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Catalytic hydrodesulfurization and hydrodechlorination of chloroethyl ethyl sulfide

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Abstract

Catalytic hydrodesulfurization (HDS) and hydrodechlorination (HDC) of chloroethyl ethyl sulfide (CEES) is carried out over a Ni–Mo/γ-Al_2O_3 catalyst and Ni and/or Mo supported on active carbon (AC) catalysts. The reactions are as follows:

$$C_2H_5\text{–}S\text{–}C_2H_4Cl + H_2 \rightarrow 2C_2H_4 + HCl + H_2S \quad \text{(i)}$$

$$C_2H_5\text{–}S\text{–}C_2H_4Cl + 3H_2 \rightarrow 2C_2H_6 + HCl + H_2S \quad \text{(ii)}$$

At 300°C and 0.1 MPa, complete conversion of CEES is achieved in a fixed bed microreactor over Ni–Mo/γ-Al_2O_3 for 100 h with gas molar composition of H_2 : CEES : He = 10 : 0.33 : 89.7 and 24,000 cm^3/h/g·cat space velocity. The reaction is 98.0% selective to pure hydrocarbons (ethylene and ethane; Reaction (i) and (ii)) and 2% to ethyl mercaptan on Ni–Mo/γ-Al_2O_3. Over Ni–Mo/AC, the reaction is more selective toward pure hydrocarbons with >99.5% selectivity. The activity order converting CEES to pure hydrocarbons at 300°C is Ni–Mo/AC > Ni–Mo/γ-Al_2O_3 > Mo/AC > Ni/AC.

For all catalysts, the concentration of chlorinated hydrocarbon (chloroethane) is much less than the concentration of sulfur-containing compounds (diethyl sulfide [DES] and ethyl mercaptan) in the product stream, suggesting that hydrodechlorination (HDC) is faster than hydrodesulfurization (HDS) of CEES. Two sulfur-containing compounds — 1,2 bis(ethylthio) ethane and 1,4 dithiane — are detected at short residence times. This indicates the reaction pathway is more complicated than simple HDS and/or HDC reactions. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Chloroethyl ethyl sulfide; Chemical warfare agent; Waste disposal; Hydrodechlorination; Hydrodesulfurization

1. Introduction

Hydrotreatment of sulfur-containing organic compounds is widely practiced in petroleum refining [1], but there are very few reported studies of hydrotreating compounds containing both sulfur and chlorine. However, these types of compounds are used in the military. For example, there are about 25,000 tons of chemical warfare (CW) agents in the US stockpile [2]. About 90% of this stockpile must be destroyed by 2004, according to a public law enacted by Congress [3]. At the present time the major disposal alternatives for these materials are incineration, neutralization, and neutralization followed by biodegradation processes [4,5]. However, it is extremely difficult to completely destroy these wastes with oxidative approaches while avoiding noxious byproduct formation. The present study focuses on the development of a hydrotreating process, which has been suggested in a recent National Research Council (NRC) study to detoxify CW

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agents [2]. Here, we investigate the gas phase catalytic hydrotreatment of cholorethyl ethyl sulfide (CEES), a simulant of CW agent HD (mustard gas), over a solid catalyst as an alternative to incineration. Unlike most oxidative destruction procedures, the reaction products from the hydrotreating reactions (hydrocarbons, hydrogen sulfide, and hydrogen chloride) which can be recovered for other applications pose a minimal environmental threat.

