



Reaction mechanisms of thioetherification for mercaptans and olefins over sulfided Mo-Ni/Al₂O₃ catalysts



Zhibing Shen^{a,b}, Ming Ke^{a,*}, Pei Yu^a, Haiqiang Hu^a, Zhaozheng Song^a, Qingzhe Jiang^a

^a State Key Laboratory of Heavy Oil processing, China University of Petroleum, Beijing 102249, China

^b College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, Shaanxi Province, China

ARTICLE INFO

Article history:

Received 5 June 2014

Received in revised form

24 September 2014

Accepted 25 September 2014

Available online 5 October 2014

Keywords:

Thioetherification

Mechanism

Mercaptan

Olefin

Sulfided Mo-Ni/Al₂O₃ catalysts

ABSTRACT

The thioetherification reaction of 1-butanethiol and 1-hexene dissolved in *n*-hexane was investigated over sulfided Mo-Ni/Al₂O₃ catalysts. The experimental results showed the catalysts have good catalytic performance for thioetherification reaction, but the isomerization and hydrogenation reactions of olefins over the catalysts can inhibit thioetherification reaction. As reaction temperature increases, the isomerization and hydrogenation reactions of olefins increase rapidly, however, the inhibition of thioetherification reaction also increases. The sulfur distribution and molecular structures of sulfur compounds in the products were analyzed by the gas chromatograph with sulfur chemiluminescence detector (GC-SCD) and the gas chromatograph/mass spectra spectrometry (GC/MS). Two possible routes of thioetherification reaction could be observed. At low temperature, the major pathway involves a direct addition of 1-butanethiol to the terminal carbon of double bond of 1-hexene. In this mechanism, the main product is anti-Markovnikov adduct. At a higher temperature, the C–S bond of 1-butanethiol can be subsequently cleaved, and the adsorbed -SH species can be formed on the catalysts. On the same time, abundant 1-hexene can be absorbed on the catalysts, as well. Therefore, the adsorbed SH species can then recombine with adsorbed 1-hexene to form new hexyl-mercaptans, which can continue to produce another kind of thioether (di-hexyl sulfide) with adsorbed 1-hexene. Similar with the first reaction route, the thioether of the anti-Markovnikov adduct still dominates in the product.

© 2014 Published by Elsevier B.V.

1. Introduction

Thioetherification (or thiol-ene reaction) is an addition reaction of mercaptans with olefins, which can convert mercaptans into thioethers [1–4] and other sulfur compounds. This process can be used to remove mercaptans in the fluid catalytically cracked (FCC) naphtha streams [2,3]. It is reported [5] that the olefins are mainly in the low boiling fraction (LCN) in the cracked naphtha, and the predominant light boiling sulfur compounds are mercaptans (RSH) in LCN. Therefore, thioetherification can be used to transform mercaptans in the light boiling range naphtha (LCN) into thioethers. The heavier molecule thioethers can go into the heavy boiling range naphtha (HCN) fractions. Then, thioethers and other sulfur compounds in HCN are removed in a subsequent HCN hydrodesulfurization (HDS) step. This process can avoid FCC gasoline octane

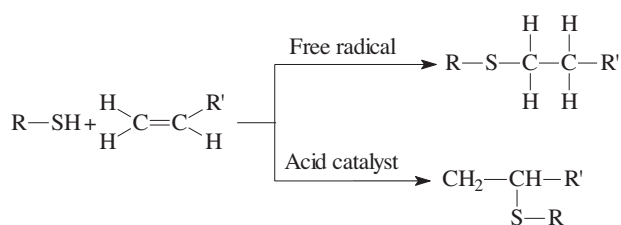
number loss caused by the olefin saturation during full fraction gasoline HDS stage [6,7]. Thioetherification process is usually performed under the H₂ atmosphere over the sulfided metal catalysts [3,8]. Therefore, diolefins in the FCC gasoline can also be simultaneously hydrogenated into mono-olefins or alkanes, which can prevent polymerization of diolefins on the catalysts of HDS unit. The gum formed by the polymerization of diolefins can reduce the activity and life of the HDS catalysts [8].

The thioetherification reactions of thiols with carbon-carbon double bonds (or simply “enes”) were noted in a much cited articles in 1905 [1], which clearly indicated the general concept of reactions between thiols and olefins. During the last century, two kinds of reaction formulas were proposed in Scheme 1: thiol free-radical addition to carbon-carbon double bonds to give the anti-Markovnikov adducts [9–11], and the acid catalyzed thiol electrophilic addition to carbon-carbon double bonds to provide Markovnikov adducts [12,13]. Applications of the thiol-ene reaction with free-radical addition are widely used in both polymer and synthetic chemistry.

Sulfided transition metals, such as Ni, Pt, Pd and Ag, have been reported to be applied into the thioetherification process in some

* Corresponding author at: State Key Laboratory of Heavy Oil processing, China University of Petroleum, No. 18 Fuxue Road, 102249 Changping District, Beijing, China. Tel.: +86 10 89733372.

E-mail addresses: keming@cup.edu.cn, shixin611@sina.com (M. Ke).



Scheme 1. General reaction formulas of thioetherification.

literature [16–20]. All those transition metals have some catalytic activity for thioetherification. Especially, Mo promoted Ni/Al₂O₃ catalysts had displayed good thioetherification reaction performance for mercaptans and di-olefins in our previous study [14,15]. However, some new reaction findings have been investigated. Mo-Ni/Al₂O₃ catalysts also have good performance for mercaptans and mono-olefins and the distribution and structures of thioethers do not obeyed traditional Markonikov Rule. At present, there is almost no literature discussing thioetherification reaction mechanisms over sulfided metal catalysts. Therefore, it is difficult to continue to study the reaction and improve its catalysts deeply.

