

Transformation of ketones over sulfided CoMo/Al₂O₃ catalyst — factors affecting thiol selectivity

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Abstract

The competitive transformation of cyclopentanone and of two thiols (cyclopentanethiol and cyclohexanethiol) was carried out on a sulfided CoMo/Al₂O₃ catalyst at 220°C under atmospheric pressure in the presence of H₂/H₂S (90/10 vol.%). The results made it possible to explain the good selectivity in cyclopentanethiol obtained in the thio-reduction of cyclopentanone. This is the consequence of the inhibition due to a competition to adsorption, of the thiol desulfurization into the corresponding olefin. The kinetic order with respect to cyclopentanone of the transformation of cyclohexanethiol into cyclohexene was found equal to -0.6 . © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thiol chemistry has known a significant development in the last decades. The main factor for this increasing interest in thiol chemistry was the necessity to produce synthetic rubbers in the 1940s. Thiol based molecules acting as polymerization transfer agents were widely used, and are still used nowadays [1]. But, the interest for thiols cannot be limited to rubber and plastics chemistry. Indeed, thiols are strongly involved in biological processes (co-enzyme A, and different amino-acids like methionine and cysteine contain thiol functions). Thiols are also present in various drugs like penicillin, its derivatives and various anti-arthritic agents [2]. It has also to be noted that thiol containing molecules are often present in synthetic herbicides and pesticides [1].

The main thiol synthesis methods involve the addition of H₂S to olefins or the substitution of alcohols and halogenocompounds [3].

In previous studies [4,5], we reported results on the synthesis of thiols by reaction of carbonyl compounds with H₂S and H₂ using a molybdenum sulfide catalyst promoted by cobalt (CoMo/Al₂O₃). These studies have led to the proposal of a reaction scheme involving a thioketone as intermediate. We have also shown that such a reaction could be carried out with good yields and selectivities.

Sulfide catalysts used in this work are mostly known for their properties in hydrodesulfurization of petroleum cuts [6]. However, the surface sulfur atoms of these catalysts are able to act as nucleophiles [7–9] and are especially mobile [10], which can predispose these catalysts for substitution reactions. The aim of this work was to study the factors determining thiol selectivity in the transformation of carbonyl compounds on cobalt promoted sulfide catalysts.

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2. Experimental

The base catalyst was a commercial CoMo/Al₂O₃ (procatalyse) with respective loadings in molybdenum and cobalt of 8.4 and 2.3 wt.% and a specific area of 200 m² g⁻¹.

The transformation of cyclopentanone, cyclopentanethiol and cyclohexanethiol was carried out at 220°C in a fixed bed microreactor made of pyrex glass at atmospheric pressure, the carrier gas was a H₂S/H₂ mixture (10/90 vol.%). The different partial pressures (in kPa) in a standard experiment were: reactant = 3.5; solvent: *n*-heptane = 8.5; H₂ = 79 and H₂S = 8.7. In experiments where a second reagent was used, the partial pressure of *n*-heptane was adapted depending on the different amounts of the competitive agent so that the partial pressure of the main reactant was constant as well as the sum of the partial pressures of *n*-heptane and of the competitive agent (8.5 kPa). Experimental tests have shown that the solvent partial pressure had no effect on the catalytic results. The catalyst weights were between 0.1 and 0.5 g. Contact time was characterized by the following parameter (θ):

$$\theta = \frac{m_c}{D}(h),$$

where m_c : catalyst weight (g); D : reactant flow rate (g.h⁻¹).

All the catalysts were presulfided in situ under atmospheric pressure at 350°C for 12 h before reaction, using a 10/90 vol.% H₂S/H₂ mixture with a 3°C min⁻¹ temperature programming.

The reaction products were analyzed using a gas chromatograph (Varian 3400) equipped with a 25 m BP1 capillary column (SGE) with a temperature program from 50°C (5 min) to 150°C (5 min) at 10°C min⁻¹. Unknown products were identified by GC-MS (Finnigan INCOS 500) and co-injection of standard samples (provided by Aldrich).

