CATALYTICALLY ACTIVE CENTERS OF ZEOLITES IN THE REACTION BETWEEN H_2S AND CH_3OH

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ABSTRACT

The reaction between methanol and hydrogen sulfide was carried out on HNaY and ZSM-5 type zeolites. Brønsted acid sites are catalytically active centers. In the absence of acidic OH groups, i.e. on NaX and NaY zeolites, sodium cations play the rôle of active sites. The selectivity of this reaction towards $(CH_3)_2S$ and CH_3SH depends on the temperature and the molar ratio H_2S : CH_3OH. Competitive with the reaction of H_2S with CH_3OH is the decomposition of methanol to hydrocarbons.

INTRODUCTION

Results of a study on the reaction between methanol and hydrogen sulfide on HNaY zeolites have been presented in an earlier paper [1]. It was found that the methoxylation of the zeolite surface is the first step of this process. The formation of the methoxyl groups requires Brønsted acid centers to be present on the zeolite surface. It seemed interesting to compare the activity of hydrogen and sodium forms of zeolites, and to find out whether the same catalytically active centers take part in this reaction on both forms of zeolites. It was the aim of this study to elucidate this problem.

EXPERIMENTAL

Catalysts. The following catalysts were used: NaX, Linde Lot No. 1360027, with Si/Al=1.21; NaY, Linde SK-40 Lot No. 3606411, with Si/Al=2.37; HNaY, prepared from NaY *via* ion exchange with 1M solution of CH_3COONH_4 (degree of exchange, δ=60 %); NaZSM-5, Ultraset T-1000/J ($Na_{4.07}Al_{2.45}Si_{93.15}O_{192}$), synthesized in the Institute of Industrial Chemistry in Warsaw, with Si/Al=38; HZSM-5, prepared from NaZSM-5 *via* ion exchange with 0.25 M solution of NH_4Cl (δ =100 %).

Reaction conditions. The continuous flow technique was used to measure the catalytic activity. The apparatus has been described in

Ref. [1]. Portions of 0.2 g of dehydrated zeolite were employed. The zeolite crystallites were tabletted without binder, ground, sieved to a 0.5-1.0 mm diameter range and 4 hours *in-situ* activated in pure and dried helium flow at 673 K.

A mixture containing Merck research grade H_2S (3-12 vol. %, depending on the desired H_2S : CH_3OH ratio), methanol (3 vol. %) and helium as a carrier gas, was passed through the catalyst bed to a gas chromatograph. The flow rate was 2.4×10^{-4} m^3h^{-1}. Each experiment was carried out twice: (i) using GC analysis with a catharometer, (ii) using GC analysis with a flame ionization detector. The first technique was applied in particular for the determination of H_2S conversion. In both analyses a 2 m Porapak Q column was employed at 423 K for separating the products.

The catalytic experiments were conducted at 623 and 673 K, using various H_2S : CH_3OH molar ratios, *viz.* 1:2, 1:1, and 4:1. The reaction between H_2S and CH_3OH was also carried out after poisoning the acidic centers with pyridine at 623 and 673 K.

IR measurements. IR spectra were obtained with a Perkin-Elmer Model 325 spectrometer. Design and operation of the IR cell has been described elsewhere [2]. The zeolite wafers, having a thickness of about 10 $mg \cdot cm^{-2}$, were activated for 12 h at 673 K under high vacuum (10^{-4}Pa). Subsequently, pyridine or water was adsorbed at 623 and 673 K.

RESULTS

Catalytic experiments. The results of the reaction between methanol and hydrogen sulfide on faujasite-type zeolites are presented in Table 1.

The highest conversion of methanol was observed on HNaY, but the selectivity towards CH_3SH and $(CH_3)_2S$ was lower than in the case of the pure sodium forms of faujasite type zeolites. It was observed that on HNaY zeolite a fraction of the methanol underwent decomposition to hydrocarbons. It was possible, however, to increase the selectivity of HNaY towards CH_3SH and $(CH_3)_2S$ by using an excess of H_2S in the feed. In the case of NaX and NaY zeolites, no products of methanol decomposition were observed. NaX zeolite exhibited higher activity than NaY.

