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# Influence of weakly coordinated cations and basic sites upon the reaction of H<sub>2</sub>S and CO<sub>2</sub> on zeolites

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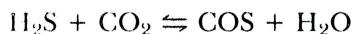
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Batch formation of COS and H<sub>2</sub>O by heterogeneous reaction of H<sub>2</sub>S and CO<sub>2</sub> on A- and X-type zeolites with various degrees of alkaline earth cation-exchange, on faujasite-type zeolites with various Si/Al ratios, and on alkaline cation-exchanged X-type zeolites, has been studied. Results obtained at different reaction times illustrate the dual function of the zeolites as selective sorbents causing a shift in reaction equilibrium and as catalysts. Correlations between the catalytic activity and population of cation sites with low oxygen coordination have been found. Furthermore, the catalytic activity could be correlated with the efficiency of dissociative H<sub>2</sub>S adsorption (literature data) and the basicity of zeolites. These correlations are regarded as being in accordance with the concept of basic catalysis on zeolites.

**Keywords:** zeolite A; zeolite X; ion-exchange; basic catalysis

## INTRODUCTION

The conversion of hydrogen sulphide with carbon dioxide to carbon oxide sulphide (carbonylsulphide) and water, as follows:



is not desired in the desulphurization processes of natural gases with molecular sieves<sup>1-3</sup>. As a main result of an extensive development programme conducted to define and control COS formation in sour natural gas processing<sup>1</sup>, it has been established that alkaline-earth cation-exchanged A- and X-type zeolites (exchange level > 45%) favour the COS formation to a lesser extent than the parent Na forms<sup>4</sup>.

To our knowledge, the H<sub>2</sub>S to CO<sub>2</sub> reaction on zeolites has not been investigated so far with regard to catalytically active sites. This is the topic of the present paper. Studies concerning catalytically active sites were reported for other reactions on zeolites involving H<sub>2</sub>S as reactant; Ono showed in a review paper<sup>5</sup> that basic sites in faujasite-type zeolites are the catalytically dominant centres for the reaction of H<sub>2</sub>S and γ-butyrolactone as well as H<sub>2</sub>S and tetrahydrofuran. An analogous conclusion was drawn by Ziólek and Dudzik<sup>6</sup> in the case of oxidation of H<sub>2</sub>S by oxygen. However, Verver and Van Swaaij<sup>7</sup> identified the active sites of the latter reaction with weakly coordinated Na<sup>+</sup> cations in faujasites.

## EXPERIMENTAL

### Materials

The sodium forms of the faujasite-type zeolites, having Si/Al ratios from 1.23 to 2.65, were synthesized at the CK Bitterfeld Research Division. The Si/Al ratios were determined by chemical analysis: SiO<sub>2</sub> gravimetrically, aluminium by e.d.t.a. titration.

Zeolites NaA and Na<sub>82</sub>X from CK Bitterfeld, as well as laboratory synthesized NaA, were used as the parent materials for ion-exchange. CaNaA (percentage of Na<sup>+</sup> exchange, 31–100%) and MgNaA (33–79%) modifications were prepared by the column ion-exchange method. CaNaX (22–72%) and SrNaX (22–98%) zeolites were produced by the batch method using aqueous solutions of appropriate chlorides (varying the volume and concentration). The exchange degree was determined by a volumetric technique and flame photometry. Preparation and analysis of the alkaline cation exchanged X-type zeolites are described elsewhere<sup>8</sup>, their compositions were Li<sub>60</sub>Na<sub>22</sub>X, Rb<sub>37</sub>Na<sub>15</sub>X, K<sub>82</sub>X, and Cs<sub>41</sub>Na<sub>44</sub>X. LaX was nearly Na<sup>+</sup>-cation free (prepared from NaX by batch cation-exchange at 90°C over three months with two-fold intermediate tempering *in vacuo* at 400°C). The purity of the gases used H<sub>2</sub>S (Fluka) and CO<sub>2</sub> (VEB TEGA) was 99.7 and 99.9%, respectively.

