PAPER

Synthesis of 2,5-dimethylhexene by isobutene dimerization with H₂S co-feeding†

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This study investigates the effect of hydrogen sulfide (H₂S) co-feeding on the synthesis of 2,5-dimethyl-1-hexene, 2,5-dimethyl-2-hexene, and 2,5-dimethylhexane (2,5-DMHs), useful compounds, using the dimerization of isobutene under mild pressure conditions. The dimerization of isobutene did not proceed in the absence of H₂S, whereas the desired products of 2,5-DMHs were produced under H₂S co-feeding conditions. The effect of reactor size on the dimerization reaction was then examined, and the optimal reactor was discussed. To enhance the yield of 2,5-DMHs, we changed the reaction conditions of the temperature, molar ratio of isobutene to H₂S (iso-$C_4^=$/H₂S) in the feed gas, and the total feed pressure. The optimum reaction condition was at 375 °C and 2/1 of iso-$C_4^=$/H₂S. The product of 2,5-DMHs monotonously increased by an increment of total pressure from 1.0 to 3.0 atm with a fixed iso-$C_4^=$/H₂S ratio at 2/1.

1. Introduction

Isobutene is an essential feedstock for methyl-*tert*-butyl ether (MTBE), ethyl-*tert*-butyl ether (ETBE), and isooctane in high-octane gasoline.[1–5] However, the requirement for MTBE and ETBE would be decreased year by year owing to the significant decrease in gasoline demand caused by the widespread use of hybrid and electric vehicles and the improvement in fuel efficiency of cars. Therefore, a novel approach to utilize the surplus isobutene is required.

The dimerization of isobutene to produce 2,5-dimethylhexene (2,5-DMH) is an attractive reaction because 2,5-DMH can be selectively converted into aromatics.[6–9] Several research studies on the dimerization of isobutene with 2,5-DMH have been reported. Behr *et al.* reported that a heterogeneous nickel complex catalyst promoted the dimerization of isobutene to produce linearly linked dimers of 2,5-DMH.[10] However, the performance of the nickel complex catalyst declined during the reaction. Therefore, improving the stability of the catalyst is an issue for the continuous production of 2,5-DMH. Taubert *et al.* developed a Bi₂O₃ catalyst for the oxidative dimerization of isobutene in the presence of oxygen.[11] The Bi₂O₃ catalyst provided a 13% yield of 2,5-DMH with 53% selectivity. Because the oxidation of isobutene produced carbon monoxide and carbon dioxide, the

catalyst demonstrated less selective performance by increasing the isobutene conversion.

The activation of the terminal carbon atom in isobutene is necessary to synthesize 2,5-DMH *via* the dimerization of isobutene. Generally, the terminal activation of isobutene is not expected in conventional carbocation reactions because of the high stability of tertiary cations.[2,11] In contrast, the radical reactions can activate the terminal carbon in isobutene because of the high chain reactivity between the radicals and the non-radical species.[12–14] Conventionally, azo compounds and organic peroxides such as azo-bis isobutyronitrile (AIBN)[15–17] and *tert*-butyl hydroperoxide,[18–20] are used as radical initiators. AIBN decomposes by thermal or photoenergy to produce cyanoisopropyl radicals, which undergo dimerization, disproportionation, and chain reactions to produce various products.[21–23] Hydrogen sulfide (H₂S) could also be a potential radical initiator for alkyl coupling. Vitzthum *et al.* determined that the pyrolysis rate of *n*-butylbenzene accelerated under high-pressure conditions during the pyrolysis of H₂S with *n*-butylbenzene.[24] The apparent activation energy of the pyrolysis of *n*-butylbenzene decreased from 66.6 kcal mol⁻¹ (pure *n*-butylbenzene) to 55.9 kcal mol⁻¹ (*n*-butylbenzene in a mixture with H₂S). Nguyen *et al.* reported on the pyrolysis properties of a mixture of *n*-octane and H₂S. Many types of thiols and heavy hydrocarbons were formed in the presence of H₂S, owing to the progress of the reaction between the hydrocarbon molecules and the radicals produced from H₂S.[25] Zeng *et al.* investigated the interaction of sulfanyl radicals (SH*) with aliphatic (C1–C4) hydrocarbons *via* calculations using CBS-QB3.[26] Regarding hydrogen extraction by SH* from the C–H bond in hydrocarbons, the hydrogen extraction from isobutene was remarkably spontaneous (300–