Hydrotreatment of CEES can include hydrodesulfurization (HDS) and hydrodechlorination (HDC) because CEES contains both sulfur and chlorine atoms. However, there have been very few prior studies of the combined HDS and HDC to detoxify organic wastes [6–9], though HDS is well-known [1]. For example, Bonnet et al. investigated HDS and HDC of halogenated benzothiophenes over a $CoO–MoO_3/Al_2O_3$ catalyst to study the role of an electronic effect from halogen groups [6]. They reported that dehalogenation reaction takes place without any observed hydrogenation or HDS. Zhou et al., on the other hand, reported the first study of adsorption and thermal decomposition of CEES over Pt(111) surfaces, but under vacuum conditions [7]. Sulfide adsorption, through the S atom, is molecular and very strong at 90 K. Molecular desorption does not occur at low coverages, but at high coverages, the multilayer desorbs at 180 K. A closely related investigation by Hagh and Allen reported the effect of H_2S on the HDC of polychlorinated biphenyls (PCBs) over presulfided NiMo-supported Al_2O_3 catalyst [10]. Although H_2S decreased the HDC reaction rate slightly, the results suggested that well-known HDS catalysts such as Ni–Mo and Co–Mo may be candidates for combined HDS and HDC of CEES. Another process developed by Kalnes and James of UOP [11] demonstrated a pilot-scale hydrogenation of hazardous organic waste containing halogens and sulfur. Although both HDS and HDC reactions proceeded during the process, no detailed information is given on the relative rates of HDS and HDC.

Our previous studies investigated the activity and stability of 3% Pt/η-Al_2O_3, Ni–Mo/γ-Al_2O_3 and Co–Mo/γ-Al_2O_3 for catalytic hydrotreatment of CEES [8,9]. These are the first reported combined HDS and HDC catalytic studies of CEES over heterogeneous catalysts under atmospheric pressure. A high-pressure process for CW agent disposal is not favorable by the military due to concern of leaks at high pressures. Although 3% Pt/η-Al_2O_3 is quite stable for HDS and HDC of CEES during the first 20 h, it deactivated rapidly thereafter [7]. Ni–Mo/γ-Al_2O_3 and Co–Mo/γ-Al_2O_3 are active and stable for HDS and HDC of CEES, but the selectivity to pure hydrocarbons is limited to 98.0% at 300°C [6]. A more selective catalyst is needed. This paper focuses on the combined HDS and HDC of CEES over AC-supported Ni and/or Mo catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

Ni–Mo/γ-Al_2O_3 catalysts were supplied by United Catalyst, Inc. Ni–Mo/AC, Mo/AC, and Ni/AC were prepared by the incipient wetness technique using PCB carbon from Calgon. PCB carbon, mesh 20–40, was first dried overnight under vacuum at 60°C before catalyst preparation. Ni–Mo/AC is prepared by loading the Mo first with ammonium heptamolybdate tetrahydrate (Aldrich) followed by nickel nitrate (Alfa).

Metal loadings and surface areas were analyzed by the inductively coupled plasma-mass spectrometry (ICP-MS) and BET technique, respectively.

2.2. Catalyst evaluation

The gas-phase heterogeneous catalytic hydrotreatment was studied in a fixed-bed microreactor. Details of the experimental setup and procedures have been described elsewhere [8,9,12]. Briefly, the reactant mixture is generated by passing a predetermined $H_2 + He$ mixture through a constant temperature saturator containing CEES. Five hundred milligrams of catalyst is loaded into a 3/8 in. O.D. Monel tube reactor. Before reaction, the catalyst is pretreated in situ with 10% H_2S in H_2 at 400°C for 1.5 h. The reactant mixture usually consists of 0.33% of CEES, 10% of H_2, and the balance He, unless otherwise specified. The total flow is 200 cm^3/min at room temperature. The reactant and product concentrations are analyzed by an on-line HP 5972 gas chromatograph-mass selective detector (GC-MSD) with an SPB-1 column for sulfur compounds and a Hayesep R column with thermal conductivity detector (TCD) for hydrocarbon (HC) products.

Table 1
BET surface areas and metal loadings of catalysts

Catalysts	BET surface area (m^2/g)	Mo loadings (wt.%)	Ni loadings (wt.%)
Ni–Mo/AC	637	7.5	1.73
Mo/AC	732	9.4	–
Ni/AC	882	–	2.68
Ni–Mo/γ-Al_2O_3	145	11.2	2.86

The conversions and product selectivites are defined as follows:

$$\text{Conversion} = 1 - \frac{\text{Reactant}_{\text{out}}}{\text{Reactant}_{\text{in}}} \times 100\%$$

$$\text{Selectivity}_i = \frac{\text{Product}_i}{\sum \text{Product}_i} \times 100\%$$

$$\text{HC Selectivity} = \text{Selectivity}_{C_2H_4} + \text{Selectivity}_{C_2H_6}$$