### Procedure

Investigations of the catalytic conversion of H<sub>2</sub>S into COS have been carried out under static conditions as follows. A reaction chamber was connected with a vacuum line, a gas mixing bulb and H<sub>2</sub>S and CO<sub>2</sub> storage vessels. The zeolite samples were activated within the reaction chamber at 673 K and 1.3 × 10<sup>-2</sup> Pa for 15 h. Then 0.29 mmol of the H<sub>2</sub>S/CO<sub>2</sub> mixture was transferred into the reaction chamber by cooling the latter with liquid nitrogen.

After fixed contact times, the gaseous and desorbate phases were analysed by gas-chromatography (Porapak Q). The masses of all zeolite samples were normalized to an equal number of supercages (0.266 × 10<sup>20</sup>). The composition of the CO<sub>2</sub>/H<sub>2</sub>S mixture was 4/1, except for the presorption experiments with NH<sub>3</sub> (composition 1/1). If not noted otherwise the experiments were carried out at room temperature.

## RESULTS AND DISCUSSION

### Shift in reaction equilibrium and catalytic effect

The equilibrium constant of the reaction between  $\text{H}_2\text{S}$  and  $\text{CO}_2$  amounts to  $6.7 \times 10^{-6}$  at 300 K<sup>9</sup>. Consequently, at a  $\text{CO}_2/\text{H}_2\text{S}$  ratio of 4/1, a conversion of only 0.5% (related to  $\text{H}_2\text{S}$ ) is possible. However, the presence of A- and X-type zeolites leads to  $\text{H}_2\text{S}$  conversions up to 70% (see Figures 1–3); under processing conditions  $\text{H}_2\text{S}$  conversions up to 90% were observed at very high  $\text{CO}_2/\text{H}_2\text{S}$  ratios<sup>2</sup>. In view of the strongly preferred sorption of the reaction product water as compared with the sorption of the other components involved into the system, it is obvious that the zeolites cause a shift in reaction equilibrium<sup>1</sup>. That is, the zeolites provide the thermodynamic basis for high COS concentrations by superposition of both adsorption and reaction equilibria. However, the quantity of COS actually formed under relevant practical conditions depends on the catalytic activity of the zeolite; this is illustrated in Figures 1 and 2.  $\text{H}_2\text{S}$  conversion is shown vs. the

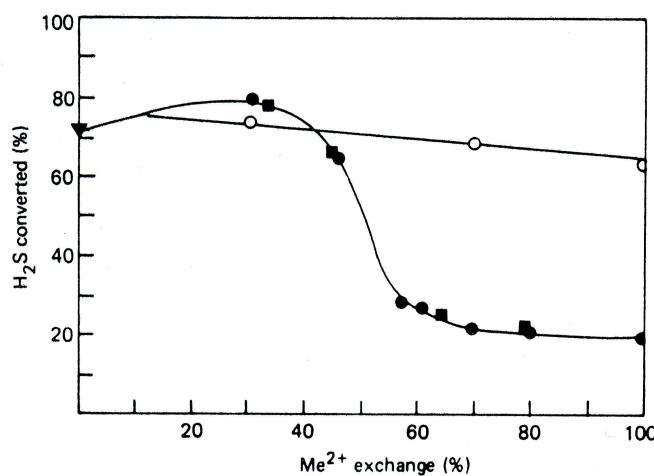


Figure 1 Conversion of  $\text{H}_2\text{S}$  to COS on  $(\text{Me}^{\text{II}}, \text{Na})\text{A}$  zeolites versus cation exchange percentage. (●), (○) CaNaA; (■) MgNaA; (▼) NaA. Reaction times: (●), (■), (▼) 6 h; (○) 320 h. Composition of the initial mixture  $\text{CO}_2/\text{H}_2\text{S} = 4/1$

