

Study on the Oxidation Mechanism of Mixed Thiols in Light Oil Sweetening. 3. Apparent Kinetics of the Catalytic Cooxidation of Mixed Thiols in Gas–Liquid–Solid Systems

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The effects of oxygen pressure, temperature, catalyst loading, and particle size of the catalyst support on the cooxidation reaction of mixed thiols were studied systematically in gas–liquid–solid systems. The results have shown that the pore diffusional resistance is the main factor limiting the reaction and the overall cooxidation reaction kinetics is zero order in oxygen and first order in mercaptan. The diffusion-controlled rate law can be represented as $r = k_{\text{obs}} C_{\text{RSH}}$. A discussion is presented for the industrial sweetening operation based on the research.

Introduction

Sweetening of gasoline by catalytic oxidation is an area receiving attention from both academic and industrial sectors. Basic research provides the preliminary knowledge and guidance for the industrial process, and a number of research studies have been made.^{1–3} Until quite recently, we focused on the research of the cooxidation of mixed thiols and found that the kinetics and mechanism of the catalytic cooxidation of mixed thiols are more reasonable than that of an individual thiol for the theoretical elucidation of the oxidation sweetening process of light oil. In homogeneous catalytic cooxidation of mixed thiols, interactions of different types of mercaptans were found to exist and the cooxidation mechanisms were proposed by us.^{4,5} To provide information concerning the practical industrial fixed-bed sweetening process in which the sour hydrocarbon distillate, together with air and alkaline base or Merox CF, is passed at the operating temperature and pressure in contact with the catalyst bed (activated carbon impregnated with cobalt-sulfonated phthalocyanine (CoSPc)) in a reactor,^{6–8} it is necessary to make a further study of the apparent catalytic kinetics of the cooxidation of mixed thiols in gas–liquid–solid systems.

The present study is aimed at understanding the influence of oxygen pressure, temperature, catalyst loading, and particle size of the catalyst support on the cooxidation of mixed thiols in heterogeneous systems.

Experimental Section

Kinetics Measurement Method. As a representative mixed thiol, the mixture of 1-butanethiol and 2-methyl-2-propanethiol was selected to be the model mercaptan. For the gas–liquid–solid ternary phase system, the liquid phase was made by dissolving the mixed thiols in petroleum ether (60–90 °C), oxygen was the gaseous phase, and the solid catalyst was CoSPc impregnated on activated carbon. In the above heterogeneous system, the catalytic cooxidation kinetics of mixed thiols was determined using the method which was described in detail elsewhere.⁴

Experimental Conditions. All reagents used in the experiments were of A.R. grade; 1-butanethiol and 2-methyl-2-propanethiol were purified by distillation under nitrogen before use. The initial total mercaptan concentration was 0.012 mol·dm⁻³, and the mole ratio of 1-butanethiol and 2-methyl-2-propanethiol in the mixture was 1:1. Three particle sizes, 20–40, 40–60, and 60–80 mesh, in most cases 40–60 mesh, of activated carbon as the catalyst support were selected, and the catalyst CoSPc loading was 0.025% (w/w). During the cooxidation, the total gaseous pressure was maintained constant at 103 kPa, and sometimes nitrogen was introduced into oxygen in order to get the desired partial pressure of oxygen. The reaction temperature was kept at 35 ± 0.1 °C. All experiments were carried out under the above conditions unless otherwise stated.

Product Analysis. After the cooxidation reaction of the mixed thiols with a mole ratio of 1:1 proceeded for 2 h under the aforementioned conditions, a sample was drawn directly from the reactor and analyzed by gas chromatography quickly. The peaks of the reaction products were compared with those of the standard disulfides. The analytical results demonstrate that three disulfides were produced in the cooxidation of 1-butanethiol and 2-methyl-2-propanethiol: *t*-C₄H₉SSC₄H₉-*t* (**1**), *n*-C₄H₉SSC₄H₉-*t* (**2**), and *n*-C₄H₉SSC₄H₉-*n* (**3**). The quantitative data show that the mole percentage of products **1–3** is 3.6%, 30%, and 66.7%, respectively. The formation of the unsymmetrical disulfide **2** reveals that the interaction between 1-butanethiol and 2-methyl-2-propanethiol also exists in heterogeneous catalytic systems. But the smaller mole percentage of unsymmetrical disulfide in the heterogeneous system than that in the homogeneous system^{4,5} implies that the 1-butanethiol radical and the 2-methyl-2-propanethiol radical do not easily approach each other on the surface of the catalyst support because of steric hindrance.