3. Results and discussion

3.1. Catalyst characterization

BET surface areas and metal loadings are measured and summarized in Table 1. Among the three AC-supported catalysts, Ni–Mo/AC shows the lowest surface area, with 637 m^2/g. Mo/AC and Ni/AC are 731 and 882 m^2/g, respectively. The surface areas of AC-supported catalysts are much higher than the surface area of Ni–Mo/γ-Al_2O_3. The metal loadings of AC-supported catalysts are slightly lower than the commercial alumina-supported catalyst.

3.2. Catalyst evaluation

3.2.1. Ni–Mo/AC and Ni–Mo/γ-Al_2O_3

The conversions of CEES and hydrocarbon (HC) selectivity over Ni–Mo/γ-Al_2O_3 catalysts were studied at temperatures from 200 to 350°C. The results are summarized in Fig. 1 and Table 2. At 300°C, Ni–Mo/γ-Al_2O_3 is active and stable for HDS and HDC of CEES to pure hydrocarbons with >99.9% conversion of CEES. It shows no sign of deactivation with 98.0% selectivity to ethylene and ethane throughout the 100 h run, as shown in Fig. 1. The activity and stability of Ni–Mo/γ-Al_2O_3 for HDS/HDC of CEES to pure hydrocarbons are greater at 300°C than they are at 250°C. As shown in Fig. 1, the HC selectivity of Ni–Mo/γ-Al_2O_3 decreases slowly, from 95.0 to 90.0% after 20 h at 250°C though the conversions are close to complete. The activity, however, decreased rapidly at 200°C. It is likely that the hydrogenation of coke precursors is relatively slower at low temperature than that of at high temperature which causes deactivation. However, the coke content of used catalysts were not analyzed. As summarized in Table 2, the HC selectivity decreased from 90.0 to 14.0% after 20 h on stream at 200°C. On the other hand, increasing the reaction temperature to 350°C the HC selectivity (Table 2) increased then only from 98.0 to 99.0% while the conversion of CEES is close to complete. The result suggests that although Ni–Mo/γ-Al_2O_3 is active and stable for HDS and DSC of CEES, the selectivity to ethane and ethylene is limited.

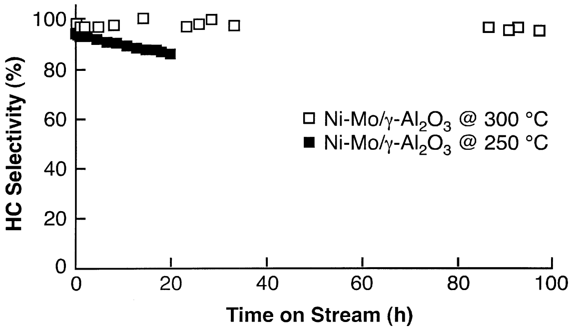


Fig. 1. Illustration of product selectivity to hydrocarbon formation during the first 20 h of CEES conversion over a Ni–Mo catalyst at 250°C and the first 100 h over a Ni–Mo catalyst at 300°C. H_2 : CEES : He = 10 : 0.33 : 89.7; 24,000 cm^3/h/g.

The conversions and HC selectivity of Ni–Mo/AC for HDS/HDC of CEES were studied at 200 and 300°C (Table 2). Ni–Mo/AC is most active and stable at 300°C for HDS and HDC of CEES to pure hydrocarbons. The HC selectivity is >99.5% (limited by the analytical system) at 300°C and is >98.0% over Ni–Mo/Al_2O_3 at the same temperature, as shown in

Table 2
Temperature effect on hydrotreating of CEES over Ni–Mo/γ-Al_2O_3 and Ni–Mo/AC catalysts[a]

Catalysts	Temperature (°C)	CEES conversion (%)	HC selectivity (%)
Ni–Mo/γ-Al_2O_3	350	>99.9	99.0
	300	>99.9	98.0
	200	90.0	14.0
Ni–Mo/AC	300	>99.9	>99.5
	200	97.0	20.0

[a] 0.33% CEES, 10% H_2, and balance He 200 cm^3/min, 0.5 g catalysts, 20 h on stream.

