ALKYLATION OF THIOPHENE WITH METHANOL OVER SYNTHETIC ZEOLITES

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ABSTRACT

The behaviour of Na-, H-, Ca-, Mg-, K-, La-, totally or partially ion-exchanged X, Y and ZSM5 zeolites and of silicalite in catalysing the methylation of thiophene with methanol was systematically compared and the effect of the most important reaction parameters on catalyst performance was studied, within the 240-300°C temperature range. Interesting selectivity to mono-methyl-thiophenes, coupled with reasonable life, was obtained with partially protonated NaY zeolite, other catalysts giving less satisfactory results. Some correlations were found between physico-chemical properties and activity of the catalyst, which can be easily regenerated.

INTRODUCTION

It is well-known that methanol (M) may be easily converted into hydrocarbons over some zeolite catalysts [1,2]. Furthermore, owing to its particular reactivity [3], thiophene (T) tends to polymerise when put in contact with acidic substances. In spite of this, some data have been published, concerning the alkylation of T with alcohols, including M, on X- and Y-zeolite-based catalysts [4-6]. Unfortunately, these studies were performed in different conditions, so that it is not easy to compare the results and to find correlations between catalyst properties and performance. Therefore, it seemed interesting to carry

out a systematic comparison of the behaviour of catalysts prepared from X, Y, ZSM5 zeolites and from silicalite, in promoting the methylation of T with M. Some preliminary data were recently reported [7]. In the present work, the comparison has been further extended, in order to put in evidence the limitations connected with a process based on such a reaction.

EXPERIMENTAL

Catalysts. X- and Y-zeolite-based catalysts were prepared from commercially available powder cake (LZY-52, SK-45, SK-500 and Na13X from Union Carbide). ZSM5 and silicalite were prepared in our laboratory, following the well-known procedure [8]. XRD showed that both the latter materials were fully crystalline, their diffraction patterns matching perfecly the corresponding ones reported in the literature. "Analytical grade" pure chemicals were used for the preparation of catalysts and of ion-exchange solutions, as described elsewhere [9]. After ion-exchange, drying and calcination, the powder was pressed (maximum pressure 200 MPa) in ca. 1 mm thick wafers, which were then gently crushed and sieved, collecting the 40-60 mesh fraction. The ion-exchange degree was determined by AA spectrometry. Surface acidity was determined by titration with n-butyl-amine (n-BA) in anhydrous solvent, after pretreatment at 500°C in a slow flow of dry air. The main characteristics of the catalysts employed are summarised in Table 1.

Apparatus, procedure and analysis. Alkylation runs were carried out in a continuous, fixed-bed microreactor, previously described [10]. Hydrogen was used as carrier gas. Before each run, the catalyst was activated "in situ" overnight in a slow flow of nitrogen at 500°C. Standard reaction conditions were as follows: 240°C; molar ratio (R_H) of carrier gas to liquid feed = 3; WHSV (g of liquid feed/g of cat.x h) = 1; feeding T/M molar ratio ($R_{T/M}$) = 2; catalyst weight 1.5 g. Reaction products were collected in traps cooled to -80°C and analysed by GC, on a capillary glass column, 0.3 mm I.D. and 50 m long, coated with Carbowax 20M and kept at 60°C. Usually four samples for analysis were collected, after 1, 3, 5 and 10 h on-stream, respectively.

Table 1

Main characteristics of catalysts employed and results of activity comparison runs in standard conditions. Data after 1 h on-stream.