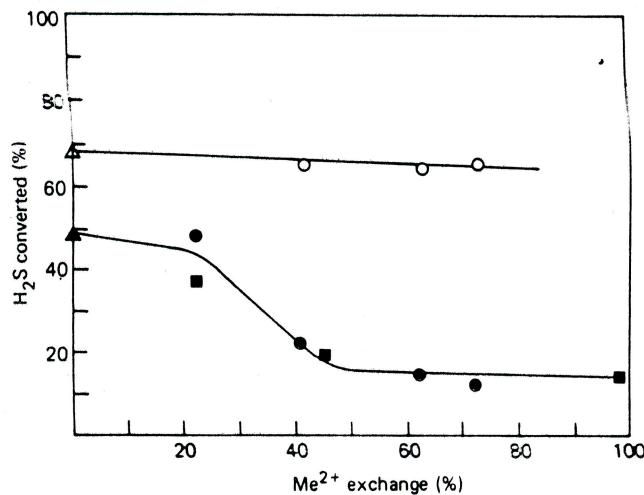


Figure 2 Conversion of  $\text{H}_2\text{S}$  to COS on  $(\text{Me}^{\text{II}}, \text{Na})\text{X}$  zeolites versus cation exchange percentage. (●), (○) CaNaX; (■) SrNaX; (▲), (△) NaX. Reaction times: (●), (■), (▲) 6 h; (○), (△) 320 h. Composition of the initial mixture  $\text{CO}_2/\text{H}_2\text{S} = 4/1$

percentage of cation exchange in  $\text{CaNaA}$  and  $\text{MgNaA}$  (Figure 1) and  $\text{CaNaX}$  and  $\text{SrNaX}$  (Figure 2) for different reaction times. The conversion data obtained for long reaction times (320 h) represent the equilibrium state, whereas the catalytic feature of the zeolites is given by conversion values after reacting times of 6 h. Obviously, the catalytic properties depend strongly on the degree of cation exchange, whereas the equilibrium conversion on the investigated zeolites does not differ significantly. That means, all zeolites presented in Figures 1 and 2 cause a shift in reaction equilibrium, but only  $\text{NaA}$ ,  $\text{NaX}$  and samples with a low exchange degree show high catalytic activity.

The dual function of the zeolite influence on COS formation (as sorbents and catalysts) is further reflected by the temperature dependence of  $\text{H}_2\text{S}$  conversion. As shown in Figure 3, for the catalytically active  $\text{Ca}_{2.75}\text{Na}_{6.5}\text{A}$  zeolite,  $\text{H}_2\text{S}$  conversion passes through a smooth maximum at 70°C. Such behaviour could be interpreted by superposition of two processes: the increase of  $\text{H}_2\text{S}$  conversion with temperature due to its endothermicity ( $\Delta H = 35.7 \text{ kJ mol}^{-1}$ ) and promotion of catalytic activity, and the decrease of  $\text{H}_2\text{S}$  conversion because of the diminishing equilibrium shift (caused by increasing the water concentration in the gaseous phase).

### Nature of active centres

The major applications of zeolites in catalytic systems are related to their acidic properties. The following results demonstrate that the reaction of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  cannot be promoted by Brønsted acid sites:

- (i) On  $\text{LaX}$  with appreciable Brønsted acidity after 6 h we observed a  $\text{H}_2\text{S}$  conversion of only 1%. After 320 h, 30% of the initial  $\text{H}_2\text{S}$  was converted. These two conversion values indicate that  $\text{LaX}$  causes a shift in reaction equilibrium, but this zeolite does not catalyse the process.
- (ii)  $\text{NaA}$  and  $\text{NaX}$  with very low concentrations of hydroxylic groups<sup>10</sup> are active catalysts for the  $\text{H}_2\text{S}$  to  $\text{CO}_2$  reaction. The introduction of bivalent cations into A- and X-type zeolites generates structural OH groups<sup>11</sup>, their number in  $\text{Me}^{\text{II}}$   $\text{NaA}$  and  $\text{Me}^{\text{II}}$   $\text{NaX}$  zeolites being proportional to the number of  $\text{Me}^{\text{II}}$  cations<sup>12</sup>. However, as shown

