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NOTE

Hydrogen Sulfide Oxidation on A-Type Zeolites: Some Conclusions from an Infrared Study

During several infrared spectroscopic investigations of the adsorption of hydrogen sulfide on various adsorbents it was observed that water was formed simultaneously (*1–4*). While Deo *et al.* (*1*) and Liu *et al.* (*2*) considered it to be the result of oxidation by chemisorbed molecular oxygen, Slager and Amberg (*3*) proposed an exclusive participation of oxygen atoms of the adsorbent. Here we present data and conclusions, which make it seem probable that oxygen impurities in the gaseous adsorbate are responsible for the oxidation.

The experimental arrangements and methods have been described elsewhere (*5*). Six samples were investigated under different conditions, and details are in Table 1.

We noticed a decrease of the intensity of the SH (SD) band with time and a corresponding increase for the OH (OD) stretching and the H_2O (D_2O) bending modes. There was no formation of water in a control run without gas inlet. According to the experimental conditions, the absorbance E of the ν_{SH}, ν_{OH}, δ_{H_2O} bands or their deuterated analogues were recorded as a function of time. All the E–t curves showed saturation, but we believe for several reasons that the mechanisms proposed by Deo *et al.* (*1*) or Slager *et al.* (*3*) are not applicable in our case:

There are no adjacent aluminum atoms in the zeolite A framework [Si–Al = 1, Loewenstein's rule (6)].

Under our experimental conditions (*5*) there are virtually no surface hydroxyls on the outgassed zeolite.

There was no oxygen pretreatment in our experiments, the oxidation was proceeding even after hydrogen pretreatment.

There is no satisfactory explanation for the strikingly small slope of run No. 4 (NaA, 10 Torr D_2S) in the log $(E_t - E_\infty)/t$-diagram.

The insertion of sulfur should give rise to an expansion of the lattice and destruction of the three-dimensional network, which has not been observed (*7*).

A combined ir/MS analysis shows that every 600th H_2S molecule is converted into an SO_2 molecule, its formation from lattice oxygens being virtually impossible.

In our opinion the adsorbed hydrogen sulfide reacts with molecular oxygen from the gas phase, a reaction which is thermodynamically favored, and which according to Addison and Walton (*8*) goes well if oxygen is admitted to zeolite A after it has been exposed to H_2S. In the first instance, the surrounding air was considered as an oxygen source. The mass spectroscopic analysis showed that the leak for oxygen does not exceed 10^{-9} Torr l s^{-1}, thus revealing atmospheric leaks inadequate to explain H_2S oxidation.

Consequently, only the possibility remains that oxygen is present as an impurity in the gaseous adsorbate. Table 2 shows a comparison of the degree of conversion estimated from ir data and the estimated amount of oxygen referring to an

TABLE 1

DETAILS OF THE KINETIC EXPERIMENTS

No.	Zeolite	Mass (mg)	Gas	Pressure (Torr)	Duration (hr)
1	NaA	55	H_2S	1.5	3
2	NaCaA	18	H_2S	10	16
3	NaCaA	24	D_2S	10	20
4	NaA	32	D_2S	10	66
5	NaA	31	H_2S	1	46
6	NaCaA	23	H_2S	1	46

TABLE 2

COMPARISON OF THE OXYGEN AMOUNT NECESSARY FOR THE H_2S OXIDATION WITH THAT BASED ON AN IMPURITY CONCENTRATION OF 0.2%[a]

No.	Estimated adsorbed amount (10^{-5} mol)	Fractional conversion	Corresp. amount n_0 of oxygen (10^{-6} mol)	Estimated oxygen amount n_0' present (10^{-6} mol)	n_0/n_0'
2	2.33	0.51	5.9	2.4	2.5
3	3.19	0.22	3.5	2.4	1.5
4	3.84	0.56	11	2.4	4.5
5	1.21	0.23	1.4	0.4	3.5
6	1.12	0.22	1.2	0.4	3.0

[a] The adsorbed amount of H_2S has been slightly corrected for humidity and temperature of the sample.

impurity concentration of 0.2%. The H_2S dose was calculated from the volume and area of the recipient, the pressure, and the adsorbed amount.

In view of the numerous uncertainties, a sufficient agreement actually results; the grave disadvantage of the infrared spectroscopic method for adsorption studies, however, becomes clear, namely the unfavorable relation between volume of the apparatus and amount of the adsorbent.[1]

If one assumes the intracrystalline oxygen transport to be the slowest step, a $t^{1/2}$ law should be obeyed when plotting the relative amount $(n_t - n_0)/n_\infty - n_0)$ against time (*9*). The expression $(E_0 - E_t)/(E_0 - E_\infty)$ corresponding to our conditions is shown in Fig. 1 as a function of $t^{1/2}$ for H_2S; for H_2O an analogous diagram is obtained with E_t/E_∞.

The deviation from a straight line is obvious in the case of the points for the NaA with 10 Torr D_2S, which has been mentioned above. We explain this curvature over the earlier stage in terms of the theory of hindered zeolitic diffusion of Barrer and Rees (*10*). They assume a sequence of low energy barriers interrupted by high energy barriers along each of a set of nonintersecting isolated channels. In our case, these high energy barriers are the sorbate molecules preferentially located near the windows of the α cage at S_{2A} sites (*5*) and hindering the diffusion of apolar molecules ["moderated diffusion" (*9*)], so that cut-offs are possible (*11*). On the other hand, in the NaCaA all the cations occupy inner positions and hardly influence diffusion. For a cubic array of pores Hammersley (*12*) has calculated the degree of wetting as a function of the probability p that a pore is open. When applied to our problem (*11*), $p = 0.13$, i.e.,

