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Transformation of cyclopentanone into cyclopentanethiol over a sulfided CoMo / Al_2O_3 catalyst

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The transformation of cyclopentanone in the presence of H_2S/H_2 was investigated at atmospheric pressure over a sulfided CoMo/Al_2O_3 catalyst. The main reaction products were cyclopentanethiol and cyclopentene, the relative amounts of which depended on the reaction temperature and on the H_2S to cyclopentanone molar ratio. The best results were obtained at 220°C, with a 2.5 H_2S to cyclopentanone molar ratio: under these conditions, the cyclopentanethiol molar selectivity remained at about 90%, in a range of cyclopentanone conversion of 10–70%.

Keywords: cyclopentanone; cyclopentanethiol; sulfide catalysts; CoMo/Al_2O_3

1. Introduction

Various methods have been used to synthesize thiols [1–6], each method having specific advantages concerning activity, selectivity [2,3], or separation of the products [4,5]. For example, the reaction of H_2S with primary alcohols can produce selectively, primary thiols, but secondary thiols cannot be obtained from secondary alcohols owing to the dehydration of the latter [3]. However, Lucien et al. [1,7] found that both primary and secondary thiols could be obtained selectively from aldehydes and ketones over a K_2O/Al_2O_3 catalyst using both H_2S and a thiol as reducing agent. A two-step reaction scheme was proposed [7]. This scheme involved first the transformation of the carbonyl compound by H_2S into a thiocarbonyl compound which was then reduced through hydrogen transfer from the added thiol.

Sulfided CoMo/Al_2O_3 catalysts have been widely used for the hydrodesulfurization of petroleum fractions [8]. It is now well established that SH groups exist after sulfidation on the surface of Mo [9,10] or CoMo/Al_2O_3 catalysts [10]. These SH groups not only play a role in the catalytic activity for reactions involving Brønsted acidity [9,10], but can also be a source of hydrogen during catalytic reactions [10,11] or act as nucleophiles for displacement reactions [12–14]. This led us to study the possibility of using sulfided CoMo/Al_2O_3 catalysts for the thiolation of carbonyl compounds. Indeed, one could imagine that the carbonyl compounds would be first transformed into thiocarbonyl compounds by H_2S, these compounds being in turn hydrogenated into thiols by hydrogen.

2. Experimental

All the experiments were carried out in a fixed bed microreactor at atmospheric pressure. Cyclopentanone dissolved in *n*-heptane was injected by means of a plunger pump, the carrier gas being a 10 vol% H_2S/H_2 mixture. The different partial pressures (in bar) were: $H_2 = 0.79$, $H_2S = 0.088$, cyclopentanone $= 0.035$ and *n*-heptane $= 0.085$. Further experiments were also carried out, using cyclopentanol or cyclohexanethiol as reactants. The catalyst used was a commercial CoMo/Al_2O_3, containing 3.4 wt% CoO and 13.4 wt% MoO_3. It was presulfided in situ by H_2/H_2S (10%) at 350°C for 12 h before reaction.

The reaction products were analyzed by gas chromatography (Varian 3700) using a 25 m CPSil-5 capillary column (Chrompack), with a 50 to 170°C (15°C/min) temperature programme. All the reaction products were identified by GC-MS (Finnigan Incos500).

H_2/H_2S (10%) was obtained from Air Liquide. All the reactants were purchased from Fluka.

3. Results

The main product of transformation of cyclopentanone over sulfided CoMo/Al_2O_3 was cyclopentanethiol (C_5H_9SH). The other products were cyclopentene (C_5H_8), cyclopentanol (C_5H_9OH), and condensation products such as 1-cyclopentylcyclopentanone, 1-cyclopentenylcyclopentanone, and 1-cyclopentenylcyclopentanethiol.

3.1. *Effect of reaction time*

The experiment was carried out at 220°C with a

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2.5 H_2S/cyclopentanone molar ratio. Fig. 1a shows that the catalyst was very active at the beginning of the reaction (100% conversion of cyclopentanone), but its activity decreased rapidly before reaching a stable level after about 8 h reaction. On the other hand, fig. 1b shows that the product distribution only changed slightly with time-on-stream, probably because of the decrease in conversion. However, cyclopentanethiol remained the main product with 90% selectivity at steady state of activity.

