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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 27(3), 157-166
Issue Date	1980-03
Doc URL	<a href="https://hdl.handle.net/2115/25068">https://hdl.handle.net/2115/25068</a>
Type	departmental bulletin paper
File Information	27(3)_P157-166.pdf



## ABOUT THE SINTERING OF UNSUPPORTED POLYCRYSTALLINE COBALT CATALYST

By

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(Received August 20, 1979)

### Abstract

The activity of the fresh catalyst samples of different preparations was tested in the decomposition of  $H_2O_2$  for which a mechanism was suggested. The kinetics of sintering in the range of 300-450°C was studied through the change in activity and surface area. A new empirical equation was suggested to summarize the sintering results. The second order mechanism of sintering as well as the activation energy (15-16 kcal/mole) were also discussed.

### Introduction

The effect of thermal treatment on catalytic and surface characteristics of supported  $Co/Al_2O_3$  hydrocracking catalyst was studied in a previous publication.<sup>1)</sup> During this study, it became necessary to investigate the behaviour of sintering of the unsupported polycrystalline cobalt catalyst which determines its industrial use.

Some work<sup>2-6)</sup> has been reported in this direction from a different point of view, yet the additional information provided in the present communication concerned mainly with testing the activity of freshly prepared catalyst samples of different preparations and studying the mechanism of sintering of one of them by following the changes in activity and texture during the heat treatment.

### Experimental

#### *Catalyst*

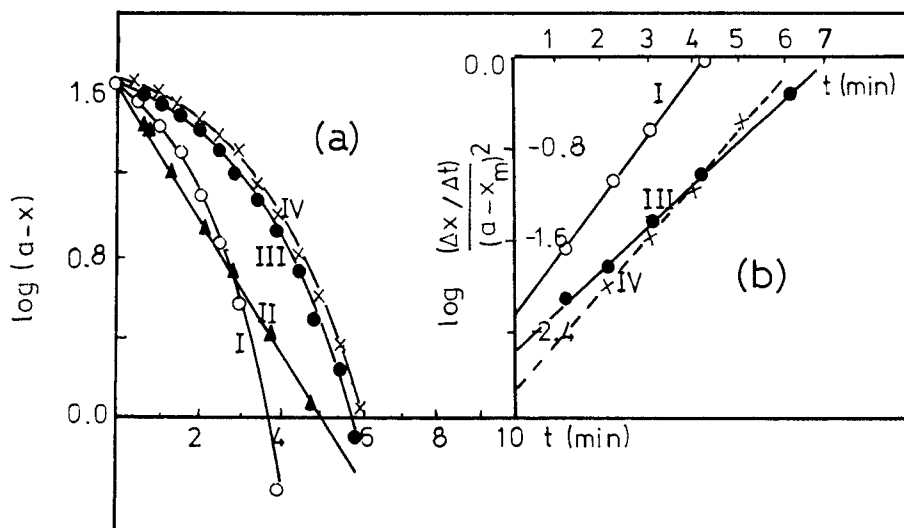
Four different samples of the polycrystalline cobalt catalyst were prepared from cobalt nitrate as follows: (I) By ignition of the starting material at 400°C for 4 hours in atmospheric air, (II) by precipitation as oxalate, (III) by precipitation as hydroxide, and (IV) by precipitation as carbonate.

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**Fig. 1.** (a) First-order plots of the decomposition of  $\text{H}_2\text{O}_2$  over the surface of the fresh cobalt catalyst samples of different preparations: I) from  $\text{NO}_3^-$ , II) from oxalate, III) from  $\text{OH}^-$ , IV) from  $\text{CO}_3^{2-}$ .  
 (b) Auto-catalytic plots for the catalyst samples: I, III and IV.

$[X]$  is an undefined surface intermediate compound which is accumulated during the reaction, and  $\text{Co}_n\text{O}_m$  is the oxide left at the end of the reaction as a result of the side oxidation step.

