Conversion of 2-Methylfuran to 2-Methylthiophene over Molecular Sieves

Part 1.—Alkaline Y-Zeolites

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The use of Me¹ Y zeolites (Me¹ = Li, Na, K, Rb, Cs) for the title reaction has been studied at 623 K and atmospheric pressure, looking at the effect of the nature of monovalent alkali-metal ions on both physico-chemical and catalytic properties of the resulting catalyst. The catalyst is very active and selective and, after ageing, it can be regenerated quite easily by a proper redox treatment. Besides the desired product, small amounts to traces of *ca*. 30 byproducts were detected, the structure of which can be explained only by admitting two different parallel reactions, one based on an ionic-type and the other on a radical-type mechanism. Some hypotheses are proposed on the possible start-up of such mechanisms, based on different adsorption modes of H₂S onto the catalyst surface.

Synthetic zeolites are very effective and selective catalysts for the vapour-phase ring transformation of oxygen-containing heterocycles to the corresponding nitrogen- or sulphurcontaining heterocyclics.¹ The reaction of furan and its derivatives with hydrogen sulphide to produce thiophene and its homologues has been reported by Venuto and Landis.² An infrared study by Karge and co-workers³⁻⁵ showed that hydrogen sulphide is adsorbed dissociatively at room temperature on NaX zeolite, suggesting that the adsorption occurs on the cations weakly bound to the AlO_4^- basic sites of the zeolitic structure. The dissociation was clearly observed on alkaline Me^IX zeolites, while no dissociation was observed on Me^IY having an Si/Al atomic ratio higher than 2.5. This fact was explained by considering that the population of these basic sites becomes smaller, the higher the Si/Al ratio of the zeolite. For a similar reaction between alcohols and H_2S_1 , alkali-metal cations were found to behave as active sites in two different ways: as centres favouring the formation of acidic OH groups by dissociation of H₂O and H₂S, and as sites for the adsorption of H₂S.⁶

In the present work the catalytic activity of Me^IY zeolites (Me = Li, Na, K, Rb, Cs) for the conversion of 2-methylfuran (MF) to 2-methylthiophene (MT) by reaction with H₂S has been studied at atmospheric pressure, looking at the effect of the nature of the monovalent alkali-metal cation on both physico-chemical and catalytic properties of the resulting catalyst.

Experimental

Catalysts

Y-Zeolite catalysts were prepared from commercially available powder cake (LZY-52 from Union Carbide) by the usual procedure,⁷ *i.e.* by repeated ion-exchange treatment in refluxing 1 mol dm⁻³ aqueous solution of the corresponding chlorides until no further exchange was noticed. Washing in distilled water, drying at 383 K and calcination in air at 773 K followed. The degree of ion exchange was determined by atomic absorption spectrometry on the solution obtained after attack of the solid with hot HF-HClO₄ mixture (1 : 1 by volume). The data are given in table 1. The catalysts were also analysed by ESR, on fresh, aged and variously treated samples, by means of a Varian E-line Century Series spectrometer. All the spectra have been recorded at room temperature, after activation of the catalysts in flowing air for 8 h at 773 K, followed by various pretreatments. Most of the pretreatments were carried out at low temperature (323 K) with each of the two reagents (H_2S or MF) alone or with the standard feeding mixture of the two substances for 0.5 h, followed by purging in flowing N₂ for 1 h at the same temperature. The last set of spectra were recorded after 0.5 h on-stream in standard conditions, followed by purging in flowing N_2 for 1 h at the reaction temperature (623 K). Some XPS analyses were also done on selected catalysts, by means of a VG Escalab MKII spectrometer, X-ray source Al K_a (1486.6 eV). For this analysis the samples were mounted on double-sided adhesive tape and cooled with liquid N₂. The internal standard was the C 1s signal at 284.0 eV, relative to the carbon of the supporting tape. Adsorption of H_2S on the catalysts was studied by TPD, with He as the carrier gas, at the conditions reported in detail elsewhere.8

Apparatus, Procedure and Analysis

The activity comparison runs were always carried out on fresh catalyst samples, in a continuous, fixed-bed micro-reactor, described previously.⁹ Unless otherwise specified, standard reaction conditions were: reaction temperature = 623 K, feeding molar ratio $H_2S/MF = 5$, catalyst

Table 1. Characteristics of the catalysts employed

catalyst	residual Na ⁺ /meq g ⁻¹	ion exchange ^a (%)	$\delta_0{}^b$	$E_{\rm i}r^{-1}/{\rm eV}~{\rm \AA}^{-1}$
LiNaY	1.5	61	-0.347	7.93
NaY ⁴	4.0		-0.349	5.28
KNaY	0.4	89	-0.371	3.26
RbNaY	1.1	73	-0.381	2.84
CsNaY	1.0	76	-0.394	2.30