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1200 K, $\Delta_r G^\circ < -20$ kJ mol^{-1}) owing to weak allylic hydrogen bonds. This study implies that the formation of terminal isobutene radicals may occur in the presence of H$_2$S-derived SH*. Based on these results, we estimated that applying a radical reaction by the coexistence of H$_2$S under high-pressure conditions could promote the formation of terminal radicals derived from isobutene and contribute to the production of 2,5-DMH. In petrochemical industries, hydrodesulfurization is performed to remove sulfur species from sulfur-containing compounds. A large quantity of hydrogen sulfide (H$_2$S) gas is exhausted during this hydrodesulfurization process. The exhausted H$_2$S is generally removed using the well-known Claus process (2H$_2$S + O$_2$ → 2S + 2H$_2$O). However, global sulfur-supply could exceed demand by about several million tons, suggesting the need for a new application of H$_2$S.[27] If the expected reaction proceeds with the utilization of H$_2$S, it could lead to new ways of using H$_2$S.

Therefore, this study focused on the synthesis of 2,5-DMHs through the dimerization of isobutene *via* the activation of the terminal carbon of isobutene in the presence of H$_2$S. The product yield and selectivity were evaluated by changing the reaction conditions, such as temperature, feedstock ratio, and reaction pressure.

2. Experimental

2.1. Reaction apparatus and synthesis conditions

The dimerization of isobutene (iso-C$_4^=$) was performed using a batch-type reactor composed of a stainless-steel tube (SUS316) with a total volume of 145 mL. After inert gas has been supplied to the reactor for a sufficient time before dimerization of iso-C$_4^=$, reactants were fed at room temperature by the specified feed rate until completely filling the reactor by the reaction gas. After that, the needle valve on the reactor outlet side was closed and the reaction gas was continuously fed until the desired initial pressure was reached and followed by closing the valve on the inlet side. The batch reactor filled with the feed gas was then installed in an electric furnace and the temperature was increased to start the reaction. Specific reaction conditions were the following: the reaction temperature was from 350 to 450 °C; the molar ratio of iso-C$_4^=$ to H$_2$S (iso-C$_4^=$/H$_2$S) was from 1/5 to 5/1; and the total feed pressure was from 1.0 atm to 3.0 atm. The reaction was then performed for 3 h, 6 h and 12 h. The product gases were diluted with nitrogen and then placed in a polyvinyl fluoride gas bag to analyze the gas composition after the reaction. Subsequently, the diluted gas was collected using a microsyringe and injected into an offline flame ionization detection (FID) gas chromatograph (GC-2014, Shimadzu Corporation, Japan). The iso-C$_4^=$ conversion and yield of the product (YP) were calculated using the following equations:

$$\text{Conversion} = \frac{n_i - n_f}{n_i} \times 100 \tag{1}$$

$$\text{Yield} = \frac{N \times n_a}{4 \times n_i} \times 100 \tag{2}$$

where, n_i (mol) represents the material amount in the filled iso-C$_4^=$, n_f (mol) represents the material amount in the iso-C$_4^=$ remaining after the experiment, n_a (mol) represents the amount of product A with carbon number N.