Integrating equation (1) yields,

$$kt = \ln \frac{k_0 + k_1 x}{(a-x)} + C,$$

where  $k = k_0 + k_1 a$  and  $C = \ln a/k_0$ . Thus,

$$kt/2.303 = \log \frac{\Delta x / \Delta t}{(a-x)^2} + \log a/k_0. \quad (2)$$

The autocatalytic plots derived from equation (2) are illustrated in Fig. 1 (b) and the calculated results of  $k_0$  and  $k_1$  are summarized in Table 1. It is clear that the catalyst samples I and II are the most active ones in this reaction.

The activation energies of the decomposition reaction measured in the temperature range  $30 \sim 50^\circ\text{C}$  are given also in Table 1. It seems that the activation energy ( $E_1$ ) calculated from  $k_1$  values decreases in a reversed order to that calculated from  $k_0$  ( $E_0$ ). The energy of activation ( $E_1$ ) indicates most

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TABLE 1. Activity of various freshly prepared samples of unsupported cobalt catalyst in the decomposition of  $\text{H}_2\text{O}_2$  (at  $40^\circ\text{C}$ )

Catalyst sample	$k_0$ ( $\text{min}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$E_0$ (kcal/mole)	$E_1$ (kcal/mole)
I	0.38	0.018	15.0	9.0
III	0.16	0.012	19.5	6.2
IV	0.10	0.016	23.5	4.0
II*	0.65		15.0	

\*  $k$  is calculated from the simple first-order equation.

likely that the oxidation step becomes more easier on the samples III and IV.

## 2. Sintering Isotherms at $350^\circ\text{C}$ in *vacuo* and in air

The behaviour of the sintering isotherms of the catalyst sample I at  $350^\circ\text{C}$  (*i. e.*,  $k_0$  and  $k_1$  as a function of  $t_{\text{sint.}}$  in hrs) in *vacuo* and in air are shown in Fig. 2. It is clear that the rate of sintering, as judged from  $k_0$  values, is the same in air and in *vacuo*. On the other hand, the rate of sintering, as judged from  $k_1$  values seems to be different in the two atmos-

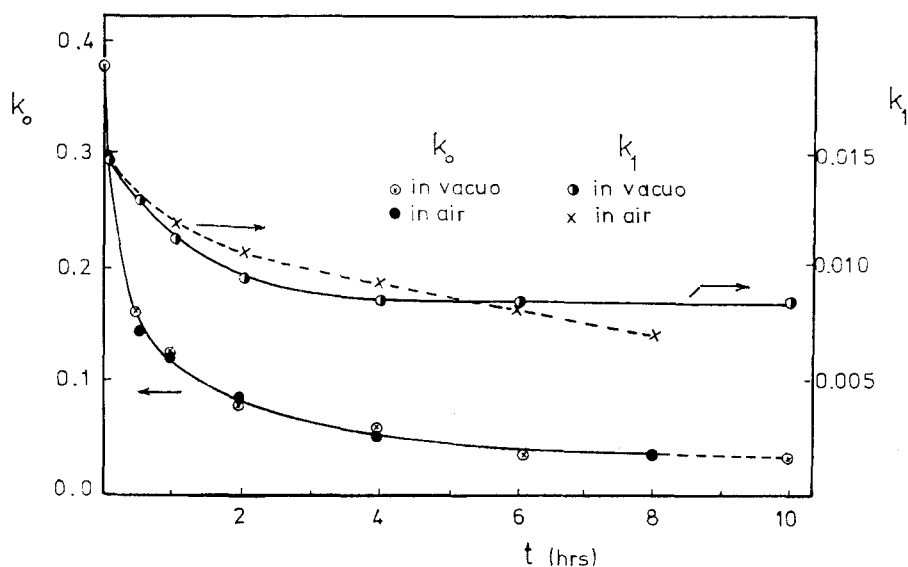


Fig. 2. Activity ( $k_0$  and  $k_1$ ) of unsupported cobalt catalyst as a function of time of sintering at  $350^\circ\text{C}$  in *vacuo* and in air.

