilitated by a strong electron withdrawing group, C≡N, of acetonitrile and also by the resonance effect of the triple bond:
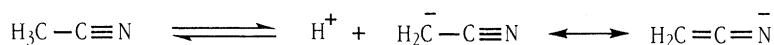
In addition to the basic strength of the active sites, high polarity of the reaction medium is somewhat essential for the carbanion formation and stabilisation. The interaction between substrates and active basic sites, particularly that arising from the polar environment within the catalyst, becomes more significant when the carbon acidity of the substrate is decreased. For example MgO, a highly basic catalyst, was found to readily catalyse the alkylation of acetone with methanol [19] whilst the side-chain alkylation of toluene using the same conditions was unlikely to be promoted by this catalyst [20,21]. This was attributed, firstly, to the lack of a regular crystalline structure [22], and secondly, to an insufficient stability of the "benzyl carbanion" intermediate over MgO catalyst. Some reports [19,22,23] have also suggested that the rate of the substrate conversion having the higher α-hydrogen acidity (acetone)

was higher than that having a lower α-hydrogen acidity (acetonitrile). According to this assumption, the alkylation of acetonitrile with methanol should be easily promoted by alkali cation-exchanged zeolites as compared to toluene which has an even lower α-hydrogen acidity than acetonitrile.

3.2. Catalytic study

3.2.1. Methanol conversion: selectivity
It can be seen for most catalysts used in Table 2 that the conversion of methanol during the side-chain alkylation of toluene is higher than that during the alkylation of acetonitrile. However, the yields of alkylated products from the side-chain alkylation of toluene are less than the alkylated yields from the alkylation of acetonitrile. This can be attributed to the fact that in the side-chain alkylation of toluene, most of the methanol was converted via decomposition to carbon monoxide and hydrogen, especially when a catalyst with excess caesium cation "clusters" was used (i.e. catalyst –CsOH). The extensive decomposition of methanol in the side-chain alkylation of toluene (Fig. 5) suggests that methanol is more strongly adsorbed than toluene as demonstrated by competitive adsorption study in Fig. 1. Conversely, the inhibition by acetonitrile on the decomposition of methanol suggests a stronger interaction for acetonitrile than that for methanol on the active basic sites, which was again clearly shown by FTIR analysis in Fig. 2. The stronger adsorption of acetonitrile on the basic sites compared to that of methanol will facilitate proton abstraction at the α-carbon of acetonitrile, and consequently allow the alkylation of acetonitrile with methanol to be favourably promoted, whereas the decomposition of methanol is apparently suppressed. These features lead to a higher selectivity of methanol conversion into alkylated products (acrylonitrile and propionitrile) rather than the decomposed products (carbon monoxide and hydrogen).

Table 2
Conversion (mol%) and yield (mol%) from alkylation of acetonitrile and side-chain alkylation of methanol over basic zeolite catalysts

Catalysts	Side-chain alkylation of toluene					Alkylation of acetonitrile				
	Conversion		Yield		EB/SR[a] ratio	Conversion		Yield		PN/AN[a] ratio
	Toluene	Methanol	EB[b]	SR[b]		Acetonitrile	Methanol	PN[b]	AN[b]	
CsNaX–CsOH	9.2	19.5	6.8	1.8	3.8	10.7	3.1	7.9	2.1	3.8
CsNaX	3.4	7.3	0.4	3.2	0.1	9.8	0.9	4.8	4.5	1.1
CsNaY–CsOH	–	0.6	–	–	–	5.8	2.8	4.6	0.9	5.7
CsNaEMT–CsOH	0.1	4.1	0.1	–	–	6.1	7.9	4.7	0.9	5.2
Na-silicalite	–	–	–	–	–	3.7	3.1	0.2	3.2	0.06

