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Vapour-phase synthesis of n-butanethiol from n-butanol and carbon disulfide over alkali-promoted chromia on γ-alumina catalysts

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The vapour-phase reaction of n-butanol and carbon disulfide was performed in a fixed-bed flow reactor in the presence of a potassium-carbonate-promoted chromia on γ-alumina catalyst, namely G41P from Girdler. A high selectivity to n-butanethiol (85%) was obtained at 250 °C with a 1 : 1 n-butanol : carbon disulfide molar ratio, a contact time of 6 s and a flow rate of 0.03 ml/min. Under these conditions no isomeric mercaptans were obtained. The amount of secondary products, di-n-butyl sulfide and di-n-butyl disulfide, is relatively low and decreases with decrease of n-butanol conversion. However, the catalyst was shown to deactivate relatively rapidly.

Keywords: n-butanethiol, n-butanol, carbon disulfide, chromia on alumina catalysts, thiolation

1. Introduction

Various heterogeneous catalytic methods of synthesizing mercaptans from alcohols or olefins and H_2S are known [1]. Primary mercaptans are generally obtained in good yields through nucleophilic substitution of the corresponding primary alcohols by H_2S on alkali-promoted alumina catalysts [2–6], whereas they are obtained in low yields in the presence of acid catalysts which mainly tend to dehydrate the starting alcohol. By contrast, according to the Markovnikov rule, secondary mercaptans are obtained from olefins on acid catalysts.

When carbon disulfide is used as the thiolating agent, very low yields in n-butanethiol were obtained from n-butanol on an alkali-promoted chromia on γ-alumina catalyst. Indeed, the major product of the reaction of n-butanol and carbon disulfide at 500 °C is thiophene [7,8]. However, during the course of our work on thiolation of crotonaldehyde by carbon disulfide on alkali-promoted chromia on alumina catalysts [9], we have found that n-butanol could also react with carbon disulfide over that kind of catalysts to yield n-butanethiol as the main product at a temperature between 200 and 300 °C. Although small amounts of diethylthiophenes, olefins and sulfides are formed, n-butanethiol is the only thiol obtained from this reaction, which is important with respect to the purification of the products.

2. Experimental

All starting materials were reagent grade. n-butanol and carbon disulfide (Aldrich) were used without further purification.

The catalyst used (Girdler G41P from Süd Chemie) was crushed to particle size 0.063–0.125 mm, which ensured working in the kinetic region, and calcined in air at 450 °C for 3 h.

All the experiments and analyses were carried out as previously described [9], using a fixed-bed reactor working at atmospheric pressure. The reaction was conducted at temperatures from 200 to 300 °C, by using a 2 g portion of catalyst. The reaction mixture was n-butanol/carbon disulfide (1/1 molar ratio) with a flow rate close to 0.03 ml/min.

3. Results and discussion

The vapour-phase reaction of n-butanol and carbon disulfide was performed at temperatures between 200 and 300 °C over the potassium-carbonate-promoted chromia on γ-alumina G41P from Girdler catalyst. The major product from this transformation was n-butanethiol, although 2,5-diethylthiophene, di-n-butyl sulfide, di-n-butyl disulfide, 1,3-butadiene, 2-methyl-2-heptene and 2-ethyl-2-hexene were obtained as by-products. The last two are products resulting from the reaction of dehydration, followed by dimerization of butenes formed. 1,3-butadiene is formed by dehydrogenation of butenes.

The relationship between products selectivity and time on stream is presented in figure 1. As shown in this figure, a selectivity to n-butanethiol of 85% is achieved. No secondary or other isomeric mercaptans were detected. The catalyst is very active during the first 2 h of the reaction and tends to deactivate after that period. The reaction was studied in the temperature range of 200–300 °C, but the highest selectivity to n-butanethiol was obtained at 250 °C. Both lower and higher temperatures tend to reduce both selectivity and yield in primary butanethiol.