3. Results and discussion

3.1. Thermodynamic study

The transformation of cyclopentanone on sulfide catalysts was reported in a previous study in

which the optimal operating conditions (220°C, $P_{\text{H}_2\text{S}}/P_{\text{cyclopentanone}} = 2.5$) were selected [5]. The main products of reaction obtained on a CoMo/Al₂O₃ catalyst were cyclopentanethiol and cyclopentanol, as well as cyclopentene. A thermodynamic study was carried out under the conditions of reaction (atmospheric pressure, 220°C). The thermodynamic equilibrium constants (K_p) could be obtained from the free reaction enthalpies (ΔG_r). These enthalpies were calculated from the enthalpies of formation (ΔG_f^0) of the various reactants and products at 220°C [11]. These results are shown in Table 1, as well as the expected conversion rates calculated from these data.

Under our operating conditions, cyclopentanone can lead to thiol and the corresponding alcohol. However under the same conditions, these two compounds can lead to cyclopentene.

3.2. Distribution of the products — effect of the conversion at 220°C

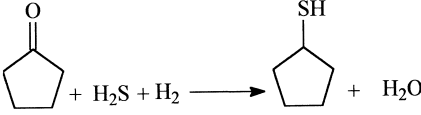
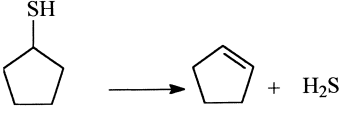
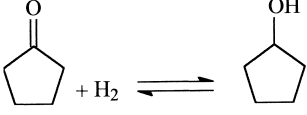
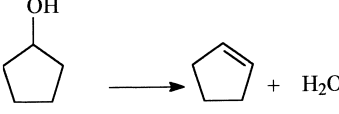
Fig. 1 shows that the transformation of cyclopentanone at 220°C over a sulfided CoMo/Al₂O₃ catalyst. The only apparent primary product which was observed was cyclopentanethiol (about 100% selectivity near zero conversion). Cyclopentene was the main secondary product. The selectivity in cyclopentanethiol which was very high even at high conversion (about 80% at a 70% conversion of cyclopentanone), contrary to what could be awaited according to the thermodynamic study (Table 1). Actually a significant conversion of the thiol into the alkene was possible, which was not observed.

As shown previously the primary product of the reaction is in fact the corresponding thione, but this intermediate is highly reactive and is observed on non-promoted MoS₂/Al₂O₃ only [5]. These results are in accordance with a reaction scheme involving a gemhydroxythiol as intermediate (Scheme 1).

3.3. Comparison of the reactivities of the reactant and products

In order to better understand the good thiol selectivity obtained from cyclopentanone at 220°C, we compared the reactivities of cyclopentanone, cyclopentanethiol and cyclopentanol under the same conditions (Table 2).

Table 1
Thermodynamic study of the transformation of cyclopentanone (atmospheric pressure, 220°C)

	K_p	Conversion (%)
	812.5	100
	3.6	99
	1.8	58
	15640.0	100

Cyclopentanol was found to be approximately 7.5 times more reactive than the corresponding thiol. This can be explained by a greater basicity of oxygen, or a greater polarization of the CO bond compared to the CS bond. In this case, the rupture of the CO bond during dehydration will be easier than the rupture of the CS bond during desulfurization. This means that the thiorreduction of cyclopentanone was much faster

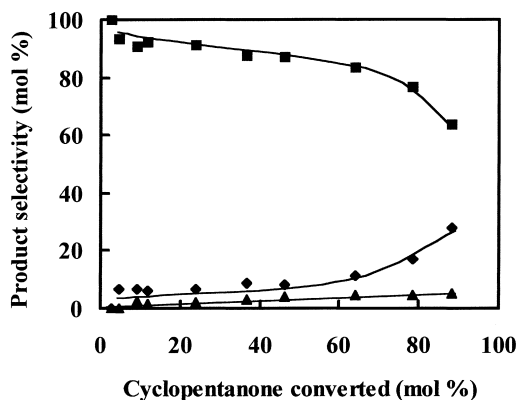
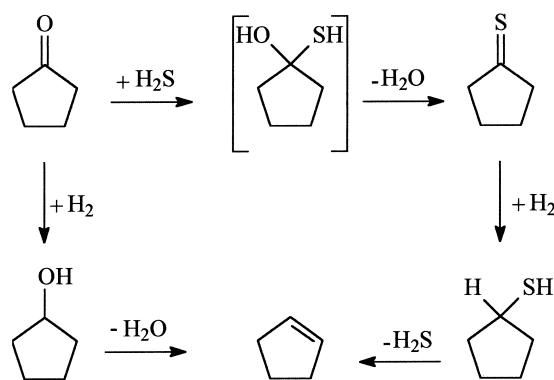