3.2. Effect of the H_2S to cyclopentanone ratio

The effect of the H_2S/cyclopentanone molar ratio was measured at 220°C on the stabilized catalyst. The flow of cyclopentanone was maintained constant, whereas the flow of H_2/H_2S changed. The conversion of cyclopentanone was not very sensitive to the H_2S/cyclopentanone ratio (fig. 2a), but the product distribution changed (fig. 2b): for low H_2S/cyclopentanone ratios, significant amounts of cyclopentene and of condensation products were formed. A H_2S/cyclopentanone molar ratio $\geqslant 2.5$ was needed to obtain a good selectivity in cyclopentanethiol.

3.3. Effect of the reaction temperature

This study was carried out using a 2.5 H_2S/cyclopentanone molar ratio. The conversion of cyclopentanone after stabilization of the catalyst increased rapidly when the reaction temperature rose from 200 to 280°C (fig. 3a). At the same time, the proportion of cyclopentanethiol decreased while that of cyclopentene increased rapidly (fig. 3b). When the reaction temperature was over 270°C, cyclopentene became the major product.

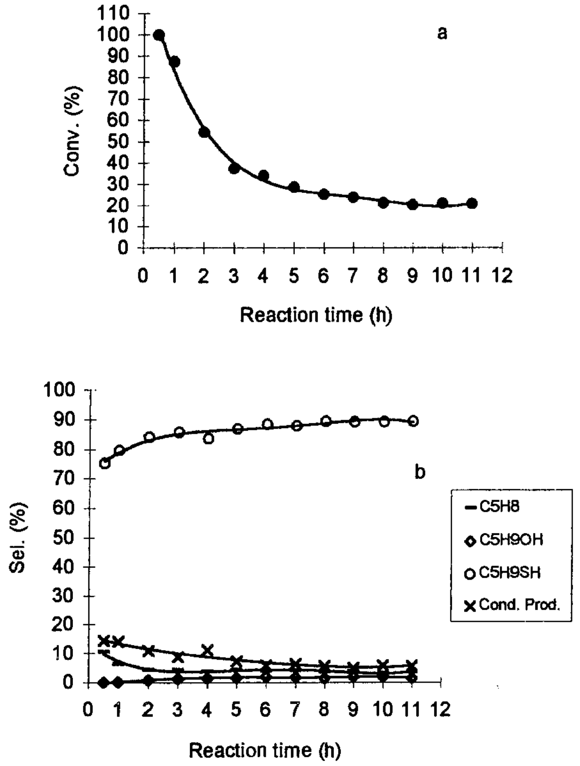


Fig. 1. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3 at 220°C: effect of the reaction time on the conversion (a) and on the molar product selectivities (b). H_2S/cyclopentane = 2.5.

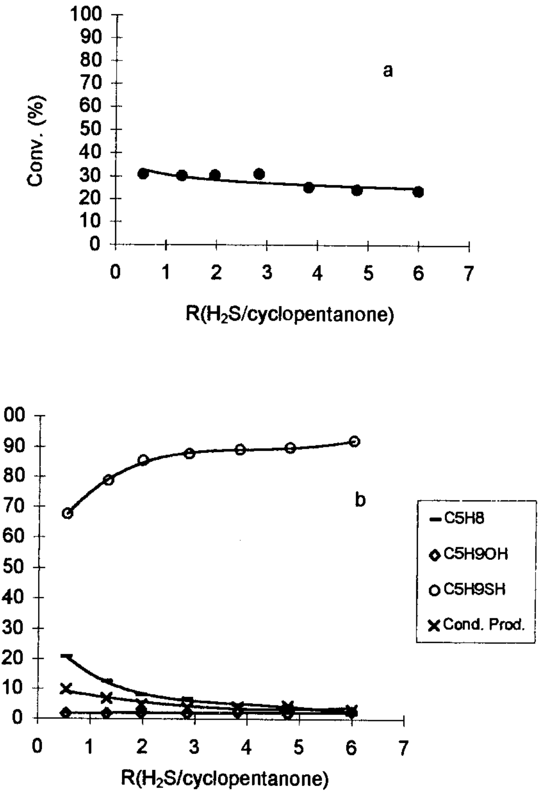


Fig. 2. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3 at 220°C: effect of the H_2S/cyclopentanone molar ratio on the conversion (a) and on the molar product distribution (b).