3. Results and discussion

3.1. Effect of co-feeding of sulfur compound on isobutene dimerization

Fig. 1(a) and (b) show the yields and selectivity of product obtained in the dimerization of isobutene (iso-C$_4^=$) with and without H$_2$S co-feeding. The reaction was performed at a temperature of 400 °C and iso-C$_4^=$/H$_2$S = 1/1, with an initial total pressure of 2.5 atm. Under dimerization conditions without H$_2$S co-feeding, 1,1,3-trimethylcyclopentane (1,1,3-TMCP), 2,2,4-trimethylpentane, and 2,4,4-trimethyl-1-pentene were produced. In contrast, the desired products of 2,5-dimethyl hexane, 2,5-dimethyl-2-hexene, and 2,5-dimethyl-1-hexene, denoted as 2,5-DMHs, were obtained with 4.1% yield and 27.8% selectivity in the dimerization with H$_2$S; isobutane, isobutyl mercaptan (iso-C$_4$SH) *tert*-butyl mercaptan were generated as byproducts. Nguyen *et al.* performed out the pyrolysis of *n*-octane/H$_2$S mixtures and proposed free-radical reaction schemes, which were initiated by the decomposition of H$_2$S into H* and SH* radicals.[25] In the present study, the formed radical species H* and SH* could activate the terminal carbon of isobutene to promote dimerization, as expected. Because 1,1,3-TMCP was produced even in the absence of H$_2$S, we followed the 1,1,3-TMCP formation pathway reported by
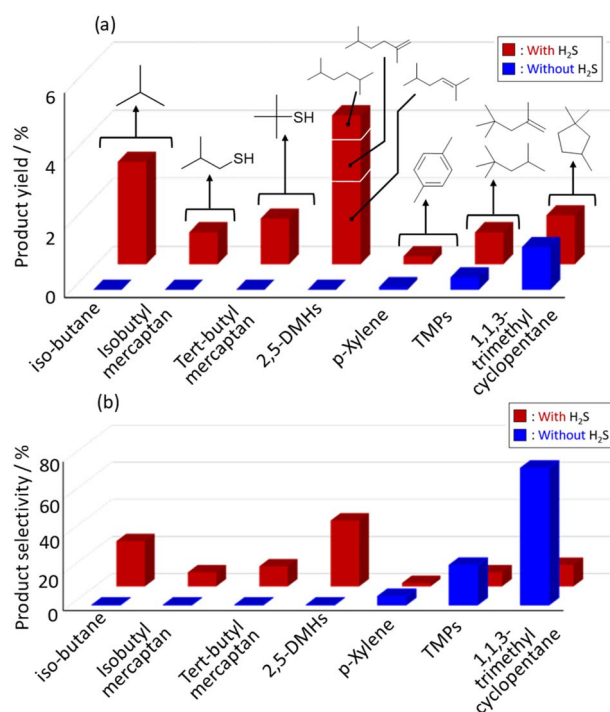

Fig. 1 (a) Yield and (b) selectivity of products in isobutene dimerization with/without H$_2$S (iso-C$_4^=$/H$_2$S = 1/1, iso-C$_4^=$/N$_2$ = 1/1) at 400 °C and 2.5 atm.

McKinley,[28] wherein iso-$C_4^=$ was dimerized to 1,1,3,3-tetramethylcyclobutane, which was further isomerized to 1,1,3-TMCP under mild temperatures.

Fig. 2 shows the effect of reactor size (reactor #1, reactor #2) on the yield of the products in isobutene dimerization with H_2S. Two types of reactors were used to study the dimerization of iso-$C_4^=$: reactor #1 has the high-volume and low-surface area (the ratio of surface area to volume of the reactor: 1.8), and reactor #2 has the low-volume and high-surface area (the ratio of surface area to volume of the reactor: 3.7); reactor #2 has approximately twice ratio of surface area/volume in reactor #1. As can be seen in Fig. 2, there is little difference in the 2,5-DMHs of the target product, and the major difference is the amount of isobutane produced. The isobutane is the result of hydrogenation of the raw material iso-$C_4^=$. The reactor contains iron component, which progress the following reaction of eqn (3).

$$Fe + H_2S \rightarrow FeS + H_2 \tag{3}$$
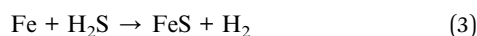
ESI data 1† shows XRD pattern of the iron component peeled off from the inner wall of the reactor after dimerization with H_2S. The component of FeS_x was found to be confirmed. Therefore, the reactor with high surface area/volume might produce high concentration of H_2. It was inferred that the isobutane formation was promoted by the increase in H_2 concentration *via* hydrogenation of iso-$C_4^=$. The result indicated the optimal reactors with small surface area per volume could reduce the formation of by-product such as isobutane.