Fig. 1. Transformation of cyclopentanone on CoMo/Al₂O₃ catalyst (220°C, atmospheric pressure). Distribution of the reaction products as a function of cyclopentanone conversion. (■): cyclopentanethiol; (◆): cyclopentene; (▲): condensation products.



Scheme 1. Transformation of cyclopentanone on sulfide catalysts.

Table 2
Comparison of the reactivities of cyclopentanone, cyclopentanethiol and cyclopentanol on a CoMo/Al₂O₃ catalyst (220°C, atmospheric pressure)

Reactivity (mmol h ⁻¹ g ⁻¹)		
Cyclopentanone	Cyclopentanethiol	Cyclopentanol
4	18	133

than its reduction into cyclopentanol otherwise the selectivity in cyclopentene should be much higher than was found. The products of the transformation of cyclopentanol were cyclopentene (97 mol.%) and cyclopentanethiol (3 mol.%).

Cyclopentanethiol was found to be approximately four times more reactive than cyclopentanone (Table 2). This compound led mainly to cyclopentene. Indeed, the reaction mixture contains 97 mol.% of cyclopentene and 3 mol.% of cyclopentanethiol. This is in accordance with the thermodynamic calculations (Table 1).

Moreover, the difference obtained between the reactivity of cyclopentanethiol and that of cyclopentanone is apparently in contradiction with the good selectivities obtained in thiol formation. This could be explained by an effect of competition to adsorption between cyclopentanone and the corresponding thiol (in favour of the ketone), which would decrease the rate of decomposition of the thiol into cyclopentene.

3.4. Competition effects

To the reaction mixture containing the cyclopentanethiol, increasing quantities of cyclopentanone were added, while maintaining constant the partial pressure of thiol.

Under the chosen experimental conditions and in the absence of cyclopentanone in the reaction mixture, the conversion of cyclopentanethiol was practically total for contact times higher than 2 h. The ketone introduction into the mixture induced a decrease in activity of the catalyst (Fig. 2). Thus, for a ratio of partial pressures of thiol over ketone equal to 14, the conversion of cyclopentanethiol was only 65%, instead of 96% in the absence of ketone at the same contact time of 2 h. The introduction of cyclopentanone did not induce any modification in the distribution of the reaction products. Cyclopentene was the main product (95 mol.%) and cyclopentane was also observed (5 mol.%).

In order to quantify more precisely the inhibiting effect of the ketone on the transformation of the thiol, the effect of cyclopentanone on the conversion of cyclohexanethiol was carried out. Under these conditions, the products of reaction of the thiol will be well differentiated from those of the ketone. Cyclohexanethiol leads primarily to cyclohexene, with a selectivity of 99 mol.%, and to cyclohexane. The ad-

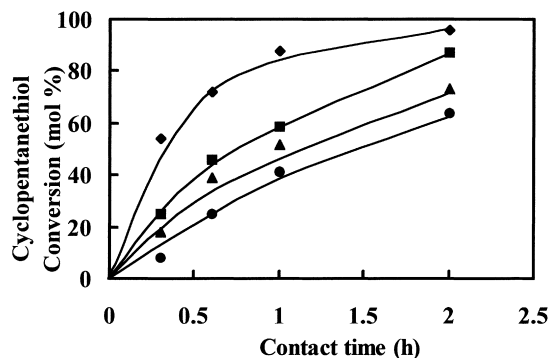


Fig. 2. Transformation of cyclopentanethiol on $\text{CoMo}/\text{Al}_2\text{O}_3$ (220°C, atmospheric pressure, $P_{\text{cyclopentanethiol}} = 3.5$ kPa). Effect of the quantity of cyclopentanone on the conversion of cyclopentanethiol. $P_{\text{cyclopentanone}}$: (◆): 0; (■): 0.02 kPa; (▲): 0.1 kPa; (●): 0.25 kPa.