Catalyst[a]	Surface acidity (mmol n-BA/g cat.)			y mol%	S_{mT} mol%	$\Delta y/\Delta t$[b] mol%/h
	$H_o \leq -1.5$	$-1.5 \leq H_o \leq 3.2$	$3.2 \leq H_o \leq 6.8$			
NaY[c]	0	0	0	no reaction		
HNaY-17	0	0.03	0.02	2	19	0.05
HNaY-30	0	0.10	0.06	4	65	<0.05
HNaY-55	0	0.65	0.81	32	13	0.5
HNaY-67	0.07	0.87	0.94	75	7	3.1
HNaY-98	0.13	0.87	1.00	82	6	3.6
MgNaY-25	0.01	0.05	0.11	12	6	0.5
MgNaY-55	0.06	0.25	0.92	30	10	0.5
MgNaY-76	0.09	0.57	1.19	50	11	1.9
CaNaY-76	0.05	0.19	0.42	10	12	0.5
CaNaY-91	0.06	0.29	0.76	26	15	2.2
LaNaY-30	0.05	0.12	0.50	29	8	2.0
REY[d]	0.12	0.18	1.53	72	8	2.6
HKY-36[e]	0	0.08	0.18	22	2	0.3
NaX[f]	0	0	0	no reaction		
HNaX-95	0	0.20	0.07	17	2	0.5
CaNaX-82	0	0.05	0.10	9	13	0.5
CaNaX-98	0.05	0.06	0.57	7	32	0.9
NaZSM5[g]	0	0	0.02	20	5	1.2
HZSM5[h]	0.18	0.14	0.56	52	4	3.0
Silicalite	0	0	0	no reaction		

[a]) figures represent the % ion-exchange degree, with respect to the original Na-form; [b]) decay rate relative to the initial 10 h on-stream; [c]) LZY-52 cake, "mother" material of the Y-series, SiO_2/Al_2O_3 wt ratio (s/a) = 2.80; [d]) SK-500 cake, s/a=2.86; [e]) from SK-45 cake, s/a=3.18; [f]) 13X cake, "mother" material of the X-series, s/a=1.73; [g]) "as prepared" ZSM5 cake, s/a=15.0; [h]) from NaZSM5, maximum obtainable ion-exchange degree.

RESULTS AND DISCUSSION

Besides 2- and 3-methyl-thiophene and unreacted M and T, usually some 2,5-dimethyl-thiophene was found in the collected liquid. In higher-temperature ($\geq 270\,^{\circ}$C) runs, various poly-methyl-thiophenes were also found, especially trimethyl-thiophenes and methyl-ethyl-thiophenes as identified by GC-MS. In any case, the ratio 2- to 3-methyl-thiophene was ca. 2:1.
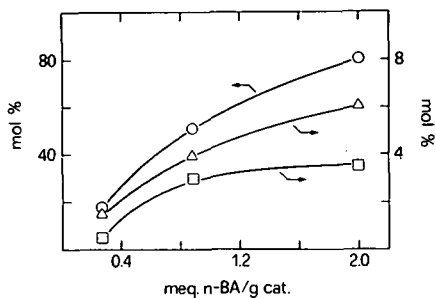

Fig.1. Conversion (O), selectivity ($\triangle$) and decay rate ($\square$, mol%/h) for fully protonated zeolites as a function of surface acidity ($H_o \leq 6.8$). T=240°C, R_H=3, $R_{T/M}$=2, WHSV=1, time-on-stream=1 h.

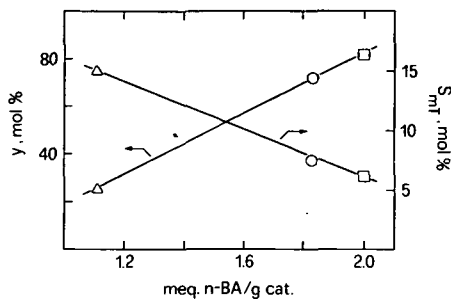Fig.2. Conversion and selectivity vs. surface acidity ($H_o \leq 6.8$) for CaNaY-91 ($\triangle$), REY (O) and HNaY-98 ($\square$) catalysts. Reaction conditions as for Fig.1.

Results have been expressed in terms of mol % conversion (y) of M and mol % selectivity (S_{mT}) to mono-methyl-thiophenes (mT), defined as follows:

$$y = (\frac{reacted}{fed})_M 100 \tag{1}$$

$$S_{mT} = \frac{mT \ formed}{M \ reacted} 100 \tag{2}$$

The carbon atoms balance, with respect to the feed and referred to liquid products collected within the sampling trap, usually ranged from 94 to 99 %. In two cases this figure was 93% and in only one case it was 91%.