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TABLE 2. Activation energies of the decomposition of  $H_2O_2$  over the surface of the cobalt catalyst samples sintered at  $350^\circ C$

Time of sintering (hrs)	$E_0$ (kcal/mole)		$E_1$ (kcal/mole)	
	<i>in vacuo</i>	in air	<i>in vacuo</i>	in air
Freshly prepared sample	15.0		9.0	
1/2	14.5	16.5	6.2	10.6
1	14.0	16.5	6.3	12.0
2	14.7	17.0	5.8	13.0
4	14.7	16.1	5.8	14.2
6	14.3	16.5	5.9	15.9
8	14.7	16.6	6.0	16.8
10	14.7	—	5.9	—

pheres. For more explanation of this phenomenon, the measured energy of activation of the decomposition reaction over the surface of sintered samples are summarized in Table 2. From this Table, it is found that the energy of activation of the decomposition reaction taking place on the non-oxidized surfaces ( $E_0$ ) remains almost constant either by treating the catalyst in air (av., 16.5 kcal/mole) or *in vacuo* (av., 14.7 kcal/mole). Similarly, during the heat treatment *in vacuo*, the activation energy of the reaction involving a side oxidation step ( $E_1$ ) remains constant but with much less values, *viz.*,  $\sim 6$  kcal/mole. This low value seems to result due to cleaning the surface during the vacuum-treatment which facilitates the side oxidation step. However, in air a continuous increase in  $E_1$  reflects most probably the accumulation of the formed surface oxide intermediate during the decomposition reaction.

### 3. Kinetics of the Sintering Process of the Catalyst Sample I

#### (a) From the change of activity:

The sintering isotherms *in vacuo* at 350, 400 and  $450^\circ C$  are shown in Fig. 3. (a) Differential analysis of the results of  $k_0$  vs  $t$  (hr) indicated that the sintering process follows the second order equation (Fig. 3 (b)). For carrying out this analysis, the method suggested before by one of the authors<sup>9</sup> was used and the activity parameter ( $A$ ) was adopted by converting  $k_0$  values according to the equation described elsewhere.<sup>10</sup> The results obtained from the analysis of  $k_1$  were not indicative.

Assuming that Arrhenius equation is applicable in the studied tempera-

ture range, the calculated activation energy of the sintering process was found to be 15.2 kcal/mole. Attention should be paid to this value in view of the heats of desorption of gases, in particular  $O_2$  and air from the catalyst surface (12 ~ 30 kcal/mole).<sup>10</sup> If this heat is supplied as minimum energy for the vacuum-sintering process, the desorption becomes therefore the rate determining step, assuming that the growth of crystal size and the elimination of active sites take place progressively in a rapid manner.

(b) *From the change of surface area:*

The adsorption-desorption isotherms of  $N_2$  at  $-196^\circ C$  on the surface of the freshly prepared catalyst sample I is illustrated in Fig. 4(a). The isotherm is of type II of Brunauer's classification<sup>12</sup> and the adsorption seems to be completely reversible on all the samples under study, exhibiting no hysteresis loop.

The sintering isotherms expressed in terms of  $S_{BET}$  vs time of sintering are also shown in Fig. 4(b). The results of this figure were analyzed according to the second order equation, *i. e.*,

$$\frac{dS}{dt} = -kS^2 \quad (3)$$

Integrating this equation yields,

$$S_i/S = S_i k_s t + 1,$$

where  $S_i$  is the initial surface area and  $k_s$  is the velocity constant for a given ratio of sintering at a constant temperature. The plots of Fig. 4(c) indicate the validity of the analysis based on the second order mechanism.