Reaction temperature: 350 °C, W/F: 40–45 g h mol^{-1}, toluene/methanol ratio: 0.2 mol/mol, acetonitrile/methanol ratio: 0.1 mol/mol. Conversions, yields and selectivities shown are the average values from the overall time on stream of each reaction.
[a] EB/SR: ratio of mole of ethylbenzene to styrene; PN/AN: ratio of mole of propionitrile to acrylonitrile.
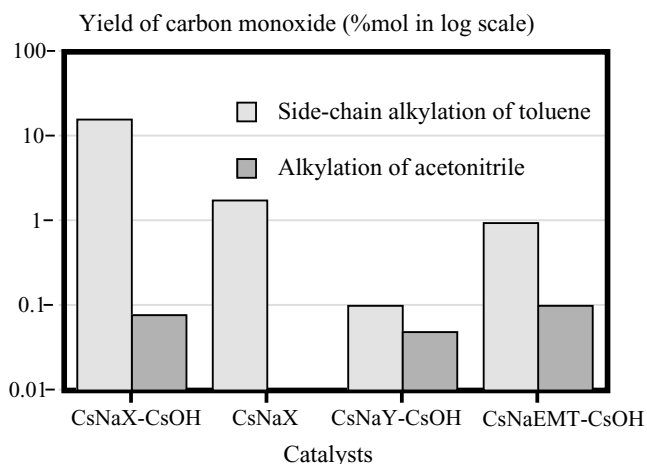[b] PN—propionitrile, AN—acrylonitrile, EB—ethylbenzene, SR—styrene.

Fig. 5. Yield of carbon monoxide in the first 60 min on stream from side-chain alkylation of toluene and alkylation of acetonitrile.

3.2.2. Effect of framework polarity

The observation that the side-chain alkylation of toluene with methanol cannot be readily promoted by CsNaY–CsOH and CsNaEMT–CsOH in the conditions of the experiment is presumably due to the inability of the catalysts to stabilise the benzyl carbanion intermediate. This deficiency was also observed in the reaction using MgO as catalyst [2]. The low polarity of the framework due to the higher silica content (low number of sites and exchangeable cations) diminishes both adsorption and proton abstraction from the poorly electrophilic toluene. In addition, there is a decreased stability for any benzyl carbanions formed. However, a polar environment in the catalyst framework is not so essential for the alkylation of acetonitrile because as discussed above, acetonitrile is more electrophilic than toluene and the intermediate carbanion can be stabilised by its functional group (–CN). Consequently, the reaction can be readily promoted by catalysts with a lower aluminium content such as CsNaY–CsOH

and CsNaEMT–CsOH. Moreover, Na-silicalite, which contains negligible amounts of aluminium and which is not effective in promoting the side-chain alkylation of toluene, can be used to promote highly selective alkylation of acetonitrile, particularly acrylonitrile. This also demonstrates that the carbanion intermediates of acetonitrile are sufficiently stable under the reaction conditions and do not require a high polar catalytic environment, such as that found in the aluminium-rich catalysts, for the reaction to proceed. On the other hand, it seems clear that a high polar catalytic environment is required for the side-chain alkylation of toluene with methanol.

Due to the reduced number of sites arising from the higher Si/Al of CsNaY–CsOH and CsNaEMT–CsOH as compared to the zeolite X counterparts, a relatively smaller surface concentration of carbanion intermediate is produced over these catalysts, leading to a lower reaction rate, and consequently, a lower conversion as shown in Fig. 6. However, CsNaY–CsOH and CsNaEMT–CsOH appear to be good catalysts for the alkylation of acetonitrile since the selectivity to a particular product (propionitrile) (Table 2) is high. The catalysts also provide selective conversion of both substrates (acetonitrile and methanol) and show less deactivation as compared to CsNaX–CsOH.