3.4. Effect of contact time

The effect of contact time (with a 2.5 H_2S/cyclopentanone molar ratio) was studied at 220°C, on a stabilized catalyst. Fig. 4 shows that the conversion of cyclopentanone increased gradually when contact time increased. On the other hand, fig. 5a shows that cyclopentanethiol seemed to be a primary reaction product and remained the main product whatever the conversion of cyclopentanone: it represented about 90% of the product mixture even at a conversion as high as 70% (fig. 6). Fig. 5b shows that condensation products were also primary products, but their amount decreased for a cyclopentanone conversion above 40%. Cyclopentene was most likely a secondary reaction product, whose formation increased when the conversion of cyclopentanone increased. Only traces of cyclopentanol could be observed.

3.5. Conversion of cyclopentanol and of cyclohexanethiol

In order to obtain further information concerning the

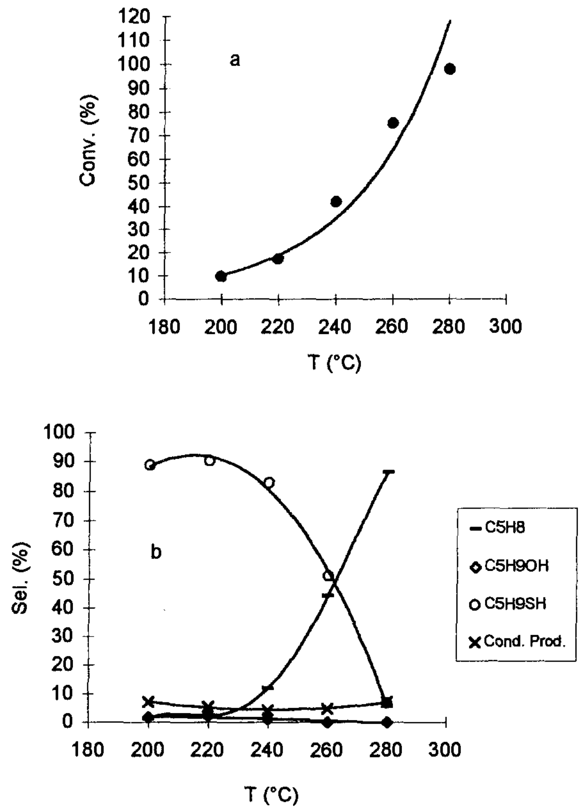


Fig. 3. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3: effect of the reaction temperature on the conversion (a) and on the molar product distribution (b). H_2S/cyclopentanone = 2.5.

