

RING TRANSFORMATION OF TETRAHYDROFURAN INTO TETRAHYDROTHIOPHENE OVER ALKALI METAL CATION EXCHANGED ZEOLITES

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The reaction of tetrahydrofuran and hydrogen sulfide to give tetrahydrothiophene over alkali metal cation exchanged zeolites has been studied. The tetrahydrothiophene yield of 94% is reached with NaX at 340 °C. The catalytic activity is considerably suppressed by adding either hydrogen chloride or pyridine to reactants feed. The reaction mechanism is proposed: Hydrogen sulfide molecules dissociate on basic sites, forming protonic acids and SH⁻ groups and protons thus formed interact with and activate tetrahydrofuran molecules, which, in turn, react with SH⁻ groups to form tetrahydrothiophene. The dissociation of hydrogen sulfide over NaX is confirmed by infrared spectroscopy.

Introduction

Synthetic zeolites usually act as acidic catalysts and have very high activity for the major hydrocarbon transformations *via* carbonium ions such as cracking, alkylation and isomerization. For these reactions, HY zeolites or alkaline earth exchanged zeolites are the most active catalysts, and alkali metal cation exchanged zeolites are the least active [1]. In a previous work, however, it was found that, for the reaction of γ -butyrolactone and hydrogen sulfide, alkali metal cation exchanged zeolites have high activity, while HY has very low, and concluded that the basic sites play important roles in the dissociation of hydrogen sulfide [2]. In another work it was reported that, for the ring transformation of tetrahydrofuran (THF) into pyrrolidine, the presence of protonic sites is essential for the ring-opening step of THF [3]. In this work, the reaction of THF and hydrogen sulfide to give tetrahydrothiophene in order to obtain further information on the role of basic sites in catalysis by alkali metal cation exchanged zeolites and on the mechanism of ring transformation reaction.

Experimental part

THF was distilled prior to each run. Hydrogen sulfide was used as received from commercial source. NaX and NaY were obtained from the Linde Division of Union Carbide Corp. Various cation forms of Y-zeolites were prepared by conventional cation exchange procedure using salt solution. The cation exchanged zeolites were pelleted without a binder and crushed and sized into 9–16 mesh. A continuous flow reactor was used under atmospheric pressure. The reactor was a silica tubing (13 mm

i. d.) placed in a vertical furnace. Tetrahydrofuran was pumped into preheating zone of the reactor containing 10 ml quartz powder. Nitrogen was used as diluent for regulating the initial pressure of reactants. The gaseous materials were fed through flowmeters. Reaction products collected in the receiver were withdrawn at certain intervals during the run and were analyzed by gas chromatography.

Results and discussion

Effect of reaction temperature

The effect of the reaction temperature on the tetrahydrothiophene yield was examined with NaX as a catalyst. The activity decreases gradually with stream hours, and the extent of deactivation increases with reaction temperature. In Fig. 1, the conversion of THF and the yield of tetrahydrothiophene were plotted as a function of reaction temperature. The values of the conversion and the yield are obtained at the stream hours of 2–3 hr. The yield increases with reaction temperature up to 350°C, and through the maximum, decreases at higher temperatures. The selectivity to tetrahydrothiophene is almost 100% below 350°C and decreased at higher temperatures.

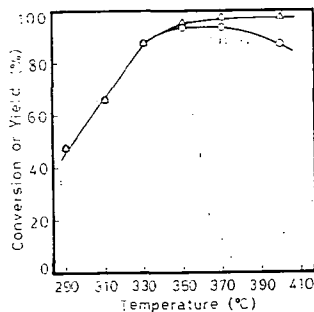


Fig. 1. Effect of reaction temperature on the conversion of THF (Δ) and the yield of tetrahydrothiophene (\circ) NaX, $W/F=15.9 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$

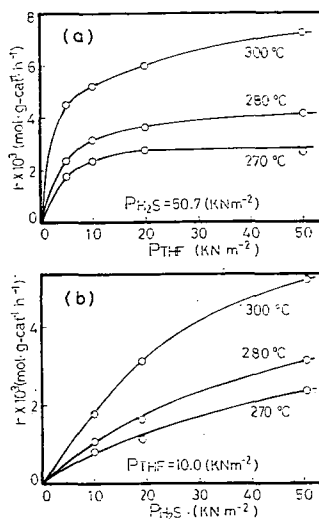


Fig. 2. Dependence of the reaction rate (a) on the partial pressure of tetrahydrofuran (P_{THF}) and (b) on the partial pressure of hydrogen sulfide

Effect of contact time

Effect of contact time [W/F , W : weight of the catalyst (g), F : molar flow rate ($\text{mol} \cdot \text{h}^{-1}$)] on the yield of tetrahydrothiophene was examined at 340°C with NaX catalyst. The yield increases with contact time and reached 92% at $W/F=15.7$ ($\text{g} \cdot \text{h} \cdot \text{mol}^{-1}$). The selectivity to tetrahydrothiophene is always 100% at this temperature.

Kinetics of the reaction

The reaction kinetics was examined with NaX catalyst in the temperature range 270–300°C under small contact time conditions. The effects of the partial pressures of THF (P_{THF}) and of hydrogen sulfide ($P_{\text{H}_2\text{S}}$) on the reaction rate (r) are shown in Fig. 2. The kinetics could be expressed as

$$r = kP_{\text{THF}}^{0.3}P_{\text{H}_2\text{S}}^{0.7}$$

The apparent activation energy is calculated to be 34 kJ·mol⁻¹.