3.2.3. Product selectivity

A higher conversion of the alkylated substrate is observed in the alkylation of acetonitrile when CsNaX is employed as a catalyst compared with side-chain alkylation of toluene over the same catalyst (Table 2). Although more saturated product is obtained from CsNaX, the propionitrile/acrylonitrile ratio for CsNaX is less than that for CsNaX–CsOH. This reveals the influence of caesium cation "clusters" in promoting the direct alkylation with methanol, which has been suggested earlier [1], as shown in Fig. 7, to be responsible for the formation of saturated product. Whilst the unsaturated product is mainly produced
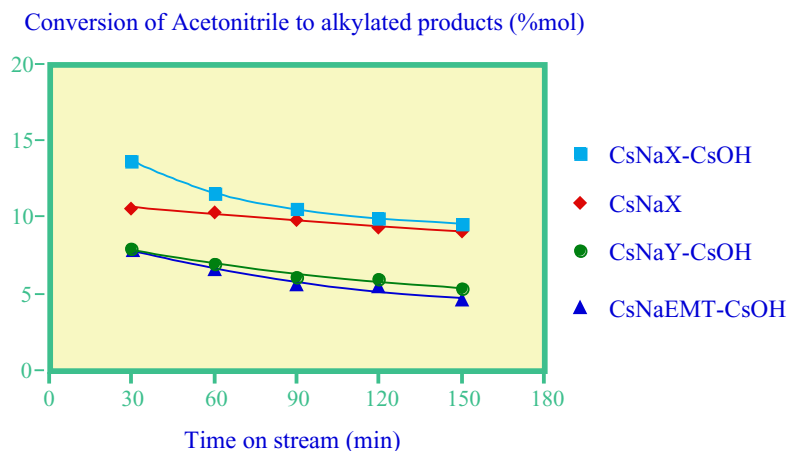

Fig. 6. Alkylation of acetonitrile with methanol over various catalysts: reaction temperature: 350 °C; W/F: 40–45 g h mol^{-1}; acetonitrile/methanol ratio: 0.1; He as carrier gas.
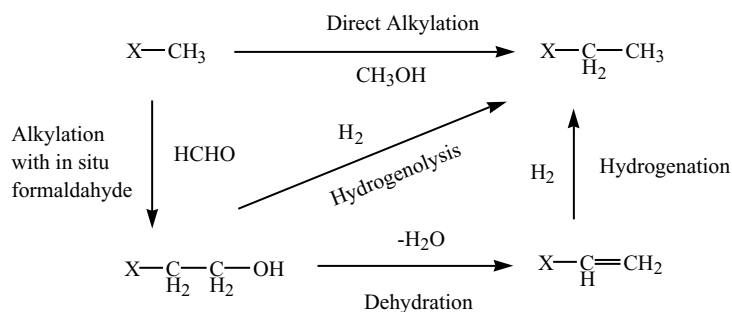
Fig. 7. Mechanistic model of overall reaction for the alkylation of toluene/acetonitrile with methanol using basic zeolite catalysts [1]; X is phenyl and –CN group for toluene and acetonitrile, respectively.

via alkylation with formaldehyde, formed in situ by partial decomposition of methanol.

By analogy with the mechanism for the formation of ethylbenzene and styrene in the side-chain alkylation of toluene with methanol [1], the formation of propionitrile and acrylonitrile presumably results from the alkylation of acetonitrile with methanol and formaldehyde. However, neither hydrogenation of acrylonitrile nor hydrogenolysis of 2-cyanoethanol (compared with hydrogenation of styrene or hydrogenolysis of 2-phenylethanol) should be involved in the formation of propionitrile because: (i) the decomposition of methanol to carbon monoxide (Fig. 5) is suppressed so that insufficient amounts of hydrogen are produced, (ii) the strong adsorption of acetonitrile would inhibit the adsorption and subsequently heterolytic dissociation of hydrogen into H^- and H^+, and (iii) if there are any active hydride anions available, the reaction would not only result in propionitrile because the cyanide group can be readily attacked by hydride anions producing amine derivatives [24,25] (and aldehydes in the presence of water [26,27]) in addition to the hydride attack at the conjugated double bond of acetonitrile [26,28]. Accordingly, the formation of propionitrile should only arise from the reaction between acetonitrile and methanol, and acrylonitrile should be formed by alkylation of acetonitrile with formaldehyde generated in situ via decomposition of methanol. A possible pathway for the formation of propionitrile and acrylonitrile can be proposed as shown in Fig. 8.