The increase of the reaction temperature did not give rise to any significant changes in the activity and selectivity of sodium forms of X and Y type zeolites. However, in the case of HNaY, the selectivity towards $(CH_3)_2S$ increased with increasing reaction temperature. This

Table 1

Methanol conversion and yield of products in the reaction of H_2S and CH_3OH on faujasite-type zeolites (data after 2h time on stream)

Zeolite	$H_2S:CH_3OH$ molar ratio	CH_3OH conv.(%)	CH_3SH yield(%)	$(CH_3)_2S$ yield(%)	After poisoning with pyridine		
					CH_3OH conv.(%)	CH_3SH yield(%)	$(CH_3)_2S$ yield(%)
		Reaction Temperature : 623 K					
NaX	1:2	65	15	40	48	15	30
NaX	1:1	70	40	30	40	30	10
NaX	4:1	85	65	20	50	45	5
NaY	1:2	50	4	18	20	4	-
NaY	1:1	33	13	20	10	10	-
NaY	4:1	50	30	20	25	20	5
HNaY	1:1	98	10	13	25	4	-
HNaY	4:1	100	15	80	50	15	15
		Reaction Temperature : 673 K					
NaY	1:2	50	6	18	20	6	1
NaY	1:1	35	13	20	15	13	2
NaY	4:1	50	30	20	35	30	5
HNaY	1:1	100	5	20	70	5	15
HNaY	4:1	100	15	55	90	6	45

was even more evident in a lower range of reaction temperatures, when no products of methanol decomposition were observed, which was described earlier [1].

Measurements of the effect of the $H_2S:CH_3OH$ molar ratio on the activity and selectivity of the reaction indicated that, on sodium forms of faujasite-type zeolites, an excess of H_2S causes an increase both in methanol conversion and selectivity towards CH_3SH. This seems to be correlated to the reaction between $(CH_3)_2S$ and H_2S. Indeed, inspection of the reaction curves (Figure 1) reveals that at the beginning of the reaction between H_2S and CH_3OH on NaX, the yield of $(CH_3)_2S$ was higher than that of CH_3SH. With increasing reaction time, the yield of $(CH_3)_2S$ decreased and the yield of CH_3SH increased.

Poisoning of the acidic centers on faujasite-type zeolites by pyridine at 623 K resulted in a significant decrease of the $(CH_3)_2S$ yield, and in a smaller one of the CH_3SH yield (see Table 1). At higher temperatures (673 K), the poisoning by pyridine did not change the yield of CH_3SH, but brought about a decrease of the $(CH_3)_2S$ yield. Hence, the formation of either product requires acidic centers, but

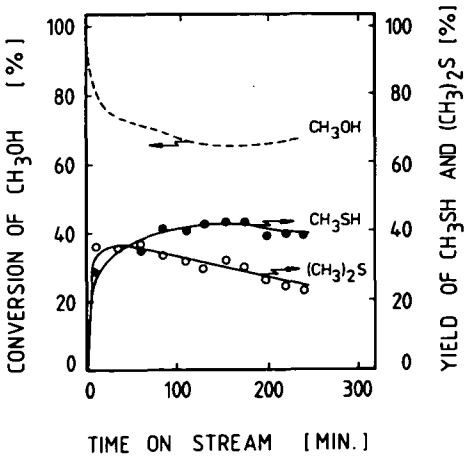


Fig. 1. Conversion of methanol on NaX at 623 K (H_2S:CH_3OH=1:1)

the reaction towards CH_3SH occurs on weaker centers than the reaction towards $(CH_3)_2S$. A fraction of the fed CH_3OH still decomposed when the catalyst was poisoned by pyridine. Again, decomposition of CH_3OH seems to proceed on weaker centers than the reaction with H_2S.

Table 2 shows the results of the reaction between H_2S and CH_3OH over NaZSM-5 and HZSM-5 zeolites. Only in the case of excess of methanol (H_2S:CH_3OH=1:2), were methanol decomposition products observed. ZSM-5 type zeolites exhibited higher activity than faujasite-type zeolites. Similarly, as was found on faujasite-type zeolites, the excess of H_2S caused an increase in selectivity towards CH_3SH. At higher temperature (673 K), the yield of CH_3SH over ZSM-5 is higher than at lower temperature (623 K), in contrast to the behaviour of faujasite-type zeolites. Similar to what was found with faujasite-type zeolites, poisoning of the acidic centers by pyridine resulted in a significant decrease of the $(CH_3)_2S$ yield and a smaller decrease of the CH_3SH yield.