Results and Discussion

Effects of Oxygen Diffusion and Catalyst Particle Size. The total mercaptan conversions of the reaction system, by using 1 g of solid catalyst, under

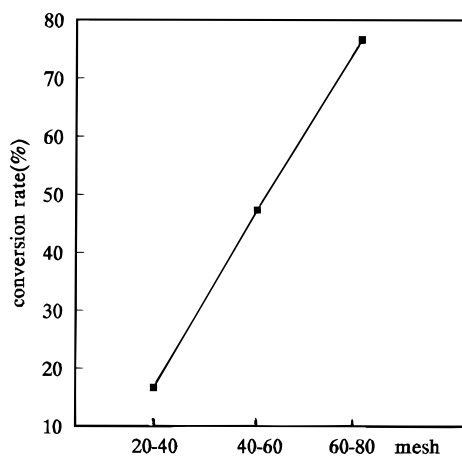


Figure 1. Influence of the catalyst particle size on the conversion rate of mercaptans.

other uniform conditions, were found to increase with an increase in the speed of agitation up to 1100 rpm and are independent of the agitation speed around 1200 rpm. It appears, therefore, that the diffusion effect of oxygen on the chemical reaction was eliminated under this agitation speed. According to Satterfield,⁹ it is difficult to eliminate the gas-liquid diffusional resistance when using large quantities of solid catalyst in the stirring slurry reactor. So the subsequent works were carried out at an agitation speed of 1200 rpm, and the quantity of solid catalyst used was reduced to 0.2 g to ensure the ruling out of the mass-transfer limitation of oxygen, as well as to get the medium reaction speed.

The effect of catalyst particle size on the conversion rate of thiols is shown in Figure 1. The conversion rates were measured at the same reaction time, 70 min, in different runs. It can be seen (Figure 1) that the higher conversion rates of the thiols were measured with smaller particle sizes of catalyst support used. The results demonstrate that the pore diffusional resistance is great. In the reaction system, the liquid phase was saturated with oxygen, and an excess of oxygen was used in order to ensure that the desired cooxidation reaction is accomplished. So in view of the molecular volume and the concentrations of oxygen and thiols, it is reasonable to conclude that the pore diffusional resistance of the mercaptan is the main factor to limit the oxidation reaction.

Effects of Catalyst Loading and the Quantity of Activated Carbon Used. An increase in the catalyst loading from 0.025% (w/w) to 0.05% (w/w) has relatively little effect on the cooxidation reaction of the mixed thiols (Figure 2), but a much greater effect on the cooxidation reaction was measured by increasing the quantity of activated carbon from 0.2 to 0.4 g with the catalyst loading unchanged (Figure 3), which revealed that the oxidation of thiols mainly occurred on the outside surface of the catalyst support and further demonstrated that the pore diffusional resistance was great. In all plots of mercaptan concentration as a function of time, the points are experimental and the lines are calculated by

$$C_{\text{RSH}} = a_0 + a_1 t + a_2 t^2 \quad (1)$$

a_0 , a_1 , and a_2 are the regression parameters.

Effect of Partial Pressure of O_2 . The effect of the partial pressure of O_2 on the rate of the cooxidation

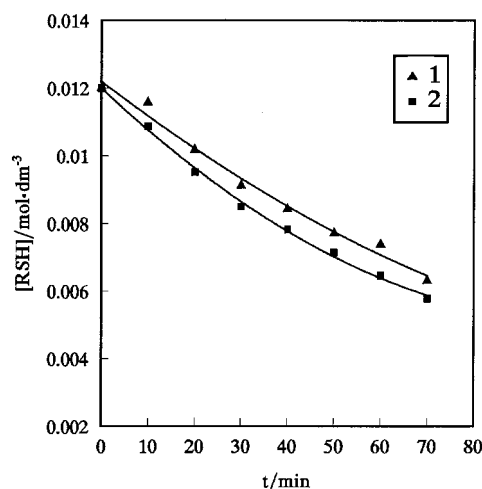


Figure 2. Influence of the catalyst loading on the cooxidation reaction of the mixed thiols. Catalyst loading: 1, 0.025% (w/w); 2, 0.05% (w/w).