Table 2. In fact, HC selectivity at 300°C (>99.5%) over Ni–Mo/AC is higher than the HC selectivity at 350°C (99.0%) over Ni–Mo/γ-Al_2O_3. The activity and selectivity of Ni–Mo/AC for HDS/HDC of CEES at 200°C are also higher than the activity and selectivity of Ni–Mo/γ-Al_2O_3 catalyst at the same temperature. This suggests that AC-supported Ni–Mo catalysts are more selective for HDS/HDC of CEES and will be more effective for hydrotreating of HD with fewer hazardous byproducts than Ni–Mo/γ-Al_2O_3.

The stoichiometry of reaction of CEES to ethylene Eq. (1) below) requires only a 1 : 1 molar ratio of H_2 : CEES, although a 3 : 1 molar ratio of H_2 : CEES is required to produce ethane Eq. (2).

$$C_2H_5\text{–}S\text{–}C_2H_4Cl + H_2 \rightarrow 2C_2H_4 + HCl + H_2S \quad (1)$$

$$C_2H_5\text{–}S\text{–}C_2H_4Cl + 3H_2 \rightarrow 2C_2H_6 + HCl + H_2S \quad (2)$$

To investigate the effect of the H_2/CEES ratio on stability and selectivity of hydrotreating of CEES, various H_2 concentrations, ranging from an H_2/CEES molar ratio of 30/1 to 3/1, were evaluated for the stability of Ni–Mo/AC catalyst. The conversions of CEES are >99.9% during the tested period at 300°C no matter what H_2/CEES ratio was used. It indicates that the reactivity of CEES is high in the presence of H_2 and catalysts. The results of hydrocarbon selectivity at various H_2/CEES ratios as a function of time are shown in Fig. 2 and summarized in Table 3. Reducing the H_2/CEES molar ratio from 30/1 to 15/1 did not change CEES conversion and HC selectivity for 20 h (Table 3). However, as the molar ratio of H_2 to CEES ratio decreases to 7.5/1, the HC selectivity decreases rapidly to 72.9% after 20 h from 99.2%. When the H_2/CEES ratio decreases further to 3/1, the HC selectivity decreases even faster to 48.6% after 20 h from 98.9%. Although the stoichiometry of reaction of CEES to ethylene Eq. (2) requires only a 1/1 ratio of H_2/CEES (a 3/1 ratio of H_2/CEES is required to produce ethane Eq. (1), a higher H_2/CEES ratio is preferred to maintain high and stable selectivity to pure hydrocarbons. It is likely that higher H_2 partial pressure minimizes the coke formation which maintains the activity converting CEES to pure hydrocarbons.

Table 3
Comparison of HC selectivity for hydrotreating of CEES over Ni–Mo/AC with various H_2/CEES ratios at 300°C [a]

H_2/CEES ratio	HC selectivity @ 1st h (%)	HC selectivity @ 20 h (%)
30	>99.5	>99.5
15	99.2	99.1
7	99.2	72.9
3	98.9	48.6

[a] 0.33% CEES and balance He 200 cm^3/min, 0.5 g catalysts.

3.2.2. *Mo/AC and Ni/AC*

Neither Mo/AC nor Ni/AC was as active or as stable as Ni–Mo/AC for hydrotreating of CEES at 300°C. The activities and selectivities of Mo/AC and Ni/AC catalysts are compared to the supported Ni–Mo catalysts in Table 4. The HC selectivities over Mo/AC and Ni/AC are lower than both the selectivities of Ni–Mo/AC and Ni–Mo/γ-Al_2O_3 (94.0 and <20%, respectively). The HC production distributions are similar for Ni–Mo/AC, Mo/AC, and Ni–Mo/γ-Al_2O_3 catalysts. Ethylene is the major product and there is some ethane. The C_2H_6/C_2H_4 ratio ranges from 0.25 to 0.30 as shown in Table 4. In the case of Ni/AC, no ethane was formed during the hydrotreating of CEES. It is known that sulfur deactivates Ni which is evident by the negligible formation of ethane (C_2H_6/C_2H_4 ratio = 0.0) and lowest CEES conversion with 51.1% after 20 h on stream.