^a Extracted/initial Na⁺. ^b Average charge on oxygen (see text). ^c E_i = ionization energy of the alkali atom, r = ionic radius of the corresponding cation. ^d Original LZY-52 powder cake. Unit cell: Na₅₆(AlO₂)₅₆(SiO₂)₁₃₆, Si/Al atomic ratio = 2.43. weight, W = 2.5 g, W/F = 20 g_{cat.} h mol⁻¹ (total). Reaction products were collected in cooled traps and analysed by an FID gas chromatograph, equipped with a capillary column 50 m long and 0.25 mm outer diameter, coated with Carbowax 20M and operated isothermally (333 K). The carrier gas was hydrogen (1 cm³ min⁻¹). The identity of the major reaction products has been confirmed by GC-MS. Owing to the low flow of liquid reagent the reactor effluent was usually collected for at least 1 h to minimise the error on the mass balance. This is the reason why 'initial' activity refers to the first sample, collected during the first hour onstream. In any case, the mass balance around the reactor was 99 $\pm 4\%$, *i.e.* within experimental error.

Results and Discussion

Ca. 30 substances were detected in the condensed effluent, including those present only in trace amounts. More than 20 have been identified through the GC-MS analysis or by comparison with mixtures of known composition.

These products have been divided into two groups on the basis of their molecular structure. The first group includes, besides MT, those substances (e.g. thiophene, 2,5-dimethyl-furan, 3-methylthiophene, 2,3-, 2,4-, 2,5-dimethylthiophene, etc.) the structure of which suggests an ionic-type mechanism of formation, for instance dealkylation, disproportionation etc.¹⁰ The second group includes the substances such as n-hexane, 2-ethylfuran, acetone, tetrahydro-2-methylthiophene, ethylbenzene, 1-ethyl-2-methylthiophene etc., which can form only through a radical-type mechanism.¹¹

Catalyst performance has been expressed in terms of overall conversion, C (mol % of the fed MF), and selectivity, S_i (mol % of the converted MF to the various products). Data referring to the initial activity are collected in table 2.

Catalyst Deactivation and Regeneration

A more or less rapid deactivation of the catalyst was observed. To enhance this effect some runs were carried out at $W/F = 47 g_{cat.} h \text{ mol}^{-1}$. A typical result is shown in fig. 1. Complete deactivation is attained within 5 h or so. This confirms that the main reaction is always accompanied by a series of secondary reactions. Indeed, it is well known that heterocyclic compounds undergo addition reactions on acid catalysts, leading to polycondensation products and rapidly ending in heavy fouling of the catalyst. These secondary reactions are of a different nature, and are a function of the surface properties of the solid. For instance, our exploratory research showed that the acid forms of both X- and Yzeolites are less active than the Na-forms for the present main reaction, and that a different mechanism can be proposed for Me¹X zeolites from that of Me¹Y.¹² Indeed, in aged NaY zeo-

Table 2. Activity^a: mean value of first hour on-stream

catalyst	C (mol %)	S _{мт} (mol %)	S _{IB} (mol %)	S _{RB} (mol %)	R/I
LiNaY	55.3	71.5	10.3	18.2	0.22
NaY	53.0	75.6	9.9	14.5	0.17
KNaY	54.1	82.5	6.5	11.0	0.12
RbNaY	63.6	86.2	3.7	10.1	0.11
CsNaY	50.6	85.6	5.6	8.8	0.10

^a C = conversion of MF, S_i = selectivity to *i* (MT = 2-methylthiophene, IB = byproducts from ionic-type mechanism, RB = byproducts from radical-type mechanism), R/I = radical/ionic mechanism products (MT is included in ionic-mechanism products). W/F = 20 g h mol⁻¹, T = 623 K, H₂S/MF molar feeding ratio = 5.

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Fig. 1. Effect of catalyst decay in stressed conditions.

lites samples the analysis by XPS puts in evidence two signals at 163.4 and 169.3 eV, connected with S^{2-} and SO_x species, respectively. The first signal indicates that at least a part of the H₂S residua does not desorb at the reaction temperature, so blocking the corresponding active centres, in addition to the ones occupied by the polyaddition species formed through the condensation of the heterocyclic reactant.

In view of a possible application of the process, two different procedures of regeneration have been attempted. The first one was carried out at 773 K in oxygen, followed by hydrogen and monitoring the formation of CO_2 or of H_2S , by bubbling the outcoming gas in Ba(OH)₂ or in lead acetate solution, respectively. This method did not prove particularly successful, permitting the recovery of only 50% of the original activity. This has been attributed to the fact that the oxidative treatment transforms the S^{2-} species into the resistant SO_x species, as confirmed by the XPS analysis, showing the complete disappearance of the signal at 163.4 eV after O_2 treatment, together with the persistence of the signal at *ca*. 170 eV.