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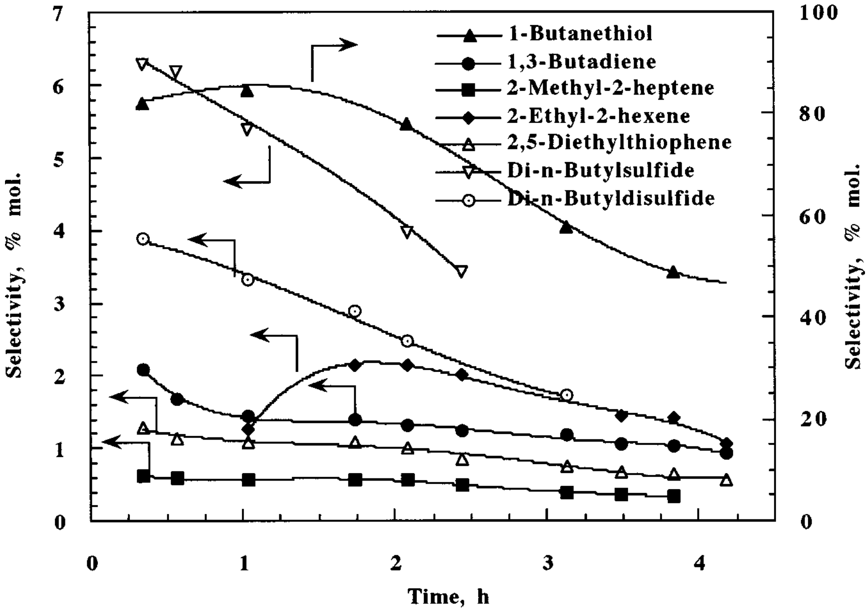


Figure 1. Products distribution resulting from the reaction of n-butanol and carbon disulfide at a temperature of 250 °C and a contact time of 6 s (n-butanol/carbon disulfide = 1/1).

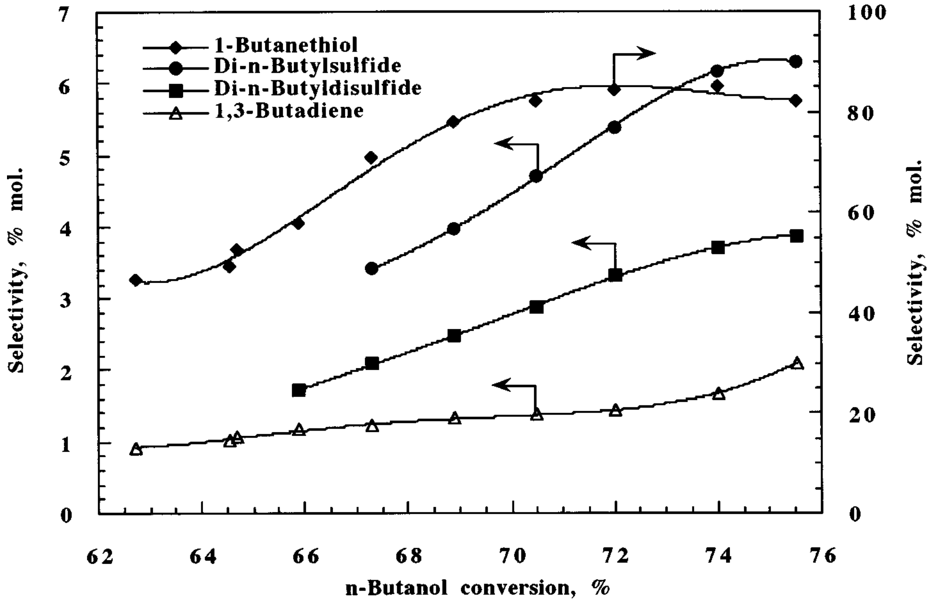


Figure 2. Selectivity to major by-products against n-butanol conversion at about 1 h on stream.

Under the operating conditions used, it was difficult to obtain a n-butanol conversion lower than 60%, even at short contact times. As it can be seen from figure 2, both increase and decrease of the conversion of n-butanol lead to a decrease in the selectivity to n-butanethiol at about 1 h on stream. However, the formation of the by-products becomes more important at higher alcohol conversion.

The formation of di-n-butyl sulfide and di-n-butyl disulfide is relatively small at low n-butanol conversion, but it also depends on the selectivity to n-butanethiol, as illustrated in figure 3. Thus, for example, the selectivity to di-n-butyl sulfide increases by a factor of 2, when the selectivity to n-butyl mercaptan goes from 70 to 85%.

It is also clear from figure 2 that all detected compounds, including n-butanethiol, appear as secondary products. According to the mechanism already proposed for the reaction of crotonaldehyde with carbon disulfide over the same catalyst and involving thiocarbonate species as primary intermediates [9], a reaction mechanism also involving thiocarbonate species can be proposed for the thiolation of n-butanol with carbon disulfide, as shown in scheme 1.