In this paper, thioetherification reaction mechanisms over sulfided metal catalysts were researched through studying and citing the reaction behaviors of thiols and olefins in other chemical reactions, such as desulfurization and hydrogenolysis of alkanethiols and disulfides [16–18] and hydrogenation of olefins over sulfided metal catalysts. Kieran et al. [18] reported catalytic reaction of ethyl mercaptan on MoS₂ catalysts. The results showed there were two ways of bond cleaving for mercaptans: cleavages of C–S and S–H. The order in which chemical bonds were activated was H–H > H–S > C–S > C–H > C–C. They also discovered that thiolates have been proposed as intermediates in hydrodesulfurization reaction, which was proved by other researchers. For example, methane-thiol could be dissociated to form methane-thiolate on the metal catalysts, such as Ni(1 1 1) [19], Pt(1 1 1) [20], Mo(1 1 0) [21], W(2 1 1) [22], Cu(1 0 0) [23] and Fe(1 0 0) [24]. And then the C–S bond of the methane-thiolate could continue cleaving on sulfided metal catalysts [25].

In this work, the thioetherification reaction for 1-butanethiol and 1-hexene in the blended oil was investigated over the sulfided Mo-Ni/γ-Al₂O₃. After the reaction, the destination of sulfur atom of 1-butanethiol, sulfur compounds distribution and molecular structures of sulfur compounds in the product were analyzed to detect possible reaction pathways of thioetherification for 1-butanethiol and 1-hexene.

2. Experimental

2.1. Catalyst and chemicals

The Mo-Ni/Al₂O₃ catalysts were prepared by the co-impregnation of the appropriate amounts of Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O precursors onto the commercial γ-Al₂O₃ support. The catalysts were obtained by drying at 100 °C for 6 h and then calcinating at 550 °C for 4 h. The textural properties of Mo-Ni/Al₂O₃ catalysts were shown in Table 1. And other physicochemical properties of the oxidated and sulfided Mo-Ni catalysts could be referenced in our previous papers [14,15].

Nickel nitrate hexahydrate (98%), ammonium molybdate tetrahydrate (97%), *n*-hexane(95%) and carbon disulfide (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., and 1-butanethiol (98%) and 1-hexene (97%) from Alfa Aesar, Johnson Matthey Company. H₂ was purchased from Beijing Haipu Gas Company.

Table 1
Textural properties of Mo-Ni/Al₂O₃ catalyst.

| Textural properties | Data |
|---|-------|
| Chemical compositions | |
| NiO (wt%) | 10.12 |
| MoO ₃ (wt%) | 5.45 |
| Specific surface area (m ² g ⁻¹) | 244 |
| Pore volume (cm ³ g ⁻¹) | 0.42 |
| Pore diameter (nm) | 7.6 |

2.2. Reaction system

The catalytic reaction of thioetherification was carried out in a fixed bed flow reactor system. This apparatus consists of a gas-feeding system controlled by a mass flow meter and a syringe pump liquid feeding system. The reactor, with an internal diameter of 10 mm, was loaded with the 5 ml catalyst sample. The catalysts were in situ presulfurized with *n*-hexane contained 2 wt% CS₂. Then, catalytic performance was tested by the mixture of 20 wt% 1-hexene, and 100 μg/g 1-butanethiol in *n*-hexane over the sulfided Mo-Ni/Al₂O₃ catalysts. The liquid feed and H₂ were input by the pump and the mass flow controller, respectively. Both reactants were mixed before they entered the reactor. The gas and liquid products were collected in a storage tank after a condenser. A back pressure valve connected with the storage tank to control the pressure of the reactor system. The experiments were carried out under the condition of the pressure 1 MPa, the volume ratio of H₂ and feed 10, and the liquid hourly space velocity 4 h⁻¹. The reaction temperatures were in the range of 70–140 °C. After a stabilization period of 10 h, reaction products were collected and analyzed per 4 h. In the experiment process, in order to improve the comparability of results of different reaction conditions, the catalysts were replaced and presulfurized under the same conditions when the experimental conditions were adjusted. All quantitative data are an average value of 5 continuous samples.

2.3. Analysis

The hydrocarbon compositions of the feed stocks and products were determined with an Agilent 1790 gas chromatograph (GC) installed with a flame ionization detector (FID) and an HP-PONA capillary column (50 m × 0.2 mm). The detector and injector temperatures are both 250 °C. The split ratio is 1/80. The column oven temperature is 40–150 °C and the heating rate is 8 °C/min.

The sulfur compounds of liquid products were analyzed by a gas chromatograph/mass spectra spectrometry (GC/MS) (Shimadzu GC17A/QP-500) for qualitative analysis (The chromatographic column is Agilent HP-FFAP (30 m × 0.25 mm × 0.25 μm), the detector of GC is also FID, the injector temperature is 250 °C, the split ratio is 100:1, the column oven temperature program is start temperature 50 °C keeping 1 min, and then rising to 240 °C in ramp of 5 °C/min; mass spectra is a full-scan in the molecular weight range of 35–400 amu) and were detected by an Agilent 6890N gas chromatograph with a sulfur chemiluminescence detector (GC-SCD) and a quartz capillary column (50 m × 0.25 mm) for quantitative analysis (Analysis conditions: the detector and injector temperatures are both 250 °C, the initial column oven temperature is 70 °C and then rises to 250 °C by the heating rate 10 °C/min).