Catalytic activity of various forms of zeolites

The catalytic activities of various zeolites were examined at 340°C and the results are given in Table I, from which one can see the following features of the reaction.

- (1) Catalytic activities of alkali cation exchanged zeolites are high, while those of acidic zeolites (HY, MgY) are low.
- (2) Alkali cation exchanged X-zeolites are more active than the corresponding cation forms of Y-zeolites.

These features are same as those found in the reaction of γ -butyrolactone and hydrogen sulfide [3], and are in sharp contrast with those found in ordinary carboniogenic reactions, for which HY is most active and alkali cation zeolites are inactive and Y-zeolites are more active than X-zeolites.

Effect of hydrogen chloride and of pyridine

The above results indicate that basic sites play an important role in the catalysis. In order to get further information on the active centers, the effects of addition of hydrogen chloride and of pyridine on the catalytic activity was examined. MATSUMOTO ET AL. [4] reported that the cracking of cumene over NaY was greatly enhanced by addition of hydrogen chloride to the system. The enhancement of the catalytic activity was ascribed to the formation of Brönsted acid sites by the interaction of hydrogen chloride with NaY. Addition of hydrogen chloride was carried out by passing the hydrogen sulfide stream over the concentrated hydrogen chloride aqueous solution. The result is given in Fig. 3(a), which shows that hydrogen chloride completely inhibits the catalytic activity as found in the reaction of γ -butyrolactone and hydrogen sulfide. It was confirmed that the treatment with hydrogen chloride does not destroy the crystallinity of the zeolite. Thus, it may well be assumed that the deactivation is associated with the poisoning of the active centers, presumably the basic sites by hydrogen chloride.

Pyridine is often used to poison acidic centers. The effect of addition of pyridine on the ring conversion was examined. As seen in Fig. 3(b), the addition

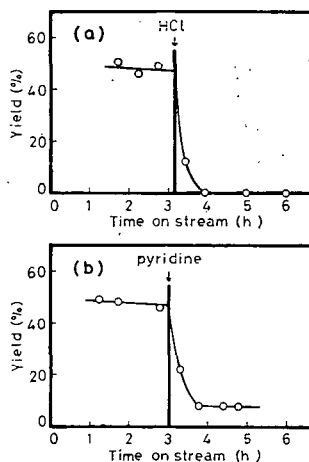


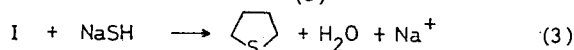
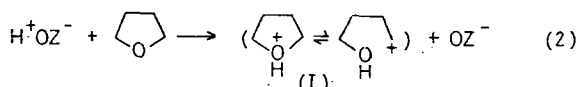
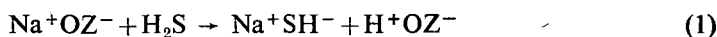
Fig. 3. Effect of hydrogen chloride and of pyridine on the reaction rate. NaX 300°C, Pyridine added 1.8 mol%

of pyridine to the reactant feed greatly suppressed catalytic activity. The extent of the activity depression depended on the partial pressure of pyridine added. This result is in sharp contrast with that found in the reaction between γ -butyrolactone and hydrogen sulfide, for which the pyridine does not poison but enhances the catalysis.

This result suggests the participation of acidic centers in the reaction. Since NaX has no acidic centers, they must be produced during the reaction, presumably by the dissociation of hydrogen sulfide.

Reaction mechanism

For the reaction of γ -butyrolactone with hydrogen sulfide, the authors proposed a mechanism in which hydrogen sulfide dissociates on the basic sites (AlO_4^-) to form protonic centers and NaSH. The protonic centers may interact with and activate THF molecules. This explains why the presence of pyridine depressed the catalytic activity. The mechanism may be written as



The steps (1)—(2), and (2)—(3) could be concerted. The mechanism is not incompatible with kinetic results.

Dissociation of hydrogen sulfide has been confirmed by IR spectroscopy. Introduction of hydrogen sulfide to NaX produced an OH band at 3650 cm^{-1} and a SH band at 2560 cm^{-1} . Furthermore, the introduction of hydrogen sulfide to NaX preadsorbed pyridine gives a band by pyridinium ions at 1540 cm^{-1} , confirming that the dissociation of hydrogen sulfide gives protonic centers. The same phenomena have been observed by KARGE AND RASKÓ [5], who showed also that the dissociation is easier over NaX than NaY. This is in conformity with the fact that the activity is higher with NaX than NaY.

The main difference of the reaction of THF and hydrogen sulfide and that of γ -butyrolactone and hydrogen sulfide [2] is that the former is retarded by pyridine,

Table I
Comparison of the catalytic activities of various zeolites

Catalyst	Yield (%)	Catalyst	Yield (%)
LiX	60	NaY	21
NaX	70	CsY	27
KX	62		
RbX	51	HY	2
CsX	49	MgY	3

340°C , $W/F = 7.95 \cdot \text{g} \cdot \text{h} \cdot \text{mol}^{-1}$, molar ratio
($\text{H}_2\text{S}/\text{THF}$) = 5

but the latter does not. This means the protonic acid is essential for the activation (probably for ring opening) of THF. Similar phenomena were observed also in the reactions of THF/ γ -butyrolactone and amines. For the ring conversion of THF to pyrrolidine, only the acidic catalysts are active [3], while for the ring conversion of γ -butyrolactone to pyrrolidinones, the alkali cation exchanged zeolites have comparable activity with HY [6, 7]. This has been attributed to the ease of the ring opening of the lactone due to the presence of polarizable carbonyl group.

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