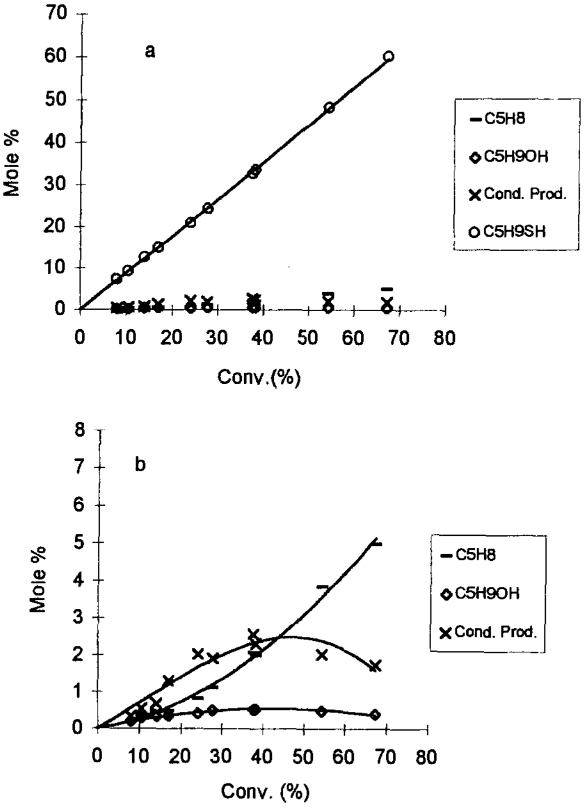


Fig. 5. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3: formation of the various reaction products (a) as a function of the conversion of cyclopentanone (220°C, H_2S/cyclopentanone = 2.5). Minor products (b).

reaction scheme, the transformation of cyclopentanol and of cyclohexanethiol (cyclopentanethiol was not available commercially) was studied under standard conditions (220°C, H_2S/reactant = 2.5).

Table 1 shows that cyclopentanol was entirely transformed, and yielded 91% cyclopentene (experiment No. 1), whereas only 70% cyclohexanethiol was transformed, into cyclohexene (experiment No. 2). The reactivities of both molecules were measured with greater accuracy using short contact times. The results obtained (experiments Nos. 3 and 4) indicate that cyclopentanol was ten times more reactive for dehydration than cyclohexanethiol for dehydrosulfidation.

4. Discussion

The sulfided CoMo/alumina catalyst is initially very

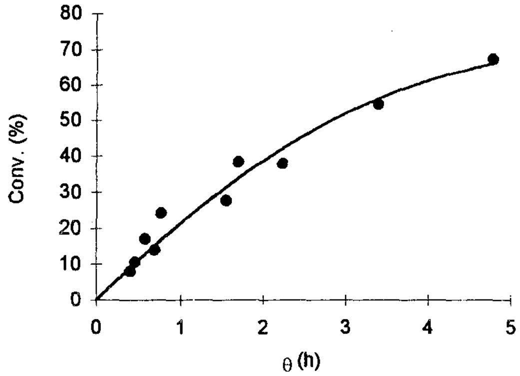


Fig. 4. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3: effect of contact time θ on the conversion (220°C, H_2S/cyclopentanone = 2.5).

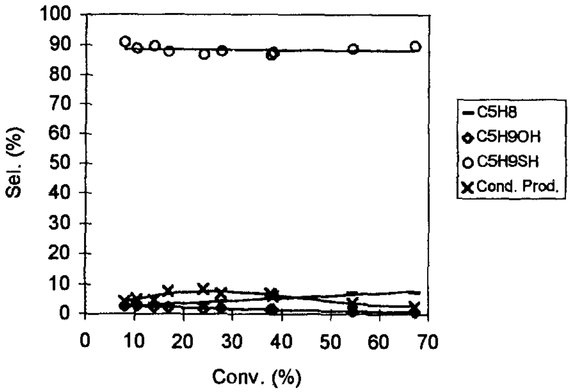


Fig. 6. Transformation of cyclopentanone over sulfided CoMo/Al_2O_3 (220°C, H_2S/cyclopentanone = 2.5). Product distribution as a function of cyclopentanone conversion.

Table 1
Transformation of cyclopentanol and cyclohexanethiol over sulfided CoMo/Al_2O_3 at 220°C. Effect of the contact time (θ). $P_{\text{cyclopentanone}}$ or $P_{\text{cyclohexanethiol}} = 0.035$ bar, $P_{H_2S} = 0.088$ bar, $P_{H_2} = 0.79$ bar, $P_{n\text{-heptane}} = 0.085$ bar

Exp. No.	Reactant	θ (h)	Product distribution (mol%)	Reactivity (mmol/(h g_{cat}))
1	cyclopentanol	0.77	cyclopentanol = 0 cyclopentene = 91.3 cyclopentanethiol = 8.7	?
2	cyclohexanethiol	0.52	cyclohexanethiol = 68.9 cyclohexene = 31.1	4.7
3	cyclopentanol	0.19	cyclopentanol = 17.3 cyclopentene = 73.4 cycopentanone = 1.6 cyclopentanethiol = 7.7	50
4	cyclohexanethiol	0.14	cyclohexanethiol = 92.6 cyclohexene = 7.4	4.6