It is shown in this experiment that the effect of caesium cation "clusters" on the selectivity of saturated products becomes more obvious in the reaction of less electrophilic substrates (toluene) than in the reaction of highly electrophilic acetonitrile. The fact that the propionitrile/acrylonitrile ratio for CsNaX–CsOH is higher than that for CsNaX clearly suggests that selectivity to the saturated products (either ethylbenzene or propionitrile) which arises from direct alkylation of the substrate with methanol, depends largely on both the excess caesium present as "clusters" and the increased stability of the carbanion. The higher the surface concentration and the more stable the carbanion intermediate, the greater the chance for direct alkylation with methanol. Therefore, the saturated/unsaturated product ratio for alkylation of acetonitrile is always higher than that for the side-chain alkylation of toluene. In a similar manner, CsNaY–CsOH and CsNaEMT–CsOH, which contain excess caesium cation "clusters", also give highly selective conversion of acetonitrile to propionitrile, but with a reduced activity due to the less framework polarity as discussed earlier.

3.2.4. Effect of temperature

Alkylation of acetonitrile at higher temperature ($\sim$400 °C) gives an increase in the conversion of acetonitrile and shows some influences on the alkylated product selectivity. However, conversion of methanol is considerably increased when the higher temperature is used producing more carbon
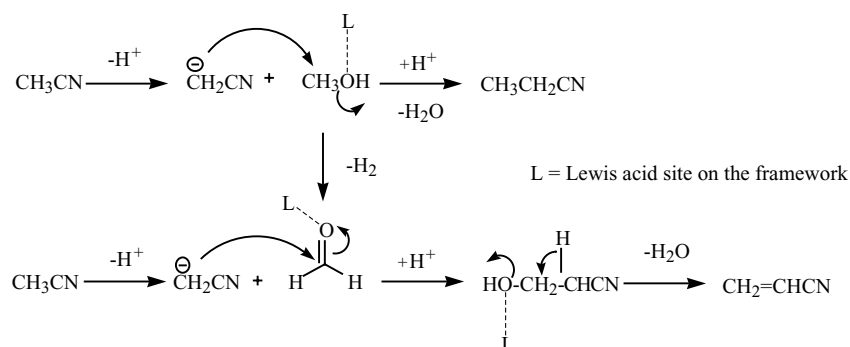

Fig. 8. Proposed reaction pathways for the formation of propionitrile and acrylonitrile from the alkylation of acetonitrile.
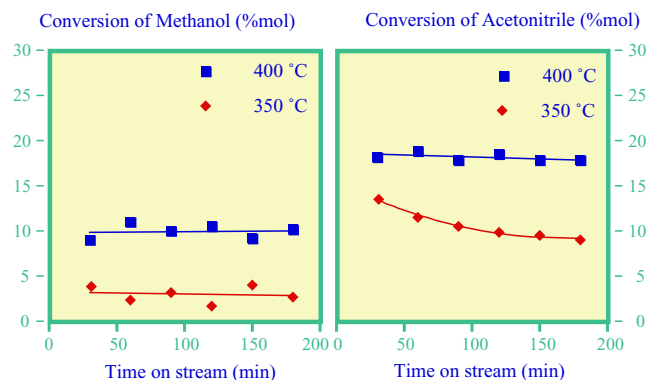
Fig. 9. Conversion of acetonitrile and methanol over CsNaX–CsOH at 350 and 400 °C.

Fig. 10. IR spectra (2000–1300 cm^{-1}) of organic matter retained in the spent catalysts (a) CsNaX–CsOH, (b) CsNaY–CsOH and (c) CsNaEMT–CsOH from the alkylation of acetonitrile.

monoxide over CsNaX–CsOH catalyst. The rate of deactivation for the reaction at higher temperature is lower than that at lower temperature reflecting complexity in the overall reaction mechanism. Fig. 9 shows the conversion of acetonitrile and methanol over CsNaX–CsOH at 350 and 400 °C.

At the higher temperature, a slight increase in selectivity to propionitrile is observed and by-products including carbon monoxide also increased. Up to 2% of aldehydes and amines are detected in the product mixture indicating that hydrogenation, hydrogenolysis and hydrolysis take place at the higher temperature. This can be attributed to the fact that, as the temperature increases, decomposition of methanol is enhanced producing more carbon monoxide and hydrogen which facilitates hydrogenation and hydrogenolysis of acetonitrile and the alkylated products, forming aldehydes and amines [24–27]. Consistent with this view, an increase in selectivity of propionitrile may be attributed to the additional yield from hydrogenolysis of 2-cyanoethanol and the decrease in formation of acrylonitrile since decomposition of formaldehyde is enhanced at high temperature [29].