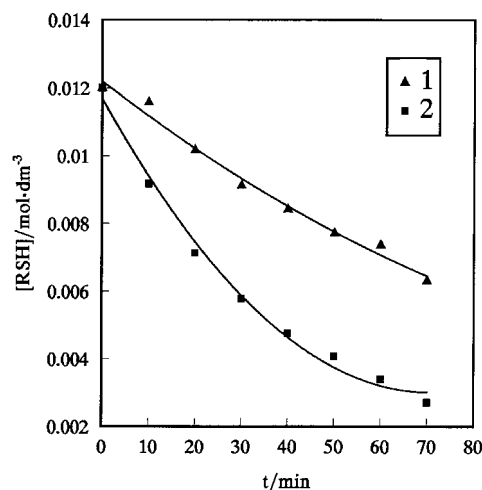


Figure 3. Influence of the quantity of activated carbon used on the cooxidation reaction of the mixed thiols. Catalyst loading: 0.025% (w/w). Quantity of activated carbon: 1, 0.2 g; 2, 0.4 g.

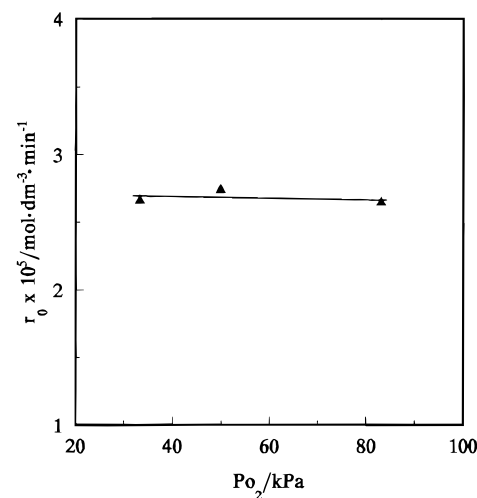


Figure 4. Effects of the partial pressure of oxygen on the reaction rate of the mixed thiols.

reaction, under otherwise uniform conditions, in the presence of 0.025% (w/w) loading of catalyst is shown in Figure 4. It clearly shows that the reaction rate is nearly independent of the change in oxygen partial pressure, and the apparent kinetics of the cooxidation

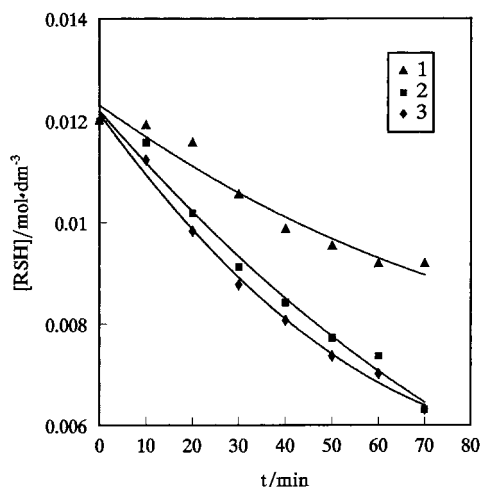


Figure 5. Plots of the total concentration of the mixed thiols versus time at different mole ratios of 1-butanethiol and 2-methyl-2-propanethiol. 1, 2-methyl-2-propanethiol; 2 and 3, mole ratio of 1-butanethiol and 2-methyl-2-propanethiol is 1:1 and 2:1, respectively.

reaction of mixed thiols is zero order in oxygen under the conditions experimented. This result disagrees with that of Cullis et al.¹ and Pal and Sharma¹⁰ for the oxidation of mercaptide in alkaline solution. They reported that the rate of oxygen uptake is proportional to the partial pressure of oxygen. A preliminary reason for this disagreement is probably the difference of the reaction medium used, which in this work was petroleum ether and theirs was alkaline solution. Xan et al.¹¹ have demonstrated that more oxygen disappeared than could be accounted for by the oxidation of mercaptan to disulfide in alkaline solution.

Catalytic Cooxidation of the Mixed Thiols with Different Mole Ratios of 1-Butanethiol and 2-Methyl-2-propanethiol. The catalytic cooxidations of the mixed thiols with different mole ratios of 1-butanethiol and 2-methyl-2-propanethiol were measured and are shown in Figure 5. It is seen that the cooxidation reaction becomes faster with an increase of the mole fraction of 1-butanethiol in the mixed thiols. This result is consistent with the product analysis, which demonstrates that the interaction between 1-butanethiol and 2-methyl-2-propanethiol takes place through the formation of unsymmetrical disulfide.

Effects of Reaction Temperature. The rates of the catalytic cooxidation of the mixed thiols, becoming greater with the rising of the reaction temperature, were measured at temperatures from 25 to 45 °C. Plotted in Figure 6 is $\ln(k_{\text{obs}})$ versus $1000/T$ (K^{-1}). The relationship between the apparent k_{obs} and temperature follows the Arrhenius equation, and the resulting apparent activation energy was found to be 12 kJ/mol.