IR measurements. The aim of the infrared study was to clarify which type of acidic centers (Lewis or Brønsted sites) is involved in the reaction between H_2S and CH_3OH and whether water (the product of this reaction) can form acidic hydroxyl groups.

After pyridine adsorption on NaX and NaY zeolites at 623 K for 1 h and evacuation at the same temperature during 15 minutes, weak-to-medium bands at 1442, 1490, and 1598 cm^{-1} appeared (see Figure 2).

According to Parry [3] and Liengme and Hall [4], the band around 1442 cm^{-1} is typical of coordinately bonded pyridine. Liengme and Hall [4] ascribed the band at 1442 cm^{-1} to pyridine coordinated to sodium ions. Therefore, the IR experiments showed that the only centers on the surface of NaX and NaY zeolite which could be poisoned by pyridine were Lewis acid centers (sodium cations); Brønsted or true Lewis sites [4-7] were not present.

Figure 3 presents the spectra obtained after adsorption of pyridine on HNaY zeolite at 623 and 673 K. Bands were observed at the following wavenumbers: 1628 and 1620 cm^{-1}, due to coordinately bonded

Table 2

Methanol conversion and yield of products in the reaction of H_2S and CH_3OH on ZSM-5 type zeolites (data after 2h time on stream)

Zeolite	$H_2S:CH_3OH$ molar ratio	CH_3OH conv.(%)	CH_3SH yield(%)	$(CH_3)_2S$ yield(%)	After poisoning with pyridine		
					CH_3OH conv.(%)	CH_3SH yield(%)	$(CH_3)_2S$ yield(%)
		Reaction Temperature : 623 K					
NaZSM-5	1:2	70	3	50	10	3	-
NaZSM-5	1:1	90	10	80	10	7	-
NaZSM-5	4:1	98	33	65	17	9	-
HZSM-5	1:1	98	5	93	25	3	-
HZSM-5	4:1	100	40	60	20	15	-
		Reaction Temperature : 673 K					
NaZSM-5	1:2	85	-	65	35	-	10
NaZSM-5	1:1	98	15	83	30	15	10
NaZSM-5	4:1	98	43	55	40	25	10
HZSM-5	1:1	100	10	90	40	8	10
HZSM-5	4:1	100	50	50	75	40	35

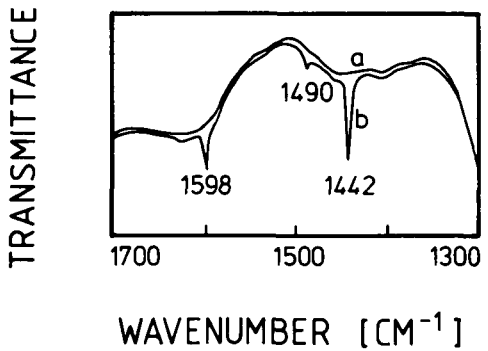


Fig. 2. Adsorption of pyridine on NaY. (a) baseline, after activation at 673 K; (b) after pyridine adsorption and subsequent evacuation, at 623 K

pyridine [4], 1545 cm^{-1} due to pyridinium ions [4], 1488 cm^{-1}, due to pyridine and pyridinium ions [4], 1452 cm^{-1}, due to pyridine coordinately bonded to true Lewis sites [3-7]. After pyridine adsorption at 623 K, a small shoulder around 1442 cm^{-1} appeared (Figure 3, spectrum b), which is assigned to pyridine coordinated to sodium ions. After heating at 673 K this shoulder disappeared (Figure 3, spectrum c). Simultaneously, the intensity of the pyridinium ion band at 1542 cm^{-1} (pyridine adsorbed on Brønsted acid centers) decreased more than the band due to pyridine adsorbed on true Lewis acid sites. The results shown in Figure 3 lead to the following conclusions: (i) After activation at 673 K, HNaY possesses both Brønsted and Lewis acid centers, which are poisoned by pyridine at either reaction temperature (632, 673 K); (ii) pyridine does not