The low bond dissociation energy of the R–SH bond of a thiol could allow the formation of radical species, such as alkyl radicals R and SH radicals,[29] which could activate iso-$C_4^=$ to produce 2,5-DMHs. Iso-$C_4^=$ was dimerized with iso-C_4SH to identify the effect of thiols on the production of 2,5-DMHs.
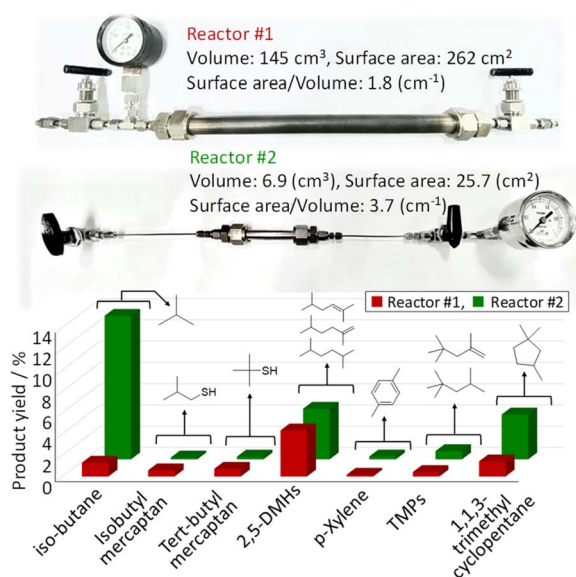

Fig. 2 Effect of reactor size (reactor #1, reactor #2) on the yield of the products in isobutene dimerization with H_2S (iso-$C_4^=$/H_2S = 1/1) at 400 °C and 2.5 atm.
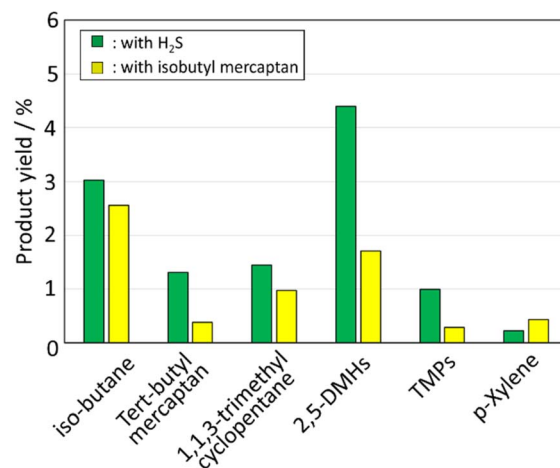

Fig. 3 Product yield in dimerization of isobutene at 400 °C under the condition of 1/1 of iso-$C_4^=$ (or iso-C_4SH)/H_2S and 2.5 atm.

Fig. 3 illustrates the yield of the product obtained from the reaction of iso-$C_4^=$ with the co-feeding of iso-C_4SH. The products are similar to those formed by the dimerization of iso-$C_4^=$ with H_2S. 2,5-DMHs were also produced, even in the presence of thiols, although the yield of 2,5-DMHs was lower than that in the presence of H_2S. These results indicate that the SH radical species generated from iso-C_4SH may activate the terminal carbon of iso-$C_4^=$, followed by the production of 2,5-DMHs. The energies of the C–S bonds in alkyl thiols probably be higher compared to those of the S–H bonds in H_2S. Thus, the generation of SH radicals by alkyl thiols was expected to lead to a slow dimerization process. Conversely, the dimerization activity is higher in dimerization with the co-feeding of H_2S, as shown in Fig. 3. Hydrogen sulfide is known to generate SH* radicals through decomposition of a single molecule and SH radicals through that of two molecules by reverse radical disproportionation ($H_2S + H_2S \rightarrow H_3S^* + SH^*$).[25,30,31] It was speculated that the yield of 2,5-DMHs was higher in the dimerization with H_2S because of the more efficient generation of radical species from H_2S *via* a direct decomposition of H_2S and/or a reverse radical disproportionation than that from iso-C_4SH.