3.2.5. Deactivation and regeneration

Deactivation of basic zeolite catalysts is usually limited as compared to that observed in acid catalysis. However, deactivation was clearly observed in the alkylation of acetonitrile with methanol, particularly with the catalyst containing excess caesium cation "clusters". It was seen from the experiment that (Fig. 6) the activity of CsNaX–CsOH, CsNaY–CsOH and CsNaEMT–CsOH were decreased in a somewhat faster rate than that of the catalyst with no excess caesium cation "clusters", such as CsNaX. In addition, it appears that the activity of CsNaX–CsOH becomes close to that of CsNaX after 120 min on stream. As a result, it can be presumed that the observed faster deactivation rate resulted from loss of activity of the excess caesium cation "clusters". The formation of stable carbonates is speculated to be the cause of the deactivation. This is in consistence with the observed increase of the band 1392 cm^{-1} in Fig. 10,
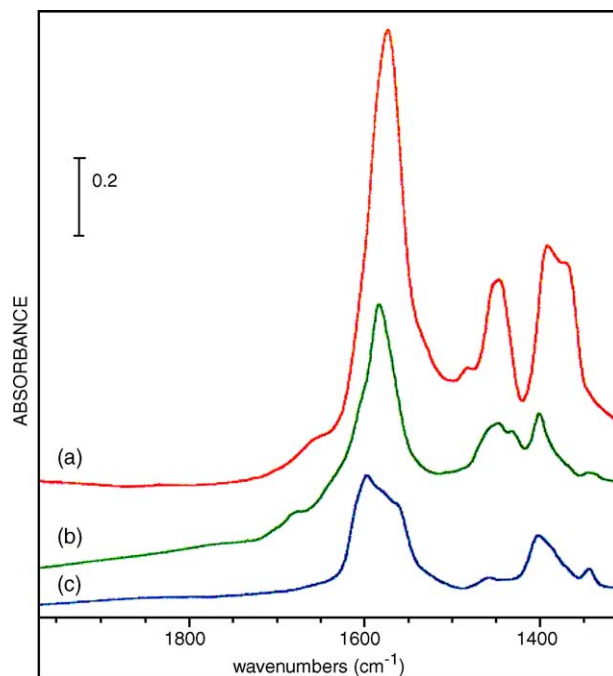
which can be assigned to some kind of carbonate-oxides, built up by additional carbon species (possibly carbon dioxide) during the reaction. This is particularly observed with CsNaX–CsOH since the catalyst is high in caesium content.

Although coking in base catalysis is found to be less than that in the reaction promoted by acid catalysts, infrared spectroscopy reveals some structural evidence concerning the organic matter retained in the spent catalysts. Fig. 11 shows that there are heteroatom-hydrogen vibrations, especially in the spent CsNaX–CsOH. These bands could, in principle, be assigned to alcohol (3200–3500 cm^{-1}), amine (3330–3400 cm^{-1}) and amide (3350–3520 cm^{-1}), but since the reactant is a nitrogen-containing compound (acetonitrile), the observed bands between 3200 and 3600 cm^{-1} presumably result from the N–H vibration frequency of amines and amides. Fig. 10 shows a strong vibration mode between 1300 and 1700 cm^{-1}, in which, the bands at 1570–1600 cm^{-1} are somewhat lower than conventional carbonyl ketones (1650–1750 cm^{-1}). However, these bands can possibly be assigned [30] to carboxylate anion (1550–1600 cm^{-1}) or C=N of imines and isocyanates (1471–1689 cm^{-1}), which may well result from hydrolysis of the –CN group of acetonitrile and its derivatives.