The second attempt was carried out by inverting the procedure, *i.e.* by eliminating first the S^{2-} adsorbed species (probably together with the HS⁻ species) by treatment of the catalyst in flowing H₂ at 873 K and then oxidizing the carbonaceous deposits by treatment in flowing O₂ at 773 K. This second procedure succeeded in recovering completely the original catalytic activity, as confirmed by a series of five successive reaction-regeneration cycles, also suggesting that the regeneration mechanism is catalysed by the zeolite.

Selectivity and Mechanism of Reaction

The data of table 2 indicate that, apart from the RbNaY sample, the conversion is practically the same for all of the catalysts, while the selectivity depends quite markedly on the nature of the alkali-metal cation. This is due to the coexistence of different competitive processes, as also revealed by the presence in the reactor effluent of products forming through a radical-type mechanism, together with those forming through the principal ionic mechanism. Both these mechanisms probably take place on the Me¹AlO₄⁻ sites present on the zeolite. The principle of equalization of electronegativity, proposed by Sanderson,¹³ permits one to calculate the value of the intermediate electronegativity S_{int} of the crystal, defined as the geometric mean of those of the component atoms forming the crystal. For a given sodic

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zeolite, for instance, the unit cell is $Na_x(AIO_2)_x$ (SiO₂)_y and the intermediate electronegativity is given by

$$S_{\rm int} = (S_{\rm Na}^x S_{\rm Al}^x S_{\rm Si}^y S_{\rm O}^{2x+2y})^{1/(4x+3y)}$$

 S_i being the values of the electronegativity of the various atoms on the Pauling scale. The partial charge $(\pm \delta_i)$ on the ith atom of the crystal can be calculated¹⁴ as the ratio of the change in electronegativity, $(S_{int}-S_i)$, undergone by the atom in joining the crystal to the change, $\Delta S = 2.08 (S_i)^{1/2}$, it would have undergone in acquiring or losing an electron. The values of S_i for calculating the partial charges on the combined atoms are given by Sanderson.¹⁵ In our case, when plotting the selectivity to the main product (S_{MT}) and the ratio (R/I) of radical to ionic products (including MT, of course) versus the partial charge δ_0 present on the oxygen atoms of the zeolite, a good correlation may be observed (fig. 2). The stronger the negative charge on the oxygen (i.e. the more basic the surface sites of the zeolite), the higher the selectivity to ionic products and the lower the amount of by-products forming through a radical-type mechanism.

Different hypotheses can be formulated on the initial mechanism triggering the desired ionic-type or the undesired radical-type reactions. In our opinion, the most convincing argument is the following. The relatively feeble charge δ_0 , present on the oxygen atoms of the zeolite (see table 1), indicates that the AlO_4^- basic sites are quite weak. As a consequence, the adsorption of reagents, particularly H₂S, does not take place through a completely ionic dissociation mechanism. Indeed, it is known⁵ that H₂S can be adsorbed dissociatively either via ionic interaction of a proton with the charged oxygen atom of an SIII zeolite site [fig. 3(a)] or by undergoing a radical-type dissociation via electronic interaction with the alkali-metal cation [fig. 3(b)], so providing the initiator for the corresponding catalytic activity of the solid. The relative preference for the two competitive mechanisms could be connected with the strength of the basic site, i.e. with the intensity of the negative charge sitting on the zeolitic oxygens. For a given mother-structure this charge depends on the ability of the alkali-metal cation to attract the electrons, which may be expressed by the value of the ratio of ionisation energy (E_i) of the alkali-metal atom to the radius (r) of the corresponding cation. Our data agree with this hypothesis: fig. 4 (upper curve) shows that the overall selectivity to ionic products $S_{\rm I}$ is higher the lower the $(E_{\rm i}/r)$ value, *i.e.* the more easily the alkali-metal atom tends to lose its electron. This is in line with the data of fig. 2, showing that the lower the strength of the negative charge on oxygen, the



Fig. 2. Selectivity to MT and ratio of radical- to ionic-mechanism products versus excess of negative charge on crystal-lattice oxygen.



Fig. 3. Hypotheses on the (a) ionic-, (b) radical-type adsorption mechanism of H_2S .

lower the amount of sites on which the ionic-type adsorption takes place, so leading to a lower selectivity of the catalyst towards the products forming through the ionic mechanism.

Our analysis by TPD of pre-adsorbed H_2S^8 showed only one peak in all the spectra (423–873 K temperature range). The most interesting result of this analysis is that the strength of the bond formed by adsorption of H_2S on the zeolitic sites is lower the lower the E_i/r ratio of the alkali-metal atom. Indeed, by plotting the value of the temperature, T_{max} , corresponding to the maximum of TPD spectra of H_2S for the various zeolites, versus E_i/r (fig. 4, lower curve) a trend opposite to that of the S_1 versus E_i/r (same figure) is observed. This means that the energy of interaction between H_2S and the zeolite site is higher for the ionic-type mechanism than for the radical-type mechanism of dissociative adsorption.