Data from activity comparison runs in standard conditions are

collected in Table 1. These results show that: i) As a general trend, conversion increases with increasing surface acidity, the "as supplied" fully-Na forms and silicalite being completely inactive. The "as prepared" NaZSM5 zeolite cannot be considered as a fully-Na form, due to the presence of protons formed during calcination, by decomposition of residual tetraalkylammonium ions. The latter are trapped within the zeo-
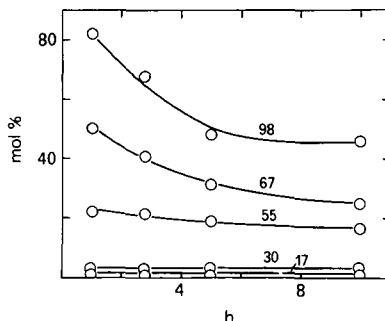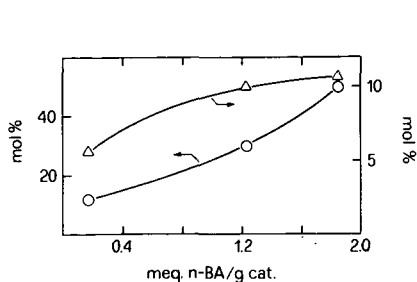

Fig.3. Conversion (O) and selectivity (△) vs. surface acidity ($H_o \leqq 6.8$) for MgNaY catalysts. Reaction conditions as for Fig.1.

Fig.4. Conversion vs. time-on-stream as a function of ion-exchange degree (figures on the curves). Reaction conditions as for Fig.1. Catalysts: HNaY series.

litic framework during synthesis. ii) When comparing HNa-type catalysts, prepared from different zeolites, one may notice that, in general, both Y- and ZSM5-based catalysts are more active, the former showing also a better selectivity. HNaX catalysts, on the other hand, are less active (see also Figure 1). The different behaviour of HNaY, with respect to HNaX catalysts, seems clearly due to different concentration of surface acid centres. The lower selectivity of ZSM5-based catalysts is very likely connected also with the well-known ability of such a zeolite in catalysing the conversion of M into hydrocarbons [1]. Indeed, some tests, performed by feeding pure M in our standard conditions, confirmed that, with any catalyst based on such a zeolite, no more than 80% of the alcohol could be recovered unconverted, even at temperatures as low as 210°C. iii) A net increase in performance

seems to be conferred by Ca^{2+} ions in the case of X-zeolite. On the
other hand, exchange by either Mg, Ca, La or K ions does not change sub
stantially the performance of Y-zeolite catalysts, with respect to the
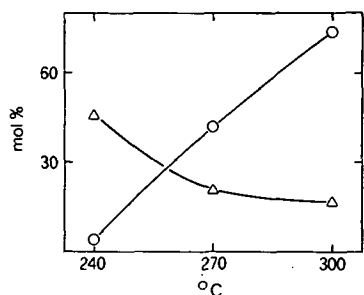HNaY series. However, some interesting correlations; may be found when

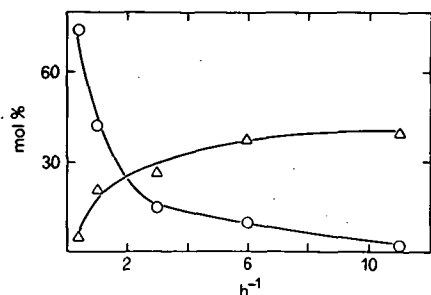Fig.5. Conversion (O) and selectivity (Δ) vs. reaction temperatu-
re. HNaY-30 catalyst.

Fig.6. Effect of WHSV. T=270°C. Catalyst and symbols as for Fig.5.

considering Y-based catalysts. By comparing the results obtained at the
highest ion-exchange degree, (HNaY-98, REY and CaNaY-91) one may see
(Figure 2) that conversion regularly increases and selectivity decrea-
ses with increasing surface acidity, in agreement with an early corre-
lation reported by Venuto |11,12|. Mg- and Ca-exchanged series behave
differently: both conversion and selectivity increase with increasing
acidity (see e.g. Figure 3). This may be explained when considering
that alkylation of T, as well as undesired coking or polymerisation
reactions, are catalysed by acid centres, although of different
strength. It is known [13] that a different distribution in acid site
strength is conferred to the zeolite by bivalent Ca^{2+} and Mg^{2+} ions,
with respect to that conferred by H^+, the latter favouring stronger
sites. This is confirmed by our data (Table 1): a higher concentration
of both stronger ($H_o \leq -1.5$) and medium-strength ($-1.5 \leq H_o \leq 1.5$) sites is
usually present in HNaY zeolites, with respect to Ca- or Mg-NaY ones.
        Unfortunately, in the present case, the ion-exchange procedure
seems unsuccessful in providing selectively only the desired type of
centres at any exchange degree and with any of the ions here employed.