The sulfur contents of gas phase were detected by another Agilent 6890N gas chromatograph with a pulsed flame photometric detector (GC-PFPD) and two line of columns. One is HP1 (60 m × 320 μm × 5 μm), another is Gaspro PLOT (60 m × 320 μm). Analysis conditions: the detector and injector temperatures are 100 °C and 250 °C, respectively. The initial column oven temperature is 70 °C and stays 4 min, then rises to 250 °C by the heating rate 20 °C/min for another 10 min.

The contents of total sulfur in the feed stocks and products were measured by a WK-2C micro-coulombmeter (Jiangsu Jiangfen Electroanalytical Instrument Co., PR China). The process was operated according to ASTM D3120-82. The mercaptan-sulfur contents of the feed and products were analyzed by the potentiometric titration method according to ASTM D3227-83.

3. Results and discussion

3.1. Reaction performance over sulfided Mo-Ni/Al₂O₃ catalysts

Table 2 gives the contents of total sulfur and 1-butanethiol in the feed and reaction products which were collected at the reaction temperatures of 80 and 110 °C, respectively. 1-Butanethiol is the only sulfur source in the feed. From Table 2, it can be noted that, after the reaction, the content of 1-butanethiol decreases and the total sulfur content remains stable in the products. Therefore, it can be concluded that the reduction of 1-butanethiol is not caused by direct desulfurization, but caused by the transformation of mercaptans to thioethers. In addition, it also can be observed from Table 2 that the carbon-carbon bonds of 1-hexene has been isomerized and hydrogenated in the thioetherification process. The terminal C=C bond of the olefins has been transformed into internal olefins (2-hexene and 3-hexene) over the sulfided Mo-Ni/Al₂O₃ catalysts. The isomerization of 1-hexene was discovered and confirmed by GC analysis as shown in Table 2. As the temperature increases, 1.72 wt% of hexene is hydrogenated to *n*-hexane and the conversions of isomerization and hydrogenation are also gradually improved. Table 2 also displayed that no H₂S and other sulfur compounds were detected in gas phase of the products, which proved further that 1-butanethiol is not hydrodesulfurized. So, we can conclude that sulfided Mo-Ni/Al₂O₃ catalysts have good thioetherification reaction performance and selectivity.

Fig. 1 demonstrates the trends of the conversions of mercaptans and 1-hexene in the blended oil over sulfided Mo-Ni/Al₂O₃ catalysts as the reaction temperature increases. It can be seen that the temperature has a great impact on the thioetherification and conversion reactions of 1-hexene. When the reaction temperature is below 110 °C, the conversion of mercaptans increases quickly with the temperature and reaches the maximum value 97 wt% at 110 °C. However, the conversion of mercaptans decreases slightly after 110 °C. Due to steric effect, it may be expected that the reactivity of terminal olefins is higher than that of internal olefins in the thioetherification. Therefore, the reduction of 1-hexene in the reaction system does not favor of the mercaptans conversion. Si et al. [26] believed that the reaction of forming thioethers and isomerization of olefins were competitive reactions on the same active sites of NiMoS/Al₂O₃. Therefore, it can be concluded that, at a higher temperature (>110 °C), the thioetherification will be inhibited, but the isomerization and hydrogenation rate of 1-hexene will be accelerated. Temperature is an important parameter to conversion and selectivity of 1-butanethiol in the thioetherification process.

Table 2
Sulfur balance and comparison of olefin content in the feed and products.

| | Feed | Product in different temperature | |
|-----------------------|--------|----------------------------------|--------|
| | | 80 °C | 110 °C |
| Liquid phase | | | |
| Sulfur content, μg/g | 101.27 | 101.12 | 100.98 |
| 1-Butanethiol, μg/g | 101.27 | 30.67 | 0 |
| 1-Hexene, wt% | 10.25 | 4.83 | 1.26 |
| 2-Hexene, wt% | – | 3.97 | 4.68 |
| 3-Hexene, wt% | – | 1.45 | 2.43 |
| <i>n</i> -Hexane, wt% | – | – | 1.72 |
| Gas phase | | | |
| Sulfur content, μg/g | – | 0 | 0 |

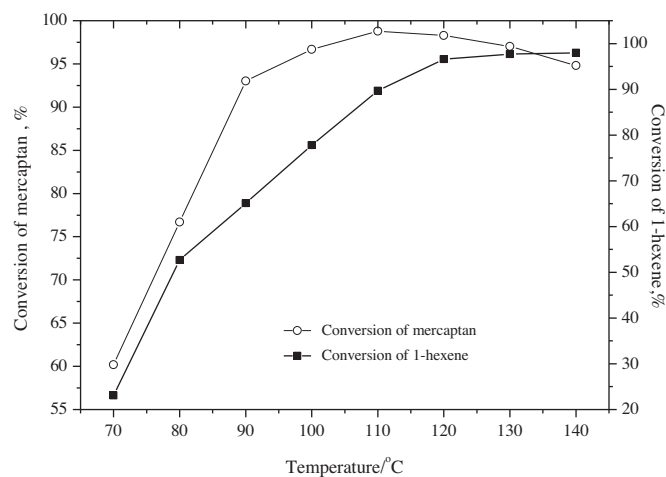


Fig. 1. Relations of the conversions of mercaptan and 1-hexene with the reaction temperatures.

3.2. Sulfur compounds distribution of the products

GC spectrum of the sulfur compounds in the feed, and products from reaction temperature 80 °C and 110 °C were given in Fig. 2, respectively. It is evident that there are different reaction pathways to transform mercaptans to other sulfur compounds at different reaction temperatures. The chromatographic peak at around 10.17 min is 1-butanethiol. The peak area decreases as the reaction temperature increases to 110 °C and the conversion of 1-butanethiol is up to 100%. The peaks at around 14.16 min and 15.45 min can be attributed to two isomers of hexylmercaptan (2-hexylmercaptan and 1-hexylmercaptan) by a comparison of mass spectrum of GC/MS analysis to the standard spectrum, as described in Fig. 3. The new mercaptans may be formed by the recombination of -SH fragments of 1-butanethiol with 1-hexene.