Apparent Kinetics of the Cooxidation Reaction of Mixed Thiols under Diffusion-Controlled Conditions. The effect of catalyst particle size on the reaction (Figure 1) shows that all kinetic measurements this paper investigated were conducted under great pore diffusional resistance, so the obtained kinetics of the cooxidation reaction of the mixed thiols is the diffusion-controlled apparent kinetics. Figure 7 shows the plots of $-\ln(C_{\text{RSH}})$ to time of several representative runs at different experimental conditions. The better linear relationships between $-\ln(C_{\text{RSH}})$ and time demonstrate that the oxidation reaction is first order with respect to thiols. In accounting for the effects of partial pressure

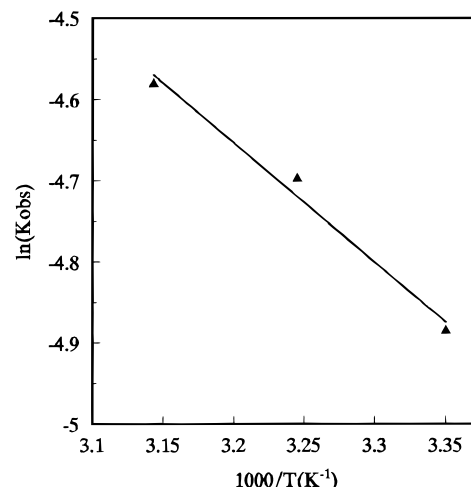


Figure 6. Arrhenius plot for the catalytic cooxidation of the mixed thiols.

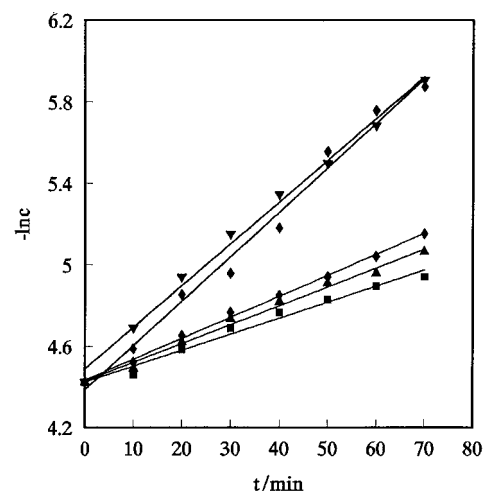


Figure 7. Plots of $-\ln(C_{\text{RSH}})$ versus time of some representative runs for the cooxidation of the mixed thiols.

Table 1. k_{obs} Measured with Different Particle Sizes of Catalyst Support^a

particle size (mesh)	20–40	40–60	60–80
$10^3 k_{\text{obs}}$ (min^{-1})	2.694	9.117	21.84

^a $t = 35 \pm 0.1$ °C.

of oxygen and mercaptan concentrations on the oxidation reaction, the diffusion-controlled kinetic equation of the overall cooxidation reaction of the mixed thiols can be represented as $r = k_{\text{obs}} C_{\text{RSH}}$.

Several apparent rate constants determined with different particle sizes of catalyst support under the diffusion-controlled conditions are listed in Table 1.

The data in Table 1 imply that the smaller the catalyst particle, the faster the catalytic cooxidation reaction of the mixed thiols. Accordingly, the selection of catalyst support in the practical industrial operation is that the size of the catalyst particle to be used in the sweetening unit should be as small as possible if the pressure drop is allowable. All the above kinetic results obtained are important for carrying out industrial applications.

Conclusion

The effects of catalyst particle size on the cooxidation reaction of the mixed thiols are great. Experimental

results show that the pore diffusional resistance is the main factor limiting the cooxidation reaction of mixed thiols in gas-liquid-solid heterogeneous systems and the diffusion-controlled kinetics for the systems investigated is zero order in oxygen and first order in total mercaptan concentration, which can be represented as $r = k_{\text{obs}}C_{\text{RSH}}$.

The interaction between 1-butanethiol and 2-methyl-2-propanethiol was found to exist in heterogeneous catalytic systems, but it is weakened because the 1-butanethiol radical and 2-methyl-2-propanethiol radical do not easily approach each other on the surface of the catalyst support because of steric hindrance.

The effects of temperature on the catalytic cooxidation reaction of the mixed thiols have been demonstrated to be great. The relationship between the apparent k_{obs} and temperature follows the Arrhenius equation, and the derived apparent activation energy is 12 kJ/mol.

Catalyst support should be as small as allowable in industrial sweetening operation in light of the results of this research.

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