dition of cyclopentanone to the reaction mixture has the same effect on the conversion of cyclohexanethiol as on that of cyclopentanethiol, the larger is the quantity of added ketone, the greater is the decrease of reactant conversion (Fig. 3). For example, with a ratio $P_{\text{cyclohexanethiol}}/P_{\text{cyclopentanone}} = 3.2$ (which corresponds approximately to the situation encountered when the conversion of cyclopentanone into cyclopentanethiol was of about 70%), the conversion of the cyclohexanethiol was limited to 35% at a contact time

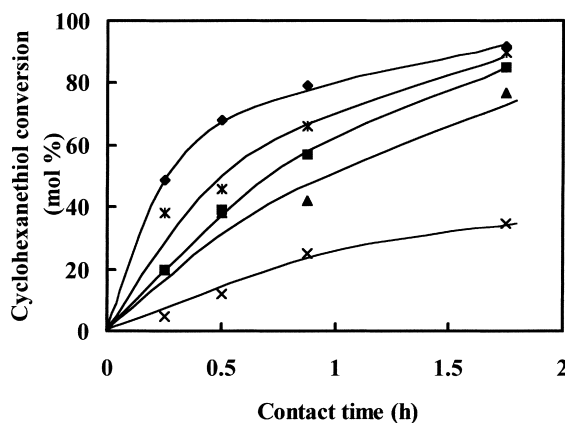


Fig. 3. Transformation of cyclohexanethiol on $\text{CoMo}/\text{Al}_2\text{O}_3$ (220°C, atmospheric pressure). Effect of the quantity of cyclopentanone on the conversion of cyclohexanethiol. $P_{\text{cyclohexanethiol}}/P_{\text{cyclopentanone}}$ ratio: (◆): 175; (✕): 64; (■): 35; (▲): 14; (×): 3.2.

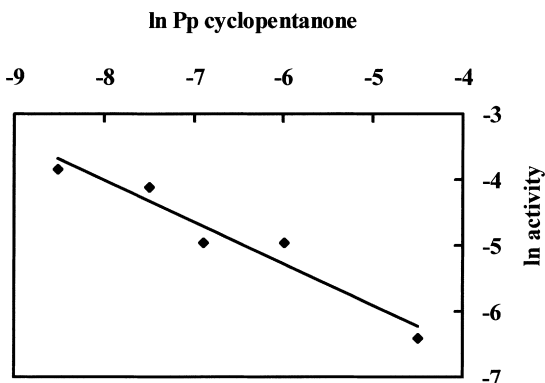


Fig. 4. Transformation of cyclohexanethiol on CoMo/Al₂O₃ (220°C, atmospheric pressure). Effect of the quantity of cyclopentanone on the conversion of cyclohexanethiol. Calculation of the reaction order of cyclopentanone.

of 1.75 h, instead of nearly 100% when the ratio was equal to 175. This inhibition effect corresponds to a reaction order with respect to cyclopentanone which could be estimated to -0.6 (Fig. 4).

4. Conclusion

The reaction of cyclopentanone with H₂/H₂S at 220°C on sulfided CoMo/Al₂O₃ under atmospheric pressure led to cyclopentanethiol with a good selectivity. Thermodynamic calculations as well as the measure of the thiol reactivity showed that, under these operating conditions the reaction should lead to a

significant extent to cyclopentene. Indeed the reactivity of cyclopentanethiol, regarding its desulfurization, was four times higher than the thio-reduction reactivity of cyclopentanone.

The competitive transformation of cyclopentanone and cyclohexanethiol showed that the selectivity in thiol obtained from cyclopentanone was due to the inhibition of the desulfurization of the thiol by the ketone (kinetic order = -0.6).

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