Additional information about the mechanism of reaction has been obtained from the analysis of our catalysts by ESR. The spectra are generally composed of the overlap of two lines (see *e.g.* fig. 5). The first, hereafter referred to as line A, is strong and narrow (linewidth *ca.* 5 G), with $g \approx 2$ (see table 3). The second (line B) is very broad (linewidth >1000 G) with a g value which is consequently difficult to evaluate. This line is most probably due to the presence of a large number of different radical species, so that no significant information can be obtained from it. Far more interesting is line A, which is absent in any of the untreated samples or in those treated with H₂S alone. It appears in the Li-, Na- and



Fig. 4. Selectivity to ionic-mechanism products and T_{max} of TPD spectra of H_2S from the substrate versus the ratio of ionisation potential (E_i) to ionic radius (r) of the alkali-metal cation.



Fig. 5. ESR spectrum (room T) of KNaY catalyst. Activation in air stream (8 h, 773 K), treatment with MF (0.5 h, 323 K) followed by purging in flowing nitrogen (1 h, 323 K). (a) Gain = 3.2×10^4 ; (b) gain = 1.25×10^5 .

K-containing samples treated with either MF or with the mixture of the two reagents at the lower temperature and in all the samples after reaction in standard conditions.

However, different characteristics are noticed in line A as a function of the conditions of pretreatment. When MF alone is adsorbed, the line is asymmetric and characterized by an average value of g decreasing from Li- to Na- to K-containing catalysts (see table 3 and fig. 6), as expected owing to the increasing size of the cation and, as a consequence, to the growing influence of this parameter on the value of the spin-orbit coupling. When H₂S is also present, different values of g are observed (table 3), indicating that different radical species are formed. Indeed, in these spectra $g_{Li} < g_{Na}$, but $g_K < g_{Li}$ and the lineshape becomes more symmetric, especially for KNaY catalyst (fig. 7). Furthermore, the value of g_K becomes closer to that of all the samples treated at the reaction temperature (table 3). For all these samples line A is very strong and Gaussian, probably due to an effective

Table 3. Characteristics of the line A (see text) of the ESR spectra (room temperature)

sample	intensity (arb. units)	linewidth/G	g					
MF 323 K								
LiNaY	64.8	10.8	2.0045					
NaY	20.0	9.0	2.0054					
KNaY	11.2	8.0	2.0059					
RbNaY	_	—						
CsNaY								
MF-H ₂ S 323 K								
LiNaY	21.6	8.3	2.0052					
NaY	21.9	8.0	2.0058					
KNaY	98.1	7.0	2.0047					
RbNaY		_	_					
CsNaY		_						
MF-H,S 623 K								
LiNaY	1850	9.5	2.0035					
NaY	845	8.0	2.0040					
KNaY	500	7.0	2.0041					
RbNaY	415	8.0	2.0042					
CsNaY	505	9.0	2.0042					



Fig. 6. ESR spectra (room T) of Me^INaY catalysts. Activation, treatment and purging as for fig. 5. (a) LiNaY, gain = 2.5×10^4 ; (b) NaY, gain = 8×10^4 ; (c) KNaY, gain = 1.25×10^5 .



Fig. 7. ESR spectra (room T) of Me¹NaY catalysts. Activation in air stream (8 h, 773 K), treatment with H₂S-MF (1 : 1 mol) for 0.5 h at 323 K, followed by purging in nitrogen stream (1 h, 323 K). (a) LiNaY, gain = 8×10^4 ; (b) NaY, gain = 8×10^4 ; (c) KNaY, gain = 8×10^3 .



Fig. 8. ESR spectrum (room *T*) of NaY catalyst. Activation in air stream (8 h, 773 K), on-stream for 0.5 h in standard reaction conditions (623 K), followed by purging in nitrogen stream (1 h, same *T*). Gain = 2×10^3 .

dipolar relaxation mechanism (fig. 8). The values of the spectroscopic factor g are in the order $g_{\text{Li}} < g_{\text{Na}} < g_{\text{K}} < g_{\text{Rb}} \approx g_{\text{Cs}}$. This indicates not only that H_2S plays an important role in the formation of radical species on the catalyst surface, but also that only in the presence of such a reagent are the radicals resulting from adsorption of the reactants on the catalyst of the same nature as those triggering the formation of the radical-type byproducts of the present reaction. Moreover, the lower the value of the spectroscopic factor g of line A the higher the concentration of radical species on the catalyst, a result perfectly in line with our selectivity data (table 2).

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