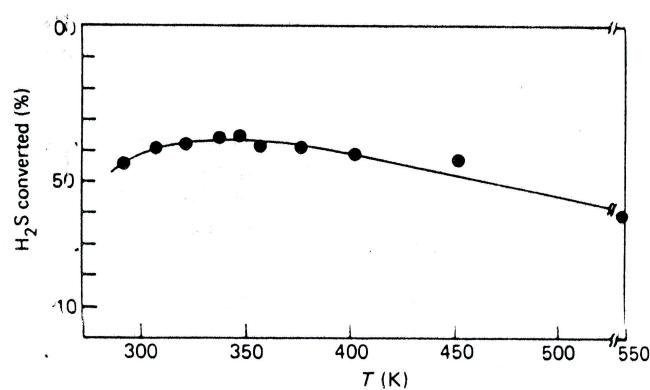


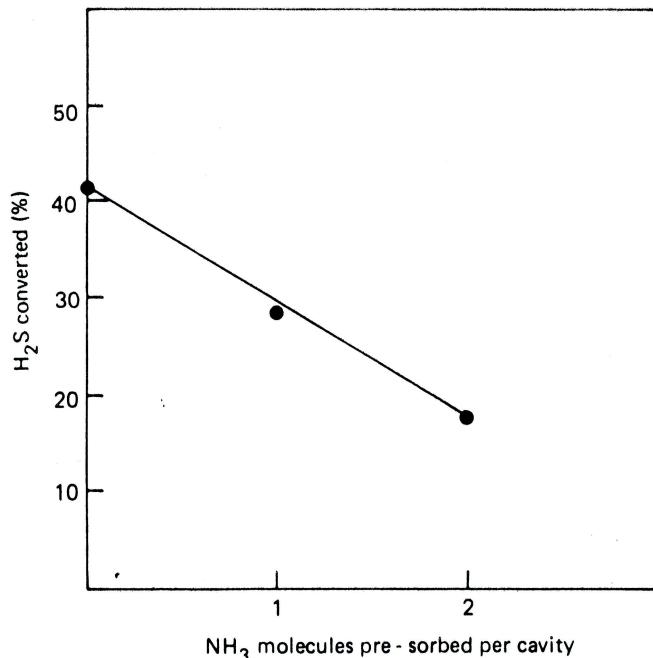
Figure 3 Conversion of  $\text{H}_2\text{S}$  to COS on  $\text{Ca}_{2.75}\text{Na}_{6.5}\text{A}$  zeolite versus temperature. Reaction time 6 h; composition of the initial mixture  $\text{CO}_2/\text{H}_2\text{S} = 4/1$

above (*Figures 1* and *2*), the catalytic activity decreases with increasing  $\text{Me}^{II}$  content.

Now it will be shown that the catalytic activity of zeolites in the reaction of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  can be correlated with the population of cation sites with low oxygen coordination:

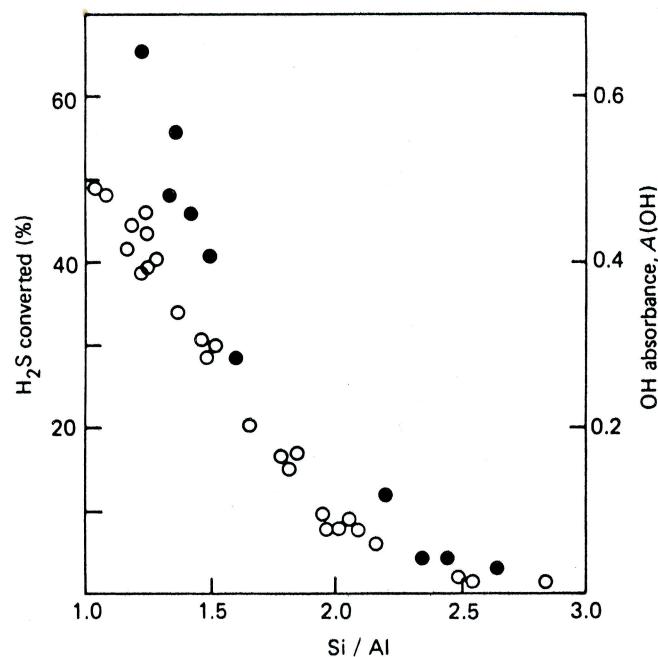
- (i) The COS formation activity of  $\text{Me}^{II}\text{NaA}$  zeolites decreases considerably at a cation-exchange percentage of approximately 50% (cf. *Figure 1*). This decrease corresponds to the removal of the last weakly coordinated  $\text{Na}^+$  ion out of the zeolitic structure. The NaA zeolite possesses four weakly coordinated  $\text{Na}^+$  ions per supercage (three within the O-8 rings (S2), one with a one-side coordination to an O-4 ring (S3))<sup>13</sup>. Introducing bivalent cations, one of them replaces both a weakly and a strongly coordinated  $\text{Na}^+$  ion (within an O-6 ring (S1)) occupying strongly coordinated sites within the O-6 rings<sup>14,15</sup>. All weakly coordinated  $\text{Na}^+$  cations are removed if the cation-exchange amounts to  $\sim 66\%$ .
- (ii) The dependence of  $\text{H}_2\text{S}$  conversion on the cation exchange degree of  $\text{Me}^{II}\text{NaX}$  zeolite (cf. *Figure 2*), can analogously be interpreted. According to Ref. 16, the number of SIII and non-localized  $\text{Na}^+$  cations per unit cell amounts to 14 for NaX with  $\text{Si}/\text{Al} = 1.37$ ; that is, there are  $\sim 1.8$  weakly coordinated  $\text{Na}^+$  cations in positions at the walls of a supercage. Taking into account that the first  $\text{Me}^{2+}$  ions to be introduced by exchange occupy positions within the  $\beta$  cages and that weakly coordinated cations should preferentially be exchanged, it can be assumed that one bivalent cation replaces both a weakly coordinated (from the  $\alpha$  cages) and a strongly coordinated (from the  $\beta$  cages)  $\text{Na}^+$  ion. Thus, at an exchange level of 35%, all weakly coordinated  $\text{Na}^+$  ions should be replaced. This value corresponds with the exchange value of  $\sim 40\%$ , which is the reason both CaNaX and SrNaX zeolites show low catalytic activity.
- (iii) Due to the preferential sorption of ammonia on weakly coordinated cations<sup>17,18</sup> presorbed  $\text{NH}_3$  molecules should block active centres, thus suppressing  $\text{H}_2\text{S}$  conversion. Corresponding experimental findings are given in *Figure 4* showing  $\text{H}_2\text{S}$  conversion vs. the number of presorbed  $\text{NH}_3$  molecules.
- (iv) *Figure 5* illustrates the dependence of  $\text{H}_2\text{S}$  conversion on the Si/Al ratio of faujasite-type zeolites (the data related to the right ordinate, see below). Results from X-ray investigations<sup>16,19,20</sup> and structure considerations<sup>21</sup> indicate a decreasing number of weakly coordinated  $\text{Na}^+$  cations ( $n_{\text{Na}^+}^x$ ) with increasing Si/Al ratio of faujasite-type zeolites ( $n_{\text{Na}^+}^x = 31, 14$  and 0 for  $\text{Si}/\text{Al} = 1.14^{19}$ ,  $1.37^{16}$  and  $2.43^{20}$ , respectively). As shown in *Figure 5*, COS formation also decreases with increasing Si/Al ratio. This supports the idea that catalytic activity is correlated with the number of weakly coordinated cations.

The higher catalytic activity of alkaline cation zeolites compared with that of the bi- and polyvalent cation exchanged forms, and NaX compared with NaY, is a

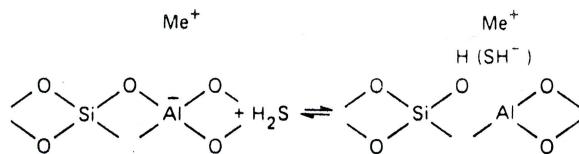


**Figure 4** Conversion of  $\text{H}_2\text{S}$  to COS on NaA zeolite versus number of presorbed  $\text{NH}_3$  molecules per supercage. Reaction time 6 h; composition of the initial mixture  $\text{CO}_2/\text{H}_2\text{S} = 1/1$

typical feature of the basic catalysis of zeolites<sup>5</sup>. For that type of catalysis, the cooperative action of both cations (preferentially weakly bound) and basic oxygen ( $\text{AlO}_4^-$  units) should be essential, leading to a polarization and dissociation of the H-containing reactant molecules with proton attachment to oxygen atoms of the zeolite lattice. In the case of  $\text{H}_2\text{S}$ , such dissociative adsorption with the formation of SH and OH groups has been shown by i.r. spectroscopy<sup>21-24</sup>:



**Figure 5** Correlation between the conversion of  $\text{H}_2\text{S}$  to COS and the concentration of OH groups formed by dissociative adsorption (data from Ref. 21) versus Si/Al ratio. (●)  $\text{H}_2\text{S}$  converted to COS; reaction time 6 h; composition of the initial mixture  $\text{CO}_2/\text{H}_2\text{S} = 4/1$ . (○) OH group concentration measured via the maximum absorbance  $A(\text{OH})$  of the OH band at  $3650 \text{ cm}^{-1}$  at  $p(\text{H}_2\text{S}) = 133 \text{ Pa}$



Therefore, it seems reasonable to assume that the COS formation proceeds by basic catalysis on zeolites involving weakly coordinated cations and basic sites as active centres.

To confirm the above assumption in addition to the correlation with weakly coordinated cations, COS formation will be related to the extent of dissociative  $\text{H}_2\text{S}$  adsorption and the basicity. From our experiments and literature i.r. spectroscopic data we have derived the following correlations between COS formation and the extent of dissociative  $\text{H}_2\text{S}$  adsorption:

- On highly  $\text{Ca}^{2+}$ -exchanged A and X-type zeolites dissociatively adsorbed  $\text{H}_2\text{S}$  molecules were not found<sup>23,24</sup>; this corresponds with very low COS formation on these zeolites as visible from Figures 1 and 2 (6 h reaction time).
- In Figure 5, the dependence of COS formation on the Si/Al ratio of faujasite-type zeolites is compared with that of the concentration of OH groups generated by dissociative  $\text{H}_2\text{S}$  adsorption as determined by Karge and Raskó<sup>21</sup>. Thus it can be seen that the trend of dissociative  $\text{H}_2\text{S}$  adsorption parallels that of COS formation.
- The amount of  $\text{H}_2\text{S}$  molecules dissociatively adsorbed on  $\text{Na}_{88}\text{X}$  zeolite (1.13 per  $\alpha$  cage) is comparable with that converted in our static experiment to COS (1.08  $\text{H}_2\text{S}$  molecules per  $\alpha$  cage)\*.
- From i.r. spectroscopic investigations of the extent of  $\text{H}_2\text{S}$  dissociation on  $\text{Me}^{\text{I}}\text{X}$  zeolites, reported by Karge *et al.*<sup>22</sup> and Möller<sup>24</sup>, the sequences  $\text{LiNaX} < \text{NaX} > \text{KNaX} > \text{RbNaX} > \text{CsNaX}$  and  $\text{LiNaX} < \text{NaX} < \text{KNaX} > \text{RbNaX} > \text{CsNaX}$ , respectively, were obtained. The first sequence corresponds closely, and the latter entirely, to the formation of COS on these zeolites (Table 1).

One contradictory result should be noted: Möller<sup>24</sup> observed a greater extent of dissociative  $\text{H}_2\text{S}$  adsorption on  $\text{Na}_{88}\text{X}$  than on  $\text{NaA}$ , whereas the  $\text{H}_2\text{S}$

\*One active site is used, obviously, for one elementary catalytic act only and is then blocked by the reaction product water. Insofar the term 'catalysis' is not used in the strong sense in this paper.