The sulfur compound at around 18.93 min of GC-SCD might be so tiny that it was not detected in the GC/MS. However, the sulfur compound could be speculated to be dibutyl sulfide based on sulfur distribution in the product. And then the standard sample of dibutyl sulfide was used to its residence time of GC-SCD under the same conditions. The result was displayed in Fig. 3. The peak position of pure dibutyl sulfide is at around 18.9 min and is according to GC-SCD of the product. Therefore, the sulfur compound at around 18.93 min was confirmed to dibutyl sulfide, which was produced by the dehydrothion of 1-butanethiols (Fig. 4).

In Fig. 2b and c, there are two kind of sulfur compounds at the retention time of both 21.4 min, 22.5 min, 24.6 min and 25.7 min, which are main products formed by the direct addition of thiols and olefins in the thioetherification. Based on the mass spectra of the GC/MS analysis (Fig. 5) and the mass spectrometric decomposition process of thioethers [27], the sulfur compounds could be speculated to be two kinds of isomers of butyl-hexyl sulfides (No. 5 and No. 6 compounds in Table 3) and di-dexyl sulfides (No. 7 and No. 8 compounds in Table 3), which are Markonikov and anti-Markonikov adduct thioethers, respectively. The anti-Markonikov adduct butyl-hexyl sulfide and di-dexyl sulfide (CH₃CH₂CH₂CH₂-S-CH₂CH₂CH₂CH₂CH₂CH₃ and CH₃CH₂CH₂CH₂CH₂CH₂-S-CH₂CH₂CH₂CH₂CH₂CH₃) are the dominant products.

Fig. 2 and Table 3 showed that as the reaction temperature increases, the major products of thioetherification reaction are gradually changed from butyl-hexyl sulfides to di-dexyl sulfides. At 80 °C, butyl-hexyl sulfides might be produced by the direct addition of 1-butanethiol and hexane. When the temperature rises to 110 °C, the C-S bond of 1-butanethiol might be cleaved and

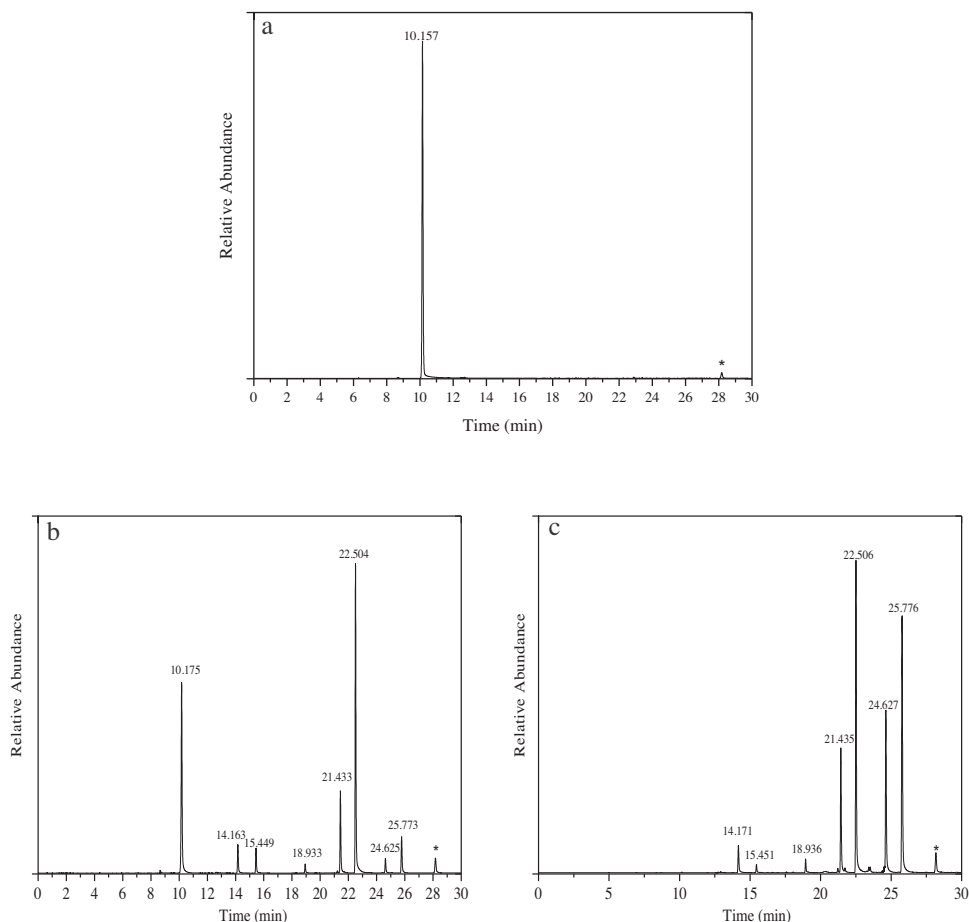


Fig. 2. The GC spectrum of sulfur compounds for the feed and the products: (a) feed, (b) product under 80 °C, and (c) product in the 110 °C, * is internal standard diphenyl sulfide.