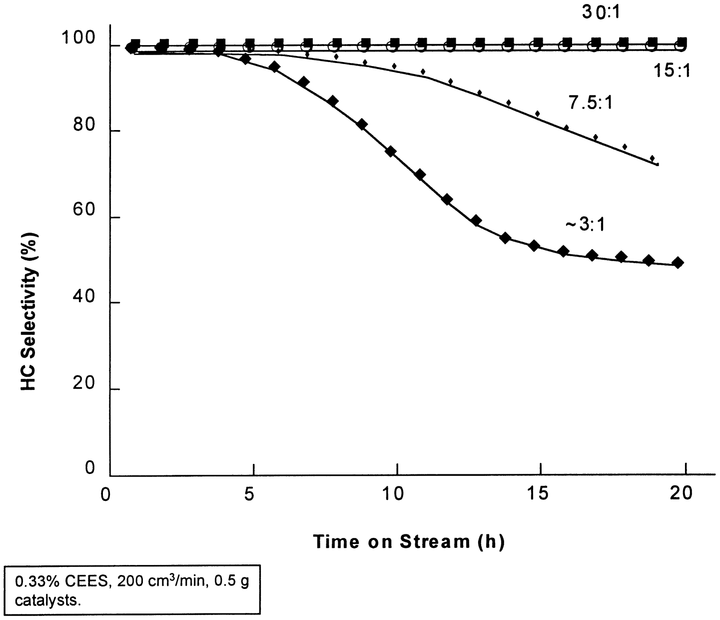


Fig. 2. Effect of H_2/CESS ratio on hydrotreatment of CEES over Ni–MoAC @ 300°C.

Table 4
Comparison of activity and selectivity for hydrotreating of CEES over various catalysts at 300°C after 20 h on stream[a]

Catalysts	CEES conversion.(%)	HC selectivity (%)	C_2H_6/C_2H_4 ratio
Ni–Mo/AC	100	>99.5	0.25
Mo/AC	100	94.0	0.30
Ni/AC	51.1	<20	0.0
Ni–Mo/Al_2O_3	100	98.0	0.28

[a] 0.33% CEES, 10% H_2, and balance He 200 cm^3/min, 0.5 g catalysts.

Table 5
Comparison of hydrotreating activities for diethyl sulfide[a]

Catalysts	DES conversion (%)	HC selectivity (%)	C_2H_6/C_2H_4 ratio
Ni–Mo/γ-Al_2O_3	58.4	78.2	0.16
Ni–Mo/AC	54.7	73.9	0.19
Mo/AC	11.6	65.2	0.43
Ni/AC	17.1	73.0	0.0

[a] 1.8% DES, 10% H_2, and balance He 300°C, 200 cm^3/min, 0.1 g catalysts.

3.2.3. Diethyl sulfide (DES) and chloroethane (CE)

It is interesting to study the HDS of DES and HDC of chloroethane (CE) since both compounds are possible intermediates of HDS and HDC of CEES. DES is produced by the removal of the one chlorine atom in CEES and the hydrogenation of the bond. CE is produced by the hydrogenolysis of the C–S bond in CEES. HDS of DES was studied over Ni–Mo/AC, Mo/AC, Ni/AC and Ni–Mo/γ-Al_2O_3 at 300°C. The molar concentration of reactant mixture are 1.8% DES, 10% H_2, and the balance He with a 120,000 cm^3/h/g·cat space velocity. The HDS activities were measured after 20 h on stream. Table 5 summarizes the DES conversions, hydrocarbon