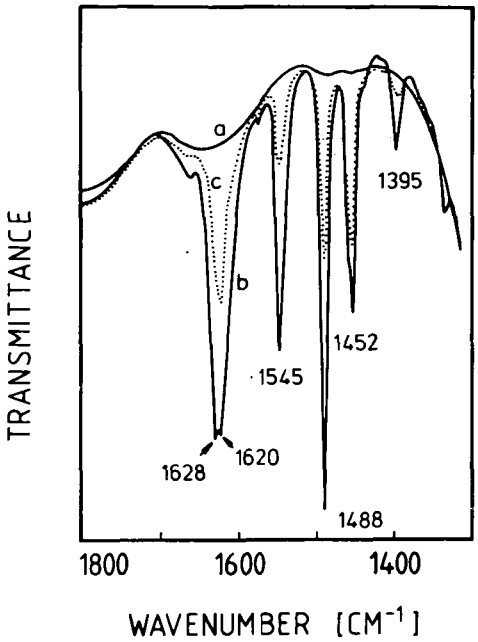


Fig. 3. Adsorption of pyridine on HNaY. (a) baseline after activation at 673 K; (b) after pyridine adsorption and subsequent desorption, at 623 K; (c) after continued evacuation at 673 K

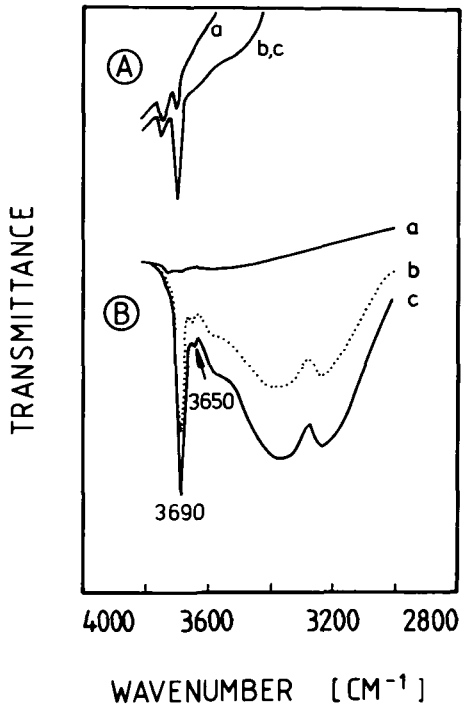


Fig. 4. Adsorption of water on NaY (A) and NaX (B). (a) baseline, after activation at 673 K; (b) after H_2O admission at 623 K (ca. 2 Pa final pressure) and subsequent pumping; (c) after subsequent heating to 673 K (1/2 h) and pumping

poison sodium cations at 673 K.

Adsorption of H_2O on sodium forms of X and Y type zeolites was carried out at 623 and 673 K. Figure 4 presents the IR results. After adsorption of H_2O on NaY zeolite at 623 K no acidic hydroxyl groups were observed. The same was true after heating at 673 K (Figure 4A, spectra b and c). Adsorption of H_2O on NaX zeolite under the same conditions resulted in formation of OH groups, since a very weak band at 3650 cm^{-1} appeared (Figure 4B, spectra b and c). However, this OH band did not disappear after adsorption of pyridine at 623 K. Simultaneously, no bands due to pyridinium ions appeared. This would mean that even if (acidic) OH groups form from the reaction product H_2O under reaction conditions, they are relatively weak, since they cannot be poisoned by pyridine at 623 K.

The results obtained after adsorption of pyridine on NaZSM-5 and

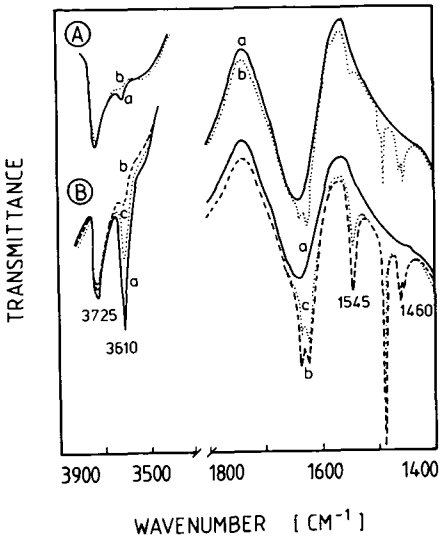


Fig. 5. Adsorption of pyridine on NaZSM-5 (A) and HZSM-5 (B). (a) baseline, after activation at 673 K; (b) after pyridine adsorption and subsequent desorption, at 623 K; (c) after subsequent desorption at 673 K

HZSM-5 zeolites at 623 and 673 K are shown in Figure 5.