Table 1 Extent of dissociative  $\text{H}_2\text{S}$  adsorption and COS formation on  $\text{Me}^{\text{I}}\text{X}$  zeolites

Data from Ref. 22		Data from Ref. 24		COS formation	
Sample*	$A(\text{OH})^{\dagger}$	Sample	$n^{\ddagger} (\text{H}^{\cdot}\text{SH}^-)$	Sample	$\text{H}_2\text{S}$ conversion (%)
$\text{LiNaX}(61)$	0.09	$\text{Li}_{81}\text{Na}_7\text{X}$	<1.13**	$\text{Li}_{60}\text{Na}_{22}\text{X}$	14
$\text{NaX}$	0.35	$\text{Na}_{88}\text{X}$	1.13	$\text{Na}_{82}\text{X}$	48
$\text{KNaX}(82)$	0.21	$\text{K}_{82}\text{Na}_6\text{X}$	1.6	$\text{K}_{82}\text{X}$	78
$\text{RbNaX}(68)$	0.14	$\text{Rb}_{63}\text{Na}_{25}\text{X}$	<1.6 **	$\text{Rb}_{37}\text{Na}_{45}\text{X}$	58
$\text{CsNaX}(61)$	0.10	$\text{Cs}_{61}\text{Na}_{27}\text{X}$	<1.6 **	$\text{Cs}_{41}\text{Na}_{41}\text{X}$	43

\*Percentage of exchange in brackets; the Si/Al ratio has not been reported

<sup>†</sup>Concentration of OH groups produced by dissociative  $\text{H}_2\text{S}$  adsorption measured via the maximum absorbance  $A(\text{OH})$  of the OH band at  $3650 \text{ cm}^{-1}$  at  $p(\text{H}_2\text{S}) = 133 \text{ Pa}$

<sup>‡</sup>Number of dissociatively adsorbed  $\text{H}_2\text{S}$  molecules per  $\alpha$  cage

\*\* $n_{(\text{H}^{\cdot}\text{SH}^-)}$  has not been determined quantitatively

conversion data are equal (Figures 1 and 4).

The following can be discussed concerning the basicity of the investigated zeolites. The basicity of  $\text{Me}^{\text{II}}\text{NaA}$  and  $\text{Me}^{\text{II}}\text{NaX}$  zeolites represented by the mean oxygen charge<sup>25</sup> decreases with increasing degree of cation-exchange. The basicity of the sodium forms of the faujasite-type zeolites decreases with increasing Si/Al ratio. That means the basicity, the number of weakly coordinated cations and the COS formation (cf. Figures 1, 2 and 4) have the same tendency, noting that the steps of the  $\text{H}_2\text{S}$  conversion curves (cf. Figures 1 and 2) can be better correlated with the presence of weakly coordinated cations than with basicity. The basicity of  $\text{Me}^{\text{I}}\text{X}$  zeolites increases according to the sequence  $\text{LiX} < \text{NaX} < \text{KX} < \text{RbX} < \text{CsX}^{5,11}$ . COS formation, however, reaches a maximum at KX (see Table 1); but this finding is not contradictory to our assumption considering the polarizing effects of the cations following the opposite order to the basicity sequence  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ . This interpretation (supposing a nearly equal number of weakly coordinated cations) combines the concepts of the zeolithic basicity<sup>6,26</sup> and the Coulomb potentials of cations<sup>22</sup> in relation to  $\text{H}_2\text{S}$  adsorption and reactions.

In the literature, chemisorption involving weakly coordinated cations and excessively charged lattice oxygen is also discussed for  $\text{CO}_2$ <sup>27,28</sup>. In view of the low extent of  $\text{CO}_2$  chemisorption (only 0.4 chemisorbed  $\text{CO}_2$  molecules<sup>27</sup> in comparison with 1.13 dissociatively adsorbed  $\text{H}_2\text{S}$  molecules<sup>21</sup> per supercage of  $\text{NaX}$ ) we assume that the dissociative adsorption of  $\text{H}_2\text{S}$  is of greater significance for catalysis of COS formation than  $\text{CO}_2$  chemisorption.

## CONCLUSIONS

It is concluded that weakly coordinated cations and basic oxygen sites in A- and X-type zeolites play the dominant role in the catalysis of the  $\text{H}_2\text{S}$  to  $\text{CO}_2$  reaction. This is shown by correlations of the catalytic activity of different zeolite modifications with the population of weakly coordinated cation sites, basicity and the i.r. spectroscopically determined extent of dissociative  $\text{H}_2\text{S}$  adsorption on these zeolites.

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