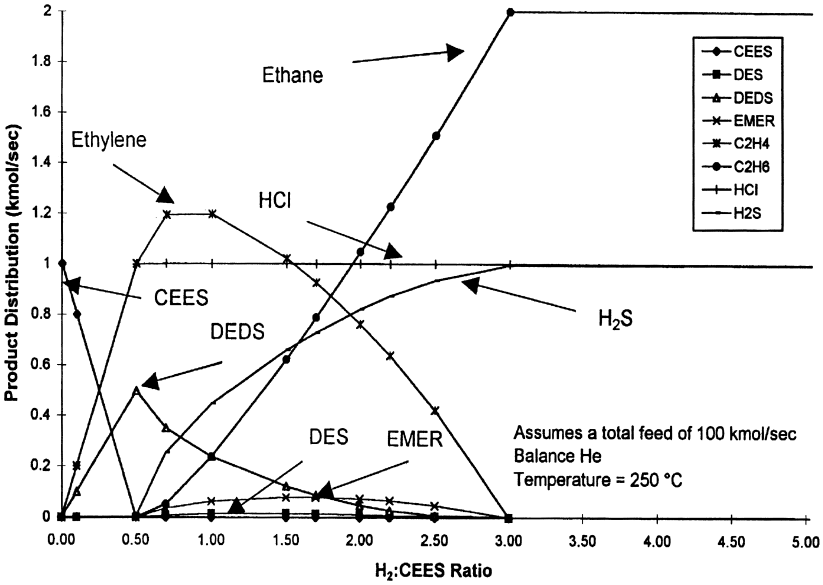


Fig. 3. Product distribution at equilibrium of hydrotreatment of CEES at 250°C.

selectivities, and C_2H_6/C_2H_4 ratios over AC-supported Ni, Mo, and Ni–Mo and Ni–Mo/γ-Al_2O_3 catalysts. Ni–Mo/AC and Ni–Mo/γ-Al_2O_3 catalysts have similar activity (54.7 and 58.4%, respectively) and selectivity (73.9 and 78.2%, respectively) for HDS of DES. However, both Mo/AC and Ni/AC have much lower activity than supported Ni–Mo catalysts with 11.6 and 17.1% DES conversion, respectively. On the other hand, the C_2H_6/C_2H_4 ratios in the product stream are similar for Ni–Mo/AC (0.19) and Ni–Mo/γ-Al_2O_3 (0.16) but are very different for Mo/AC and Ni/AC. Mo/AC is more selective to C_2H_6 than either supported Ni–Mo catalysts or Ni/AC. Its C_2H_6/C_2H_4 ratio is 0.43, compared to 0.16–0.19 for the supported Ni–Mo catalysts. Ni/AC is not active for hydrogenation at all, with a C_2H_6/C_2H_4 ratio of 0.

HDC of CE was also studied over the same group of catalysts at 300°C. The molar concentration of reactant mixture were 1.2% CE, 10% H_2, (balance He) and a 120,000 cm^3/h/g·cat space velocity was used. The results are summarized in Table 6. All catalysts were treated with 10% H_2S in H_2 at 400°C for 1.5 h, as were all catalysts used in other HDS or HDS/HDC reactions. All catalysts showed measurable conversion of CE to ethane and HCl, ranging from 3.5 to 61.2%, though Ni/AC is clearly less active for this reaction. Both Ni–Mo/AC and Ni–AC showed negligible hydrogenation activity during HDC of CE, forming only ethylene. Although Mo/AC has good hydrogenation activity during hydrotreating of CE with a C_2H_6/C_2H_4 ratio of 0.20, it is less active for CE conversion than supported Ni–Mo catalysts.

Table 6
Comparison of hydrotreating activities for chloroethane[a]

Catalysts	CE conversion (%)	C_2H_6/C_2H_4 ratio
Ni–Mo/γ-Al_2O_3	61.2	0.03
Ni–Mo/AC	32.5	<0.01
Mo/AC	20.6	0.20
Ni/AC	3.5	0.0

[a] 1.2% CE, 10% H_2, and balance He 300°C, 200 cm^3/min, 0.1 g catalysts.