There is an additional adsorption frequency observed at ∼2150–2155 cm^{-1} which is somewhat lower than the typical vibration frequencies for alkyl nitriles. This can be assigned to cyanide (CN^{-}, 2120–2170 cm^{-1}) or to cyanate
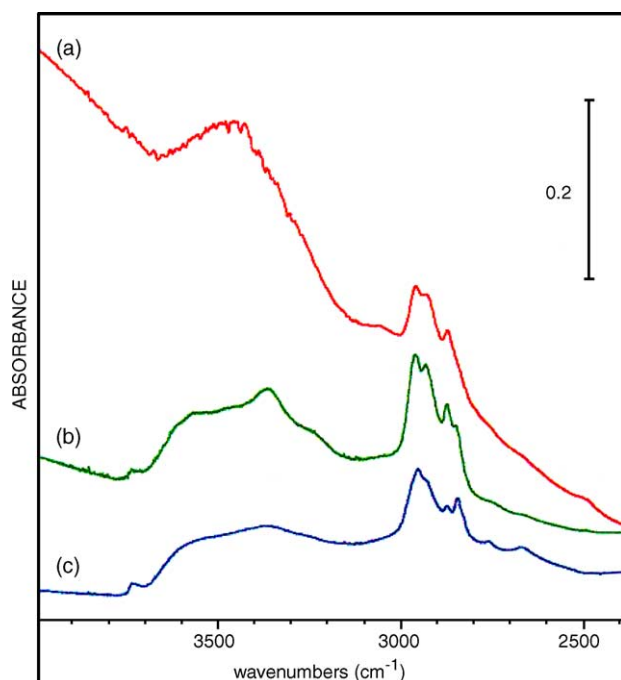
Fig. 11. IR spectra (4000–2500 cm^{-1}) of organic matter retained in the spent catalysts (a) CsNaX–CsOH, (b) CsNaY–CsOH and (c) CsNaEMT–CsOH from the alkylation of acetonitrile.

Fig. 12. Conversion of acetonitrile and selectivity to acrylonitrile for fresh and regenerated CsNaX.

anion (OCN^{-}, 2112–2165 cm^{-1}) countered by alkali cations [31,32], most probably caesium cations. These species may be decomposed from acetonitrile [33] and its derivative species, such as amides. The observed strong absorbance of the bands, which are attributed to the carboxylate and cyanide anion, indicates that dissociation of acetonitrile and its derivatives is largely promoted over CsNaX–CsOH.

The combustion/decomposition temperatures (in air) of coke retained in the spent catalysts shown in Table 3, appears to be higher than that for decomposition of the typical oxygenated coke ($\sim$300 °C) [7]. Nevertheless, it is lower than conventional decomposition temperatures of polynuclear aromatic cokes ($\sim$500 °C) produced in acid catalysis [34]. The observed decomposition temperature of the retained coke ($\sim$400 °C) suggests that the remaining organic matters are relatively small in molecular weight, as compared to typical polynuclear aromatic cokes.

In addition, the carbonyl-containing nitrogen compounds, such as amides and isocyanates, are highly electrophilic and mainly formed by reaction with water, hydrolysis. This reaction would be readily facilitated over catalysts with high aluminium content, such as CsNaX–CsOH. Conversely, amines
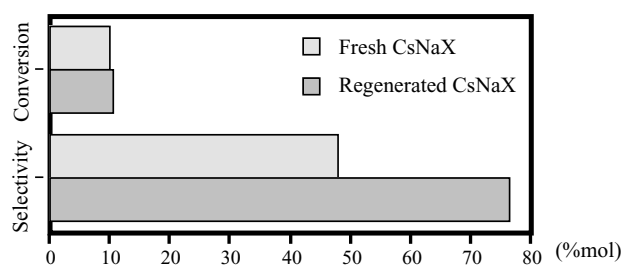
or *N*-heterocycle aromatics are highly nucleophilic and produced via hydrogenation–dehydrogenation processes. These reactions are preferably promoted by catalysts with a lower aluminium content, such as CsNaEMT–CsOH. Therefore, coke consisting of amines or *N*-heterocycle aromatics (in CsNaEMT–CsOH) should require a higher temperature (395 °C) for dissociation than that containing carbonyl compounds (in CsNaX–CsOH). Consequently, it seems clear that the decomposition temperature of the retained coke will increase with increasing Si/Al ratio of the catalyst (Table 3). In other words, it is possible to suggest that the organic matter deposited in caesium-exchanged zeolite X (low Si/Al) is composed mainly of carbonyl-containing nitrogen compounds, rather than amines or *N*-heterocycle aromatics. In contrast, the organic matter retained in CsNaEMT–CsOH (high Si/Al) appears to contain less carbonyl-containing nitrogen compounds but it is likely to be composed mainly of amines.