3.2. Effect of reaction condition on isobutene dimerization

The reaction conditions were optimized to enhance the yield of 2,5-DMHs. Table 1 shows the effect of the iso-$C_4^=$/H_2S ratios and reaction temperature on the isobutene dimerization. Based on Table 1, the maximum yield of 2,5-DMHs was *ca.* 4.6%, obtained at 375 °C and iso-$C_4^=$/H_2S = 2/1. The higher and lower reaction temperatures decreased the yield of 2,5-DMHs. The yield of 2,5-DMHs was 0.7% at a high temperature of 450 °C with iso-$C_4^=$/H_2S = 2/1; the product yield decreased, except isobutane and 1,1,3-TMCP, as shown in ESI data 2.† In addition, a liquid component was observed in the reactor after the reaction, which significantly decreased the carbon balance to *approximately* 50%. GC-MS spectrum of liquid product was shown in ESI data 3.† The compound from C5 and C7 compound was mostly included in the liquid product, which

Table 1 Effect of reaction conditions of iso-C$_4$$^=$/H$_2$S ratio and reaction temperature on (a) the yield and (b) selectivity of the products in isobutene dimerization

(a)	Reaction temperature/°C				
i-C$_4$$^=$/H$_2$S ratio	350	375	400	425	450
5/1	0.95%	4.00%	3.28%	2.11%	1.0%
2/1	1.83%	4.58%	3.32%	2.40%	0.67%
1/1	1.52%	3.29%	4.05%	1.26%	1.16%
1/2	1.83%	0.95%	0.88%	0.51%	0.20%
1/5	0.33%	0.31%	0%	0%	0%

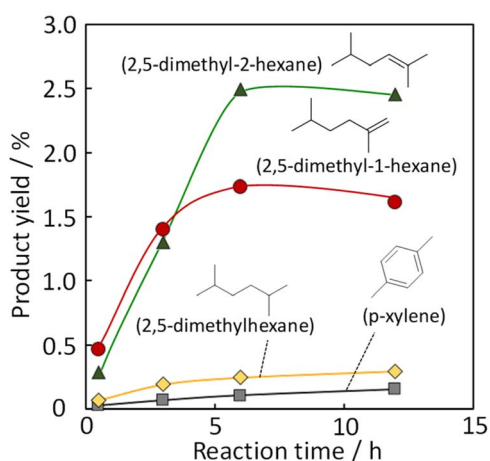| (b)	Reaction temperature/°C				
i-C$_4$$^=$/H$_2$S ratio	350	375	400	425	450
5/1	20.6%	43.6%	26.7%	12.6%	6.0%
2/1	24.3%	49.0%	16.7%	11.8%	2.7%
1/1	17.7%	31.5%	27.8%	3.3%	3.5%
1/2	32.0%	3.9%	3.7%	1.1%	0.4%
1/5	5.1%	1.3%	0%	0%	0%

Fig. 4 Product (2,5-dimethyl-2-hexene, 2,5-dimethyl-1-hexene, 2,5-dimethylhexane, p-xylene) yield with reaction time at 375 °C, 2.5 atm and iso-C$_4$$^=$/H$_2$S of 2/1.
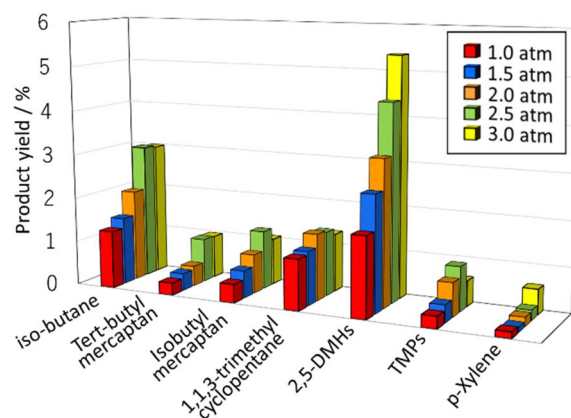