3.3. Reaction pathways

As shown in Eqs. (1) and (2), HDS and HDC of CEES can produce C_2H_6 or C_2H_4 as final products besides HCl and H_2S, depending on the H_2/CEES ratio. Thermodynamic calculations, as reported in our previous publication (Fig. 3) [6], show that C_2H_6 is the most stable product at 250°C when the H_2/CEES molar ratio is equal to or larger than 3/1. Although other products such as ethylene, DES, and ethyl mercaptan are stable when the H_2/CEES ratio is less than

Table 7
Activity summary for hydrotreatment of CEES, DES, and CE

Hydrotreatment	Conversion activity to HC	C_2H_6/C_2H_4 ratio
CEES	Ni–Mo/AC ≈ Ni–Mo/Al_2O_3 ≈ Mo/AC ≫ Ni/AC	Mo/AC ≈ Ni–Mo/Al_2O_3 ≈ Ni–Mo/AC ≫ Ni/AC
DES	Ni–Mo/Al_2O_3 ≈ Ni–Mo/AC ≫ Ni/AC > Mo/AC	Mo/AC > Ni–Mo/AC ≈ Ni–Mo/Al_2O_3 ≫ Ni/AC
CE	Ni–Mo/Al_2O_3 > Ni–Mo/AC > Mo/AC ≫ Ni/AC	Mo/AC > Ni–Mo/Al_2O_3 ≈ Ni–Mo/AC ≈ Ni/AC

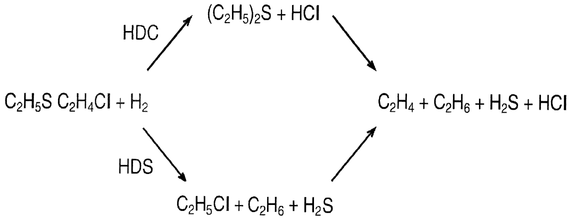


Fig. 4. Simplified reaction pathways.

3/1, they are not thermodynamically favored when the H_2/CEES ratio is $\geq$3/1. Experimentally, however, sulfur-containing components are detected in the product stream even with H_2/CEES of 30/1 at 300°C over supported Ni and/or Mo catalysts. Ethene instead of ethane is the most abundant product in the product stream under most of the reaction conditions tested. Apparently, the reaction is operated under kinetic control region far from thermodynamic equilibrium.

It is interesting to look at possible reaction pathways to understand the HDS/HDC of CEES over supported Ni–Mo catalysts. The simplified possible reaction pathways are shown in Fig. 4. The HDS and HDC of CEES could go either HDC first followed by HDS or HDS first followed by HDC. DES would be a reaction intermediate if HDC reaction proceeds first. On the other hand, CE could be a reaction intermediate if HDS proceeds before HDC reaction.

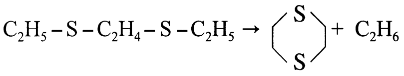
Based on the results shown in Table 4, Ni–Mo/γ-Al_2O_3, Ni–Mo/AC, and Mo/AC (except Ni/AC) have similar CEES conversion, hydrocarbon selectivity, and C_2H_6/C_2H_4 ratio in the product stream during hydrotreating of CEES. This suggests that the hydrotreating of CEES goes through similar reaction pathways over these catalysts. By examining the results in Table 5, the activity of HDS of DES shows similar hydrocarbon selectivity for all four catalysts, but the DES conversion is much higher for supported Ni–Mo catalysts than Mo/AC or Ni/AC. Furthermore, the C_2H_6/C_2H_4 ratio for Mo/AC is much higher than both Ni–Mo/AC and Ni–Mo/γ-Al_2O_3. This indicates that supported Ni–Mo catalysts are very active for breaking the C–S bonds, but not as active as Mo/AC for hydrogenation of C_2H_4 to C_2H_6 during HDS of DES. The results suggest that hydrotreating of CEES to C_2H_6 and C_2H_4 is not likely to proceed through the same reaction pathways as HDS of DES.