After activation at 673 K, two bands at 3610 and 3725 cm^{-1} were present in the infrared spectra of both zeolites (Figure 5, spectra a). Jacobs and Balmoos [8] attributed these bands at 3610 and 3725 cm^{-1} to OH groups of zeolitic Brønsted acid sites and of extrazeolitic material, respectively. Spectra b were obtained after adsorption of pyridine at 623 K on NaZSM-5 and HZSM-5. The intensities of the 3610 cm^{-1} bands were significantly decreased, but the intensities of the OH band at 3725 cm^{-1} were only very little affected. Simultaneously, in the 1400-1800 cm^{-1} region the bands of adsorbed pyridine appeared. Both the bands typical of Brønsted acid (around 1540 cm^{-1}) and Lewis acid sites (around 1452 cm^{-1}) were observed in spectra b. When, subsequent to pyridine adsorption on HZSM-5 at 623 K, the sample was heated to 673 K and evacuated, the band of pyridine coordinatively bonded to true Lewis sites (1460 cm^{-1}) did not change its intensity, but the intensity of the band due to pyridinium ions (1545 cm^{-1}) decreased (spectra c). These IR findings let us conclude that (i) after activation at 673 K both Lewis and Brønsted acid sites exist on the surface of NaZSM-5 and HZSM-5, (ii) pyridine poisons Lewis acid centers equally strongly at 623 and 673 K, but acidic Brønsted sites are poisoned by pyridine to a lesser extent at 673 K than at 623 K.

DISCUSSION

In the previous paper [1], it has been reported that the methoxylation of the zeolite surface is the first step in the reaction between H_2S and CH_3OH on hydrogen forms of Y-type zeolite. It was stated that the Brønsted acid sites of HNaY are the active centers.

After activation at 673 K, sodium forms of X and Y type zeolites do not have any acidic hydroxyl groups (see Figure 4). Nevertheless,

these catalysts, in particular NaX, show high activity for the reaction between H_2S and CH_3OH. Poisoning of the samples with pyridine caused a decrease of the yield of CH_3SH and $(CH_3)_2S$. Infrared measurements indicated that pyridine adsorbs on sodium cations of NaX and NaY which act as Lewis acid centers (Figure 2). These observations allow us to conclude that sodium cations play an important rôle in the reaction of H_2S with CH_3OH when carried out on sodium forms of faujasite-type zeolites. Two possibilities should be considered: Sodium cations might be necessary for chemisorption of H_2S or for chemisorption of methanol. As Karge and Raskó [9] found, the dissociation of H_2S to H^+ and SH^- does not occur on sodium faujasite-type zeolites with Si/Al > 2.21. Thus, dissociative adsorption of H_2S on NaY can be excluded. Therefore, we assume that sodium cations are involved in the chemisorption of methanol, even though Salvador and Kladnig [10] claimed to have ruled out this possibility. However, these authors conducted their experiments at temperatures below 623 K. On the other hand, Unland [11] did find methanol chemisorption on sodium cations of NaX zeolite at 673 K. On the basis of the present knowledge it seems difficult to propose a mechanism for the reaction between H_2S and CH_3OH which makes allowance for the rôle of sodium cations. This problem will be the subject of a subsequent investigation.