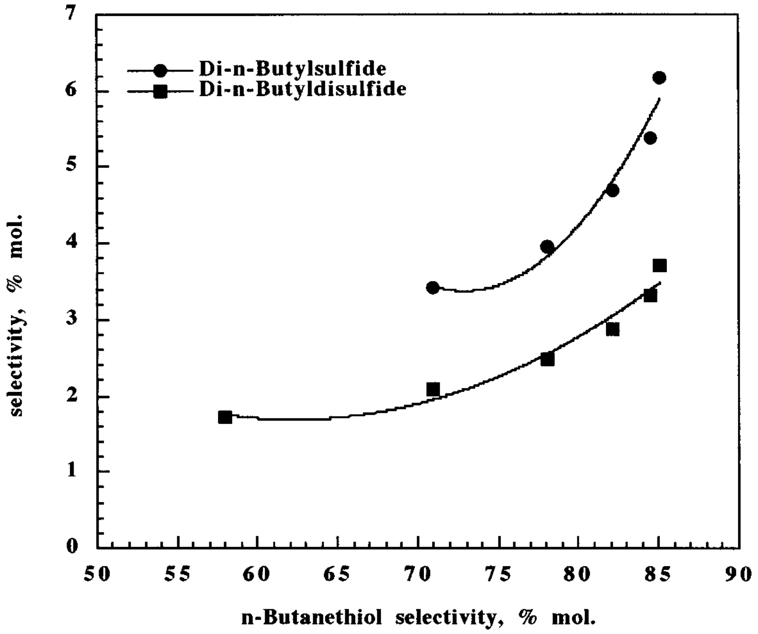
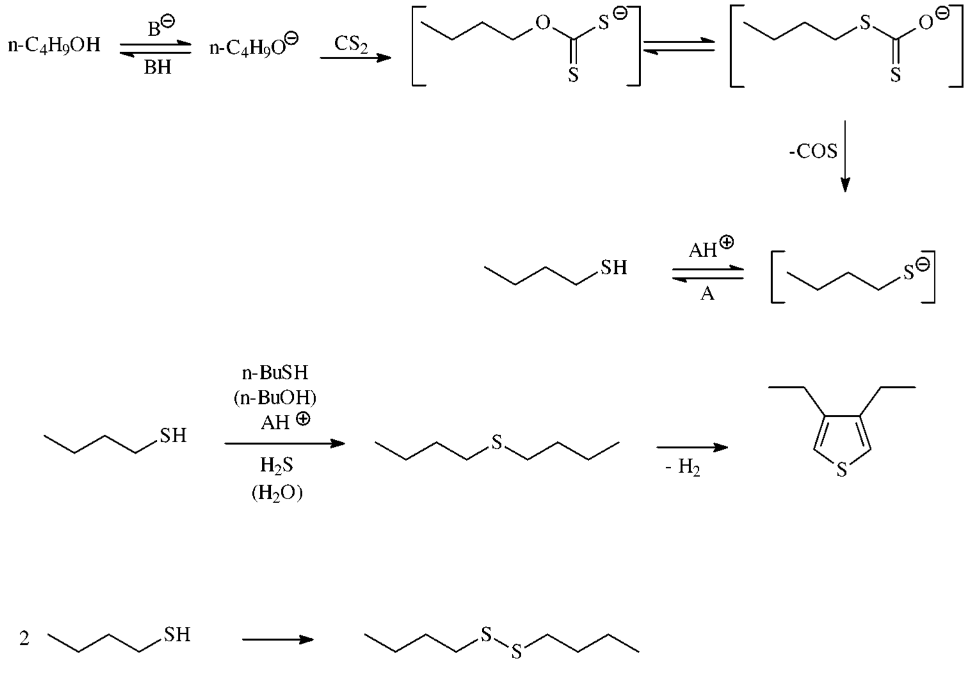


Figure 3. Selectivity to di-n-butyl sulfide and di-n-butyl disulfide against n-butanethiol selectivity.



Scheme 1. Reaction scheme proposed for the vapour-phase synthesis of n-butanethiol from n-butanol and carbon disulfide over promoted chromia on alumina catalysts.

4. Conclusion

From the results reported in this work, it appears that direct thiolation of n-butanol can work under relatively mild operating conditions using carbon disulfide as the thiolating agent. The optimization of the operating conditions, namely by using the G41P catalyst (2.1 g), a carbon disulfide/n-butanol molar ratio of 1/1, a contact time of 6 s and a temperature of 250 °C, leads to a selectivity to thiophene of around 85% with a mass balance of 90%, but with a relatively fast deactivation of the catalyst.

Acknowledgement

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