In any case, weaker sites, promoting preferentially the alkylation reaction, form first, conferring to the catalyst a higher selectivity at low conversion. However, when attempting to increase conversion, either by increasing the ion-exchange degree or by changing the ion, the unavoidable simultaneous formation of higher-strength centres confers to the catalyst a progressive ability in promoting also unwanted reactions. The result is the simultaneous decrease in selectivity, usually accompanying the increase of conversion.

From a practical point of view, the best compromise seems to be attainable with the catalysts of HNaY series. In this case overall conversion progressively increases, with increasing the ion-exchange degree, while selectivity goes through an interesting maximum (for HNaY-30). In correspondence of the latter, side reactions are still at a reasonable level, as shown by the decay rate (last column in Table 1), which attains the lowest value observed for any of the catalysts tested. Activity decay is shown in Figure 4 for the whole set of HNaY catalysts. Therefore, HNaY-30 catalyst was selected for the following analysis, aiming at the optimisation of reaction conditions.

As expected, conversion increases and selectivity decreases by increasing temperature (Figure 5) or by decreasing WHSV (Figure 6). To enhance the effect of WHSV, Figure 6 data were collected at 270°C.
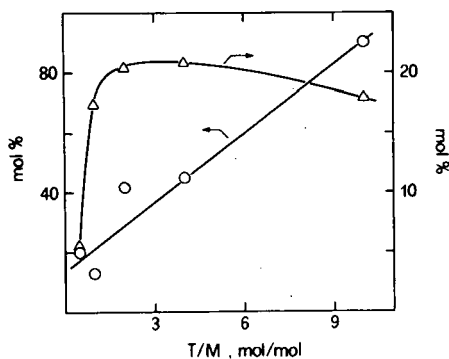

Fig.7. Effect of T/M feeding ratio (mol). T=240°C. Catalyst: HNaY-30. (O) conversion, (Δ) selectivity.

In addition, decay rate increases with temperature, particularly at 300°C, where any reaction stops within a few hours. As for the effect of $R_{T/M}$, an increase of conversion is noticed with increasing such a parameter (Figure 7), while selectivity shows a strong increase for $R_{T/M}$ going from 0.5 to 2, reaching a maximum at $R_{T/M} \sim 4$ and then decreasing slowly for higher $R_{T/M}$ values.

In view of a possible application, since the activity of any of the zeolites tested decays more or less rapidly, it is important to ascertain if the catalyst may be regenerated. This aspect was investigated by performing a series of reaction-regeneration runs on the same sample of HNaY-30 catalyst. To speed up the test, only standard reaction conditions were considered and time-on-stream was limited to 30 h. After regeneration, the reaction was immediately retaken for the next 30 h run. Three reaction-regeneration cycles were carried out, so that the total working time was 90 h. After a short purging with nitrogen, regeneration was performed by simply burning-off carbonaceous deposits in a slow flow of air at 350-500°C. The formation of CO_2 was monitored by bubbling the outcoming gas in $Ba(OH)_2$ solution, that of SO_2 by bubbling in $AgNO_3$ solution. In any reaction cycle conversion remained unchanged during the first 24 h on-stream, then decaying quite slowly. The results showed that regeneration restores completely the activity shown by the fresh catalyst, the behaviour of which was perfectly matched in both the runs following each regeneration.

CONCLUSION

The results of the present work permit to conclude that;
i) Vapour-phase alkylation of T by M may be obtained over zeolites with reasonable selectivity only when acid sites of relatively low strength are present on the catalyst surface.
ii) HNaY-30 catalyst showed the best compromise between activity, selectivity and durability.
iii) Reaction temperature should not exceed 250°C and $R_{T/M}$ should not be lower than 2, to keep within reasonable limits the formation of polymethylates and coking-polymerisation.
iv) The activity decay is essentially due to fouling by carbonaceous

deposits. However, the latter can be easily burned-off with air, so restoring completely the behaviour of fresh catalyst.

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