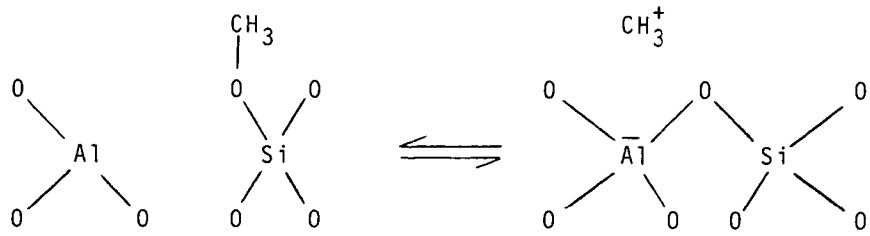
In the case of NaX zeolite we have also to take into consideration the dissociative adsorption of H_2S, which occurs on this catalyst [9]. Such a chemisorption of H_2S leads to the formation of acidic hydroxyl groups, which are active sites in the reaction of H_2S with CH_3OH [1]. Formation of acidic OH groups during chemisorption of H_2S may lead to an improved catalytic performance. Indeed, generation of such active centers (acidic OH groups) on the surface of NaX during the reaction appears to be even more favourable than employing hydrogen forms of faujasite-type zeolites. In the case of HNaY, where (strong) acidic hydroxyl groups already exist on the catalyst prior to reaction, methanol is very easily decomposed to hydrocarbons, and the selectivity of the reaction towards organic sulfur compounds is lower than it is on NaX zeolite. This conclusion is supported by the earlier investigations [1], which have shown that HNaY with a lower degree of exchange of Na^+ for H^+, is more active than a catalyst with high degree of ion exchange. Only the increase of the fraction of H_2S in the feed does result in an increase of the selectivity towards CH_3SH and $(CH_3)_2S$ over HNaY (Table 1).

Another possibility of generating OH groups is the chemisorption

of water, which is a product of the reaction between H_2S and CH_3OH. The IR experiments provided evidence that only in the case of NaX dissociative chemisorption of water might occur (see Figure 4). However, after adsorption of H_2O at 623 K on NaX only a very small band at 3650 cm^{-1} appeared. Furthermore, OH groups indicated by that band did not react with pyridine at 623 K. They obviously are very weak sites. Since pyridine adsorbed on NaX at 623 K did indeed reduce the activity of the catalyst *(vide supra)*, it can be excluded that those OH groups, generated *via* chemisorption of H_2O, are active centers for the reaction under study. In the case of NaY, where no acidic OH groups can be formed during the reaction, sodium cations are most probably the only active sites *(vide supra)*.

The infrared spectra obtained after adsorption of pyridine on NaZSM-5 and HZSM-5 catalysts (Figure 5), in correlation with their catalytic activity in the reaction of H_2S with CH_3OH before and after poisoning with pyridine (Table 2), suggest that Brønsted acid sites are the active centers.

The analysis of the results in Table 2 revealed that the selectivity towards CH_3SH increases with the increase of the reaction temperature. This fact can be explained in terms of results which were obtained by Ono and Mori [12], who studied the chemisorption of methanol on ZSM-5. These authors found that the chemisorption of methanol takes place on the acidic hydroxyl groups under formation of methoxyl groups. Methoxyl groups on the zeolite surface may be represented by two resonance structures:



The CH_3^+ carbenium ion of structure B might react with H_2S to form CH_3SH according to equ. (2)

$$CH_3^+ + H_2S \rightarrow CH_3SH_2^+ \rightarrow CH_3SH + H^+. \qquad (2)$$

Ono and Mori [12] showed that, after chemisorption of methanol, the contribution of structure (B) increases with increasing temperature.

Similarly, the increase of the yield of CH_3SH at higher temperatures, as observed in the current experiments, may be due to a preference of structure B.

CONCLUSIONS

In the case of HNaY and HZSM-5 type zeolites, the Brønsted acid sites play the rôle of active centers in the reaction between methanol and hydrogen sulfide. On the sodium forms of faujasite-type zeolites sodium cations are involved. Competitive with the reaction of H_2S and CH_3OH is the decomposition of methanol. This process predominates on HNaY when $H_2S:CH_3OH=1:1$ and was observed on ZSM-5 for an excess of methanol in the feed. The excess of H_2S leads to an enhancement of the catalytic activity of the zeolite and to an increase of the selectivity towards CH_3SH. A fraction of CH_3SH can form *via* the reaction between the reaction product $(CH_3)_2S$ and H_2S.

ACKNOWLEDGEMENT

The authors thank Mrs. Erika Popović for her valuable assistance in the IR experiments. H.G. Karge gratefully acknowledges the financial support of the Senator für Wirtschaft und Verkehr (ERP Sondervermögen) der Stadt Berlin (West).

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