Practically, reactivation at high temperature ($\sim$500 °C, air atmosphere) may well remove most of the retained organic matter but it is also possible that during the decomposition, surface defects may be formed, mostly by dislodgement of aluminium. The typical defect sites formed in basic zeolite catalysts are likely to be alkoxides of $\equiv$Al–OH or $\equiv$Si–OH species, which have been reported [26,27] to be active for the dehydrogenation of methanol to formaldehyde and additionally, for stabilisation of the formaldehyde formed. Such alkoxides may also be generated during the regeneration of basic zeolite catalysts used in the alkylation of acetonitrile with methanol. These defect sites would then facilitate an increased formation of formaldehyde when the regenerated catalysts were reused. Consequently, the alkylation of active carbanions to produce acrylonitrile as a major product was expected. This has been evidenced when a regenerated catalyst was employed as shown in Fig. 12.

Table 3
Decomposition temperature and percentage of coke retained in the catalysts used in the alkylation of acetonitrile (measured by TGA/DTA)

Catalysts	CsNaX–CsOH	CsNaX	CsNaY–CsOH	CsNaEMT–CsOH
Si/Al ratio	1.3	1.3	2.9	4.2
Coke (%, w/w)	2.2	1.8	3.7	2.5
Combustion/decomposition temperature (°C)	357	347	372	395

The increased selectivity to unsaturated products after reactivation of the used catalysts was also observed by Engelhardt et al. [16] in the side-chain alkylation of toluene with methanol. The yield of styrene increased with the number of regenerations of the catalyst, KOH–KX. This can be explained in the same manner as suggested for the alkylation of acetonitrile and could also be related to the formation of sites which are active for the formation and stabilisation of formaldehyde, subsequently resulting in the unsaturated products, such as "acrylonitrile" for the alkylation of acetonitrile and "styrene" for the side-chain alkylation of toluene.

Although defects are formed during reactivation, no significant change in the nature of basic sites can be observed. This can be seen from experiments (Fig. 12) that the conversion of acetonitrile over the reactivated CsNaX is somewhat similar to that over the fresh CsNaX. It can be suggested that when organic matter is completely removed, the basic sites, which are responsible for the formation of carbanion intermediate, remain active. In addition, the formation of defect sites discussed earlier does not significantly alter basicity of the catalysts. In other words, the defect sites are not responsible for the proton abstraction and generation of active carbanion, but in particular, they increase the stability of formaldehyde intermediates. Consequently, the reaction over regenerated catalyst results in higher selectivity to unsaturated products, acrylonitrile, whilst the conversion remain unchanged.

4. Conclusion

The ability of the basic zeolites to catalyse carbanion reaction can in fact be summarised based on the principle of hard/soft acid/base [35]. In the presence of an electrophile, a strong interaction is expected for the *hard* framework oxygen with the *hard* proton of the electrophile, and for the *soft* caesium cation with the *soft* carbanion formed. The former interaction facilitates proton abstraction and the latter facilitates the stability of the carbanion intermediate formed. It is clear that the stronger the electrophilicity of the organic substrate, the softer the carbanion intermediate and also the better its stabilisation, which plays a significant role in the intermolecular reactions proceeding via carbanions. Therefore, the reaction of the softer cyanomethyl carbanion (from acetonitrile) is relatively faster than that of the benzyl carbanion (from toluene) over the same catalyst and conditions. Moreover, a highly polar environment in the catalysts appears to be essential for base-catalysed alkylation of weak electrophiles, such as toluene, whereas this is not necessary for strongly electrophilic substrates.

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