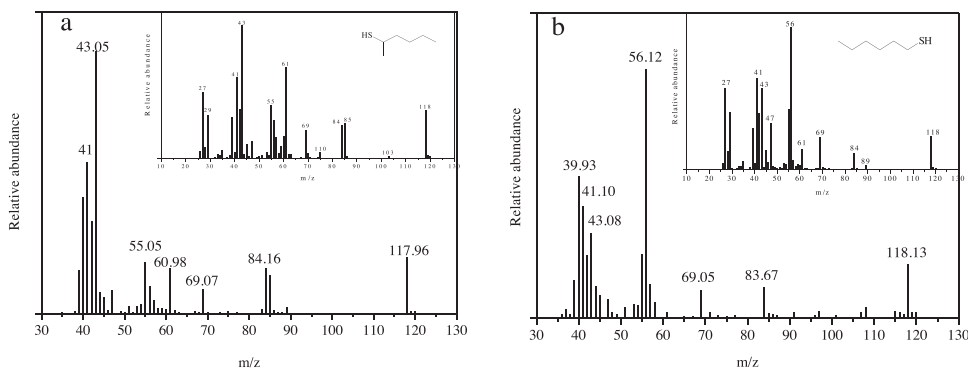


Fig. 3. Mass spectra of 14.1 min (a) and 15.4 min (b) in the product.

then recombine with hexene to form hexylmercaptans and di-hexyl sulfides, especially for di-hexyl sulfides. By comparing Fig. 2b with Fig. 2c, the mass fraction of the butyl–hexyl sulfides in the reaction system decreased slightly from 80 °C to 110 °C. Nevertheless, the mass fraction of the di-hexyl sulfides in the reaction system increased significantly from 7.83% to 48.44% as the reaction temperature increased from 80 to 110 °C. As well, conversion of 1-butanethiol was improved from 30.33% at 80 °C to 100% at 110 °C. Thus, it can be concluded that the C–S bond of 1-butanethiol has been cleaved over the sulfided Mo–Ni/Al₂O₃ catalysts. And the formation of the adsorbed SH species on the catalysts recombined with a molecule of hexene to form hexyl-thiols, which can continue to react with hexene to produce di-hexyl sulfides at the higher

temperature. In addition, the production of di-hexyl sulfides accelerates the conversion of 1-butanethiol dramatically in the thioetherification process.

3.3. Reaction pathways

From Fig. 2 and Table 3, it is shown that the distribution of reaction products are very complex, and the reaction mechanism is also contrary to the typical Markonikov adduct based on the carbenium ion reaction mechanism. It can be concluded the active sites for thioetherification are not the acid sites but the metal active sites of the catalysts. Thus, the reaction pathways for thioetherification

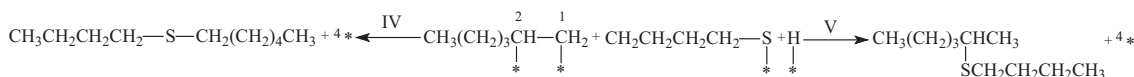
Table 3
Sulfur compounds distribution of the product.

| GC-PFPD No. | GC-PFPD residence time, min | Sulfur compounds | Relative content, wt% | |
|-------------|-----------------------------|--|-----------------------|--------|
| | | | 80 °C | 110 °C |
| 1 | 10.1 | CH ₃ CH ₂ CH ₂ -SH CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -SH | 30.33 | 0 |
| 2 | 14.1 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -SH | 4.20 | 3.31 |
| 3 | 15.4 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 3.38 | 0.84 |
| 4 | 18.9 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 1.26 | 1.34 |
| 5 | 21.4 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 11.50 | 13.10 |
| 6 | 22.5 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 41.52 | 32.38 |
| 7 | 24.6 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 2.15 | 18.02 |
| 8 | 25.7 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 5.68 | 30.42 |

can be inferred by the catalytic mechanisms of the metal catalysts to the mercaptans and olefins.

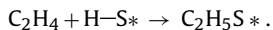
Wiegand et al. [21] studied the reactions of methane-thiol on Mo(1 1 0) and they discovered there are two ways of the S-H and

C-S bond scission under different temperature. Methyl thiolate is the only intermediate detected on the surface at 100 K and the C-S bond hydrogenolysis of the methyl thiolate intermediate is at 315 K. Wiegand et al. showed that the reaction mechanism for methanethiol on Mo(1 1 0) was proposed in Fig. 6. Therefore, the

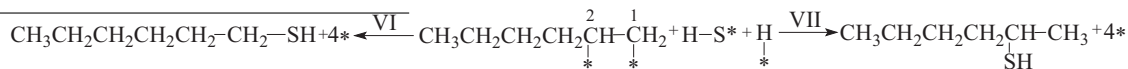


S-H bond of thiols is activated more easily than the C-S bond, which is also proved by the results of Kieran et al. [18].

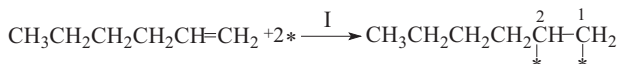
Todorova et al. [28] studied the hydrogenolysis and elimination reactions of C₂H₅SH on the catalytical active edge of 2H-MoS₂. Their calculations showed that the decomposition of ethane-thiol to ethane and ethene are fast reactions, but there is a reverse reaction pathway for the formation of another ethyl thiolate intermediate from ethane via the following sequence of reactions:



Based on the results of Wiegand and Todorova, we can speculate on the adsorbed intermediate of *n*-butyl mercaptan and 1-hexene

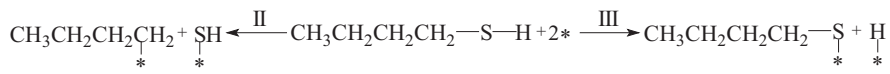


on the sulfided metal. As known to all, the olefin molecules are adsorbed easily on the sulfided metal catalysts and then π bond is opened to form olefin intermediates as follow:



N-butyl mercaptan could have two ways of bond breaking to

form adsorbed H-S* and * intermediates on the catalysts, according to



At a lower temperature (80 °C), S-H bond scission is major reaction pathway because of its lower activation energy [19]. In the meantime, the formation of butyl-hexyl sulfides from the neigh-

boring CH₃CH₂CH₂CH₂CH²-CH₂¹ and * start to be desorbed from the catalysts, according to:

Due to steric hindrance, the adsorbed CH₃CH₂CH₂CH₂CH²-S-* intermediate has priority to combining with No. 1 carbon of adsorbed hexyl intermediate to produce anti-Markonikov thioethers. Therefore, Reaction IV can be considered as a main reaction pathway in the lower temperature.