Fig. 5 Effect of the total pressure (1.0–3.0 atm) of feed gas on the product yield under iso-C$_4$$^=$/H$_2$S of 2/1, and 375 °C.

maximum yield, the yield of 2,5-DMHs decreased by an excess feed of iso-C$_4$$^=$. Hence, the feed ratio of iso-C$_4$$^=$/H$_2$S = 2/1 at 375 °C was determined to be the optimum reaction condition. Increasing the feed pressure might produce radical species of SH* by accelerating the reverse radical disproportionation.

To enhance the yield of desired product (2,5-dimethyl hexane, 2,5-dimethyl-2-hexene, 2,5-dimethyl-1-hexene, and p-xylene), we investigated the effect of reaction time and pressure on the isobutene dimerization. Fig. 4 shows the yield of 2,5-DMHs and p-xylene with reaction time. It could be seen that the yield of the desired product increased with reaction time and reached a steady state at 6 hours of reaction. Fig. 5 illustrates the effect of the initial total feed pressure on the dimerization reaction. The reaction condition was as follows: iso-C$_4$$^=$/H$_2$S was 2/1, the reaction temperature was 375 °C, and the total pressure was from 1.0 atm to 3.0 atm. An increase in the initial total pressure produces higher yield of 2.5-DMHs. No evident relationship between the initial total pressure and product yield was observed for other products. The number of SH* radical species increased when the initial pressure was increased, forming terminal isobutene radicals, which contributed to the increase in 2,5-DMHs. It is not possible to determine whether H$_2$S has catalytic function, based on the obtained results in this study. In future studies, it needs to be clarified whether H$_2$S acts as a reactant or as a molecular catalyst.

4. Conclusions

Isobutene dimerization was tested in a batch-type reactor under high-pressure conditions in the presence of H$_2$S. Dimerization in the absence of H$_2$S did not yield 2,5-DMHs, however, 2,5-DMHs were obtained in the presence of H$_2$S. Then, the dimerization reaction in the presence of H$_2$S was conducted in two reactors with different surface area to volume ratios (surface area/volume). The desired products of 2,5-DMHs were obtained with higher selectivity in the reactor with the smaller surface area/volume. This probably be because the H$_2$ produced by the reaction of H$_2$S with the Fe component in the tube wall largely reacts with isobutene to form the byproduct isobutane. By using

was considered to reduce the carbon balance. As for the lower reaction temperature of 350 °C, the product yield decreased under the condition of iso-C$_4$$^=$/H$_2$S = 2/1; the yield of 2,5-DMHs was 1.8%, as shown in ESI data 4.† Therefore, a moderate temperature of approximately 375 °C was considered optimum for the production of 2.5-DMHs. When the molar ratio of iso-C$_4$$^=$/H$_2$S was changed, the 2,5-DMH yield depended on the reaction conditions. Under the condition of iso-C$_4$$^=$/H$_2$S = 1/5 at 375 °C, the yield of 2,5-DMHs was 0.3%, as shown in ESI data 5.† The generation of the low yield of 2,5-DMHs is attributed to the progress in the hydrogenation of iso-C$_4$$^=$ to afford isobutane. Excess H$_2$S was used as the H$_2$ source. Such progress of side reaction reduce the effective utilization of iso-C$_4$$^=$ for dimerization. Furthermore, the 2,5-DMHs yield increased when iso-C$_4$$^=$/H$_2$S was increased at 375 °C. After reaching the

the reactor with low surface area/volume, we investigated the effect of reaction conditions (iso-$C_4^=$/H_2S ratio, temperature, pressure). We found that the yield of 2,5-DMHs was affected by changing the reaction conditions; in particular, the yield of 2,5-DMHs was improved by increasing the pressure. Whether H_2S has a catalytic function or not cannot be determined from the results in this study, though, the decomposition of H_2S might be accelerated at higher pressures, and generated SH radicals would activate terminal carbon of iso-$C_4^=$ to promote dimerization.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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