The CE reaction activity and selectivity over these four catalysts, as summarized in Table 6, show different conversions. There is no similarity between any two catalysts for conversion of CE. Supported Ni–Mo catalysts and Ni/AC show negligible hydrogenation activity during HDC of CE. However, both supported Ni–Mo catalysts show relatively high hydrogenation activity with C_2H_6/C_2H_4 ratios of 0.25 and 0.28 during the HDS/HDC of CEES. This suggests C_2H_6 formed during hydrotreating of CEES over supported Ni–Mo catalysts does not come from HDC of CE. CE is not likely an intermediate during the hydrotreatment of CEES. It is further supported by the fact that we have detected negligible CE concentration throughout the tests we carried out for the hydrotreatment of CEES.

The activity orders of these catalysts for converion of CEES, DES, and CE to pure hydrocarbons and their C_2H_6/C_2H_4 ratio in the product stream are summarized in Table 7. The orders for activity and C_2H_6/C_2H_4 production ratio for hydrotreating of CEES are very different from HDS of DES or HDC of CE. The results suggest that hydrotreating of CEES is not dominated by HDS of DES, HDC of CE, or a combination. In fact, we have detected two sulfur-containing compounds, 1,4 dithiane ($C_4H_8S_2$) and 1,2 bis(ethylthio)ethane (C_2H_5–S–C_2H_4–S–C_2H_5), in the product stream at low residence times. Although those two compounds were identified, they were not quantified. We believe that this is the first report on the identification of two-sulfur containing compounds from HDS of single sulfur containing reactant under gas–solid reaction conditions. We speculate that the S–C_2H_5Cl bond, due to the weakening effect from Cl, will be broken first to form C_2H_5–S^* and $^*C_2H_4Cl$ intermediates Eq. (3). In fact, Zhou et al. reported that CEES dissociation begins with cleavage of the S–C bond on the chlorine side (C_2H_5S–CH_2CH_2Cl) when multilayers of CEES are present on Pt surface. It is likely that $C_2H_5S^*$ can react with another CEES molecule to form 1,2 bis(ethylthio)ethane and 1,4 dithiane is formed by cyclization with releasing a C_2H_6 molecule Eqs. (4) and (5). On the other hand, CEES could go through dehydrochlorination to form (ethylthio) ethene which could react with another CEES molecule to form 1,2 bis(ethylthio)ethane. Presently, we do not have further evidence to suggest the details of reaction pathways. More fundamental investigations are needed to clarify the detailed reaction pathways for the HDS/HDC of CEES.

$$C_2H_5S\text{–}C_2H_4Cl + 2^* \rightarrow C_2H_5S^* + C_2H_4Cl^* \qquad (3)$$

$$C_2H_5S^* + C_2H_5\text{–}S\text{–}C_2H_4Cl \rightarrow C_2H_5\text{–}S\text{–}C_2H_4\text{–}S\text{–}C_2H_5 + {}^*Cl \qquad (4)$$



(5)

4. Conclusion

At 300°C, HDS and HDC of CEES are stable over Ni–Mo/AC, Mo/AC, and Ni–Mo/γ-Al_2O_3 catalysts with 30 : 1 H_2 to CEES ratio and 24,000 cm^3/h/g space velocity. More than 99.5% selectivity to pure hydrocarbons is achieved over Ni–Mo/AC. Ethylene and ethane are the major reaction products besides HCl and H_2S. The activity order of the catalysts for HDS/HDC of CEES to pure hydrocarbons is Ni–Mo/AC > Ni–Mo/Al_2O_3 > Mo/AC > Ni/AC for stable and selective hydrotreating of CEES. A much higher H_2/CEES ratio above the stoichiometric requirement, at least 15 : 1, is needed to maintain a high and stable selectivity to hydrocarbons.

Based on our results, hydrotreating of CEES over supported Ni–Mo catalysts does not appear to proceed similar to either HDS of DES or HDC of CE. HDC of CE does not occur ready on supported Ni–Mo catalysts as evidenced by the negligible C_2H_6/C_2H_4 ratio in the product shown. Products containing two sulfur atoms detected during low residence time reactions suggest that the reaction pathway is more complex than simple C–S and C–Cl bond cleavage followed by hydrogenation. More mechanistic studies are needed to clarify the detailed reaction pathways of hydrotreating of CEES.

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