Like Todorova's result [28], the adsorbed H-S* (or *S*) intermediate formed in Reaction II could produce new mercaptans through a reverse reaction (Reaction VI and Reaction VII) with adsorbed olefin intermediate. In the reaction system, there is abundant of hexene and adsorbed hexyl intermediates formed in the reaction process. Thus, the formation of new hexyl mercaptans are accelerated by the reaction kinetics principle, according to:

From these reaction pathways two kinds of structural isomers of hexyl mercaptans can be obtained. Similar to the formation process of butyl-hexyl sulfides, 1-hexyl mercaptan of lower steric hindrance is also major product in the reaction. Therefore, the hexyl mercaptans are also considered an intermediate. As temperature increases gradually, more and more di-hexyl sulfides were formed in Table 2 and Fig. 3. Because activation energy of C-S is higher than that of S-H. The C-S was gradually easily cleaved as temperature rising. It was inferred that more C-S bond takes carbon-to-sulfur

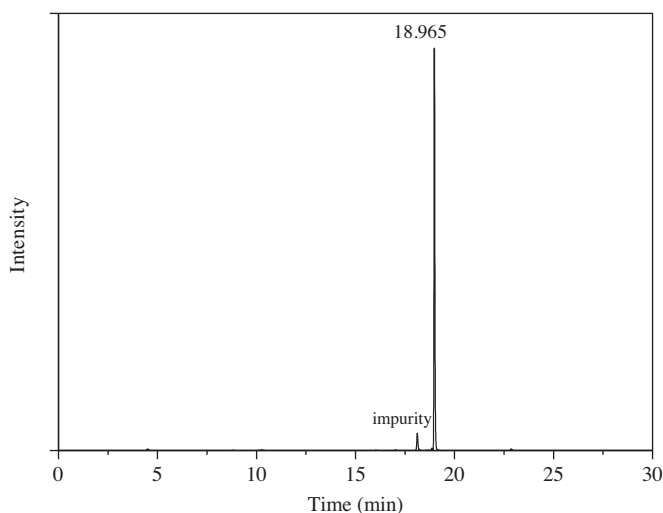
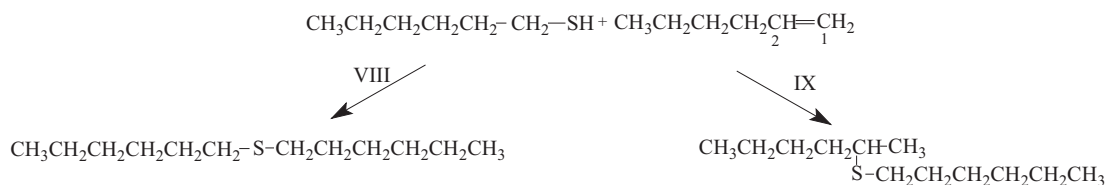


Fig. 4. The peak position confirmed by the standard di-butyl sulfide.

rupture reaction to form more and more new hexyl mercaptans when temperature increases. New hexyl mercaptans, including 1-hexylmercaptan and 2-hexylmercaptan, continue to react with

hexene to form di-hexyl sulfides via the pathways of butyl–hexyl sulfide. Similar to addition mechanism of 1-butanethiol and 1-hexene, the anti-Markovnikov adduct is obtained as major product. The reaction scheme can be displayed as follows:



These reaction mechanisms could elucidate the reason for the structures and distributions of the sulfur compounds in the