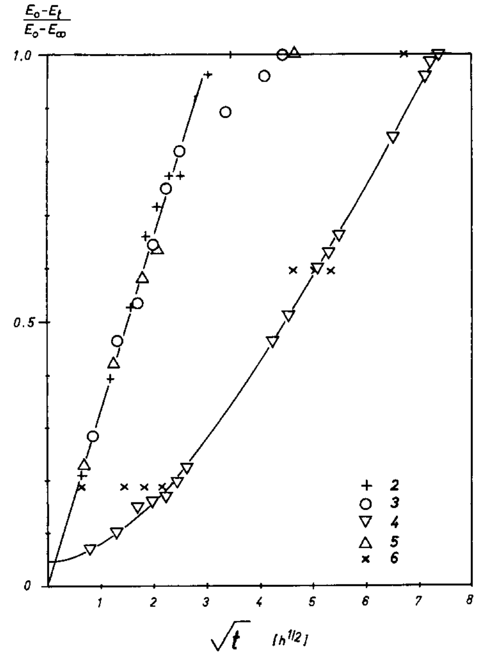

FIG. 1. Rate of H_2S (D_2S) conversion on zeolites A.

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[1] A direct determination of the gas composition is rather difficult, a later gc-MS analysis however, indicated a high impurity level.

vanishing sorption capacity, if it is assumed that one window is blocked by one H_2S molecule. Therefore, the possibility to by-pass high energy barriers is drastically reduced, and the analysis of Barrer and Rees (*10*) should then be applicable. The intercept obtained by extrapolation of the linear part of the graph was reported to contain information on the height of the modifier barrier (*10*). Taking $N_s = 1.6$ and $\nu = 10^{12}$ s^{-1} one finds $E_A = 26$ kcal mol^{-1} (1 kcal = 4.1868 kJ), hence quite a high value.

The oxygen transport seems to be unhindered in the other cases, in agreement with estimates utilizing Hammersley's (*12*) model. The initial slope is proportional to the square root of the diffusion coefficient D (*9*), whatever its meaning here; there are apparently negligible differences between NaA and NaCaA. The diffusion of oxygen into the crystallite formally fulfills the boundary conditions for a constant pressure sorption, although it is operated under constant volume conditions. Because of the irreversible consecutive reaction at the surface, equilibrium according to the law of Henry-Dalton cannot be achieved [see also Barrer (*13*)]. Taking a volume of the sorbent of about 0.05 cm^3 and an external surface of 1 m^2 (determined with N_2 at zeolite NaA) 10^{-15}–10^{-16} cm^2 s^{-1} is obtained for the diffusion coefficient. Higher values are reported in the literature (*11, 14, 15*), after an extrapolation to our conditions they fall in the range 10^{-10}–10^{-12} cm^2 s^{-1}.

The following arguments seem appropriate to us to understand the differences:

Rees and Berry (*11*) have found in their work that the diffusion coefficient falls rapidly with the further addition of only a small amount of the modifier molecules, although the activation energy remains constant or even falls. Hence the preexponential factor must have decreased because of the longer diffusion paths into the sorbent. An alternative approach may leave the diffusion coefficient for oxygen unchanged (10^{-12} cm^2 s^{-1}), but takes into account the fact that only the changes of the *converted* oxygen with time are accessible and thus a lower value may result. In the jump diffusion picture this means that there is only a low concentration of sites suitable for a jump and hence a reduction of the frequency factor. An only 40-fold excess of the incorporated over the recorded oxygen suffices for an explanation due to the quadratic dependence of D on the sorbed amount of O_2.

The presence of elementary sulfur was detectable mass spectroscopically as SO_2 after the reaction by treating the outgassed sorbent with 15 Torr oxygen (1 Torr = 133.3 N m^{-2}) at 725 K. It is obviously firmly bound even at high temperatures, which has been already reported by Dudzik and Cvetanovic (*16*). To get some further insight into the mechanism we have estimated the degree of conversion that should occur under the assumption of a Poisson distribution of the H_2S molecules within the zeolite. Moreover, the presence of one O_2 molecule together with two H_2S molecules in one cage has been assumed to suffice for accomplishing a reaction. If N denotes the number of available cages, θ the coverage in molecules per unit cell, and k the number of molecules together in one cage, the total number of the H_2S molecules then is

$$N_0 = Ne^{-\theta} \sum_k \frac{\theta^k}{(k-1)!} = N\,\theta$$

and

$$N_r = Ne^{-\theta}\left(0\,\frac{\theta^0}{0!} + 0\,\frac{\theta^1}{1!} + 2\,\frac{\theta^2}{2!} + 2\,\frac{\theta^3}{3!} + \ldots\right) = N_0 - \frac{Ne^{-\theta}}{2}\,(e^{\theta} - e^{-\theta})$$

are reacting.

Hence follows the relative conversion

TABLE 3
COMPARISON OF THE FRACTIONAL CONVERSION x OF H_2S ON ZEOLITES A[a]

No.	2	3	4	5	6
x_{calc}	0.82	0.82	0.81	0.50	0.57
x_{obs}	0.51	0.22	0.56	0.23	0.22

[a] Taken from infrared data and calculated assuming a Poisson distribution, respectively.

$N_r/N_0 = 1 - \frac{1}{2\theta}(1 - e^{-2\theta})$. In Table 3, the so calculated degree of conversion is compared with the term $(E_0 - E_\infty)/E_0$ obtained from our ir data. This simple approach shows that the measured degree of conversion is always lower mechanism with an O_2/H_2S ratio of 0.5, cf. (8), than the calculated value; thus a mechanism with an O_2/H_2S ratio of 0.5, cf. (8), does not seem to be in conflict with the ir data. It rather appears that the small supply of oxygen limits the extent of the reaction, apart from insufficient duration of the measurements.

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