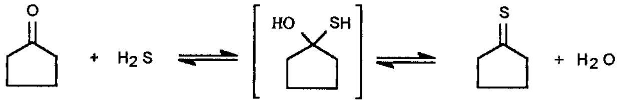
active for the conversion of cyclopentanol in the presence of H_2S at temperatures as low as 220°C, and yields mainly cyclopentanethiol. However, the activity of the catalyst decreases substantially during the first hours of reaction, but the selectivity for cyclopentanethiol formation is not affected: on the contrary, it increases (fig. 1b), owing to a decrease in conversion which limits the formation of cyclopentene and to a decrease in the quantity of condensation products. On a stabilized catalyst, a high selectivity in cyclopentanethiol can be obtained, even at a conversion as high as 70%, by increasing contact time. At high conversion levels, the main difference between the fresh catalyst and the stabilized catalysts lies in the quantity of condensation products formed (cf. figs. 1b and 5). The best selectivity for cyclopentanethiol formation is obtained at 200–220°C, with a H_2S/cyclopentanone ratio $\geqslant 2.5$.

On the other hand, fig. 5 shows that cyclopentanethiol and the condensation products are apparently primary reaction products, whereas cyclopentanol and cyclopentene are secondary products. The production of cyclopentanethiol increases linearly when the cyclopentanone conversion increases, that of cyclopentene increases also, while that of cyclopentanol and of the condensation products goes through a maximum.

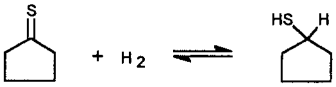
Even if the presence of cyclopentanethione is not observed under our reaction conditions, this molecule is most likely the reaction intermediate for the production of cyclopentanethiol, as was proposed for the transformation of alcohols into thiols over K_2O/Al_2O_3 [1]. Indeed, the addition of H_2S to a ketone to yield an α-hydroxy thiol or a thioketone is very rapid [15]. The products obtained are very unstable, and can hydrogenate rapidly into the thiol.

Thus, the reaction scheme would be:

(1) thiolation of cyclopentanone to cyclopentanethione:



(2) hydrogenation of cyclopentanethione to cyclopentanethiol:



Another means for obtaining cyclopentanethiol from the thioketone is a hydrogen transfer reaction from cyclopentanol to the thioketone yielding cyclopentanethiol and cyclopentanone:

This reaction is known to be very rapid in the presence of K_2O–Al_2O_3 [7]. Cyclopentanol is always present in the reaction products, but in small amounts, which indicates that it either forms slowly or is rapidly consumed. This consumption could occur by either the above hydrogen transfer reaction or dehydration into cyclopentene. The results given in table 1 indicate that cyclopentanol is totally converted, mainly into cyclopentene, under our reaction conditions. Consequently, if cyclopentanol was formed in significant amounts from cyclopentanone, a greater amount of cyclopentene should be obtained.

These observations, together with the shape of the curves in fig. 5, suggest that cyclopentene could be produced through decomposition of the condensation products, at least at 220°C (at higher temperatures, the production of cyclopentanol and its dehydration as well as the dehydrosulfidation of cyclopentanethiol can become more significant). The condensation products can result from crotonisation reactions through either a basic or an acid mechanism. These reactions can be catalyzed either by S^{2-} or by SH groups.

5. Conclusion

– $CoMo/Al_2O_3$ catalysts can be very active and selective for the transformation of ketones into the corresponding thiols.

– The reaction mechanism involves probably a thioketone as an intermediate, although no evidence of this was found in the present study. Complementary experiments are under progress on this subject.

– The reaction temperature and the molar ratio H_2S/ketone affect drastically the reaction selectivity. A reaction temperature not higher than 220°C and a H_2S/ketone molar ratio of at least 2.5 are required to obtain a good selectivity in thiol.

Acknowledgement

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