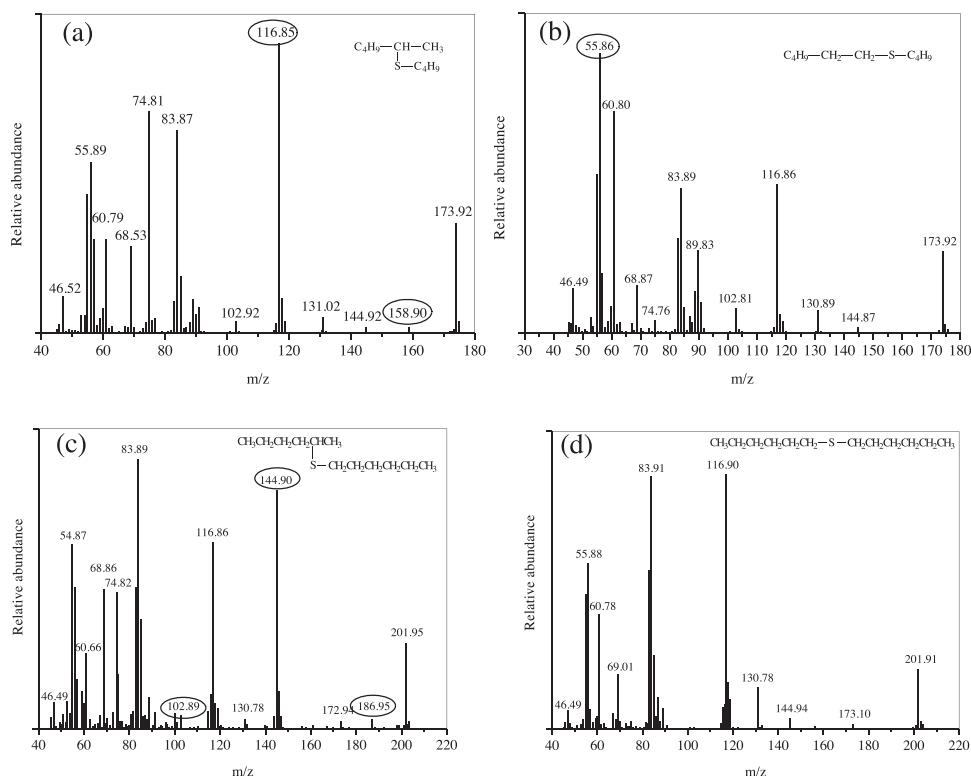


Fig. 5. MS spectra of 21.4 min (a), 22.5 min (b), 24.6 min (c) and 25.7 min (d) in the product.

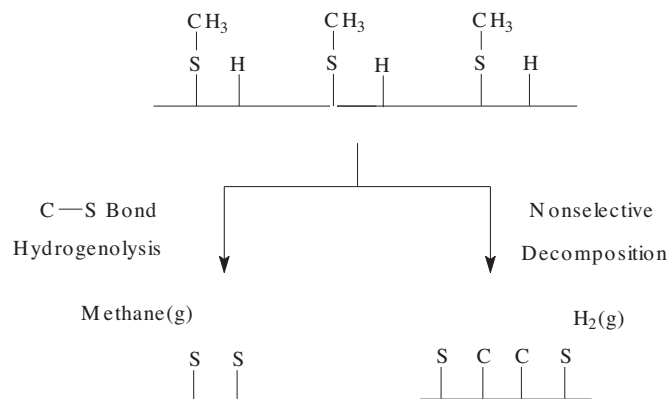


Fig. 6. Proposed reaction mechanism for methanethiol on Mo(1 1 0).

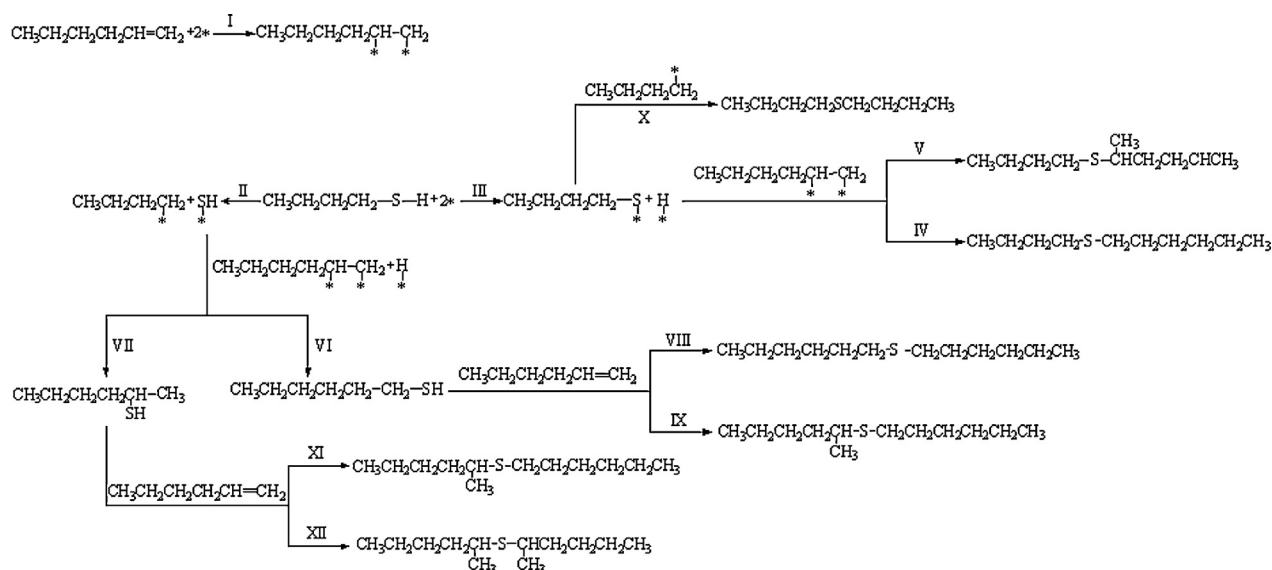
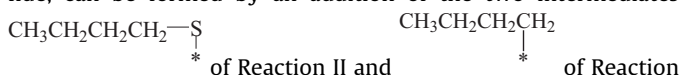


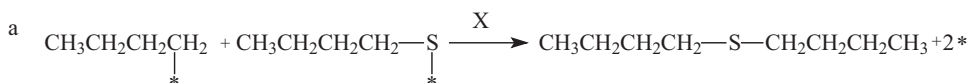
Fig. 7. Proposed reaction mechanisms of 1-butanethiol and 1-hexene.

products during the different reaction temperature, especially for the reaction behavior of mercaptans in the higher temperature.

At last, another sulfur compound in the product, di-butyl sulfide, can be formed by an addition of the two intermediates



according to:



From the above, the proposed reaction network for thioetherification of 1-butyl mercaptan and 1-hexene over the sulfided Mo-Ni catalysts can be described in Fig. 7. The network contains two pathways at different reaction temperatures: at low temperature, the major pathway involves a direct addition of 1-butanethiol to the terminal carbon of double bond of 1-hexene, which may be caused by steric effect. This process provides anti-Markovnikov adduct as a main product. As temperature increases, the C-S bond of 1-butanethiol is subsequently cleaved and the adsorbed SH species is formed on the catalysts. At the same time, there are abundant of adsorbed 1-hexene on the catalysts in the system. The adsorbed SH species can recombine with adsorbed 1-hexene to form hexyl

mercaptans. And then the new mercaptans continue to produce di-hexyl sulfides with adsorbed hexene. Similar to the production of butyl-hexyl sulfides, the straight-chain of di-hexyl sulfide is a major product.

4. Conclusions

The thioetherification of 1-butanethiol and 1-hexene in the blended oil was studied over sulfided Mo-Ni/Al₂O₃. The experimental results suggest that sulfided catalysts demonstrate good capability to catalyze thioetherification reaction. Meanwhile, the C=C bond of olefin can be isomerized from the terminal position to an internal position and can also be hydrogenated to alkane on the same active site of thioetherification reaction. This can inhibit thioetherification reaction and decrease the conversion of

mercaptans. As reaction temperature increases, the isomerization and hydrogenation reactions of olefins gradually increase but more inhibition on thioetherification also occurred.

There are two possible routes of thioetherification reaction which can be observed at different reaction temperatures. At low temperatures, the major pathway involves a direct addition of 1-butanethiol to the terminal carbon of double bond of 1-hexene, which may be caused by steric effect. This process leads to anti-Markovnikov adduct as a main product. As reaction temperature increases, the C–S bond of 1-butanethiol is subsequently cleaved, and then the adsorbed S species is formed on the catalysts. At the same time, there are abundant adsorbed 1-hexene on the catalysts in the system. The adsorbed S–H species can combine with other two molecules of 1-hexene to form new thioethers (di-hexyl sulfides). Meanwhile, a few of the hexyl-mercaptans are side products in the process. The di-hexyl sulfides are dominated products by the anti-Markovnikov adducts. The experimental results also identify that the high temperature pathways can promote thioetherification reaction and thus improve the conversion of thiols in the thioetherification.

Acknowledgement

Financial support by the National Natural Science Foundation of China (Granted No. 21276276) is gratefully acknowledged.

References

- [1] T. Posner, *Ber. Dtsch. Chem. Ges.* 38 (1905) 646.
- [2] T. Imai, J.C. Bricker, US Patent: 1988/4775462.
- [3] S.J. Frey, US Patent: 1998/5759386.
- [4] T. Skourlis, R.J. Gartside, R.E. Trubac, US Patent: 2010/20100059413.
- [5] C. Song, *Catal. Today* 86 (2003) 211.
- [6] A.R. Gardner, NPRA Annual Meeting, AM-01-39, 2001.
- [7] J.L. Nocca, Q. Debuisschert, NPRA Annual Meeting, AM-02-12, 2002.
- [8] C. Bouchy, F. Picard, N. Marchal, US Patent: 2010/7718053.
- [9] A.A. Oswald, K. Griesbaum, W.A. Thaler, B.E. Hudson Jr., *J. Am. Chem. Soc.* 84 (1962) 3897–3904.
- [10] T. Lanza, M. Minozzi, A. Monesi, D. Nanni, P. Spagnolo, C. Chiappe, *Curr. Org. Chem.* 13 (2009) 1726–1732.
- [11] C. Rissing, D.Y. Son, *Main Group Chem.* 8 (2009) 251–262.
- [12] B. Saville, *J. Chem. Soc.* (1962) 5040–5045.
- [13] M. Bellef, R. Zamboni, *J. Org. Chem.* 54 (1989) 1230–1232.
- [14] Z. Shen, M. Ke, P. Yu, S. Liu, Z. Song, Q. Jiang, *Transit. Met. Chem.* 37 (2012) 587–593.
- [15] Z. Shen, M. Ke, P. Yu, S. Liu, Z. Song, Q. Jiang, *Adv. Mater. Res.* 550 (2012) 347–353.
- [16] L. McLaughlin, E. Novakova, R. Burch, C. Hardacre, *Appl. Catal. A: Gen.* 340 (2008) 162–168.
- [17] R.L. Wilson, C. Kemball, *J. Catal.* 3 (1964) 426–437.
- [18] P. Kieran, C. Kemball, *J. Catal.* 4 (1965) 380–393.
- [19] T.S. Rufael, D.R. Huntley, D.R. Mullins, J.L. Gland, *J. Phys. Chem.* 99 (1995) 11472–11480.
- [20] T.S. Rufael, J. Prasad, D.A. Fischer, J.L. Gland, *Surf. Sci.* 278 (1992) 41–50.
- [21] B.C. Wiegand, P. Uvdal, C.M. Friend, *Surf. Sci.* 279 (1992) 105–112.
- [22] J.B. Benziger, R.E. Preston, *J. Phys. Chem.* 89 (1985) 5002–5010.
- [23] B.A. Sexton, G.L. Nyberg, *Surf. Sci.* 165 (1986) 251–267.
- [24] M.R. Albert, J.P. Lu, S.L. Bernasek, S.D. Cameron, J.L. Gland, *Surf. Sci.* 206 (1988) 348–364.
- [25] C.M. Friend, D.A. Chen, *Polyhedron* 16 (1997) 3165–3175.
- [26] X. Si, D. Xia, Y. Xiang, Y. Zhou, *J. Nat. Gas. Chem.* 19 (2010) 185–188.
- [27] Q. Deng, L. Liu, H. Deng, *Tutorial to Spectrum Analysis*, second ed., Science Press, Beijing, 2007, pp. 258.
- [28] T. Todorova, R. Prins, T. Weber, *J. Catal.* 246 (2007) 109–117.