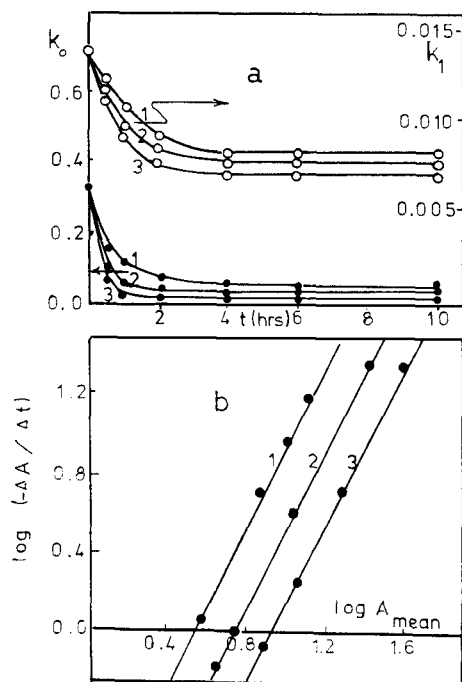
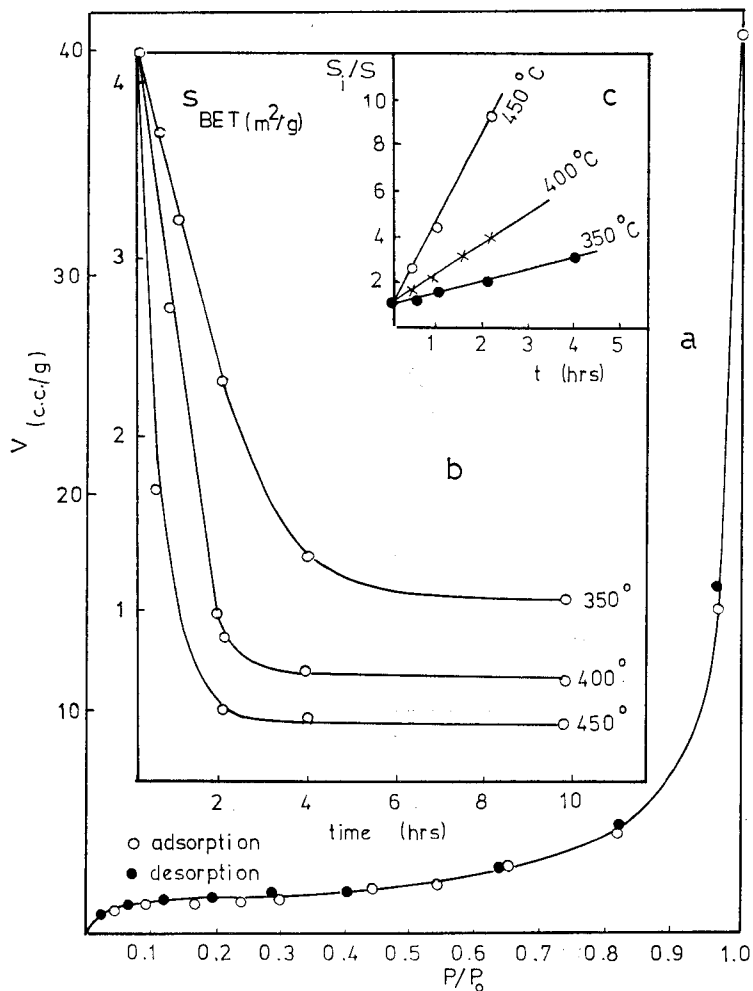


Fig. 3. (a) Sintering isotherms ( $k_0$  and  $k_1$  vs  $t_{sint}$ ) for the unsupported cobalt catalyst at: 1-350°C, 2-400°C and 3-450°C.

(b) Differential treatment of the sintering isotherms ( $k_0$  vs  $t_{sint}$ ) at: 1-350°C, 2-400°C and 3-450°C, for determining the order of sintering.

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**Fig. 4.** (a) Adsorption-desorption isotherm of  $N_2$  at  $-196^\circ C$  for the freshly prepared cobalt catalyst (I).  
 (b) Specific surface area of unsupported cobalt catalyst as a function of time of sintering at 350, 400 and  $450^\circ C$ .  
 (c) Validity of the second-order equation ( $S_i/S$  vs  $t_{sint}$ ).

On the other hand, it was assumed by Huttig<sup>13</sup> that the velocity constant  $k_s$  for a given degree of sintering is inversely proportional to the time taken to reach this degree of sintering at constant temperature ( $t_s$ ), *i. e.*,  $k_s = K/t_s$ , where  $K$  is constant. Applying this assumption in Arrhenius equation, it follows that,

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$$\log t_s = \Delta E_s / (2.303 RT) + C,$$

where  $\Delta E_s$  is the activation energy of the sintering process and  $C$  is the integration constant. In Fig. 5,  $\log t_s$  calculated for different percentages of sintering is plotted against  $1/T_{\text{sint.}}$  ( $^{\circ}\text{K}$ ), from which the activation energy

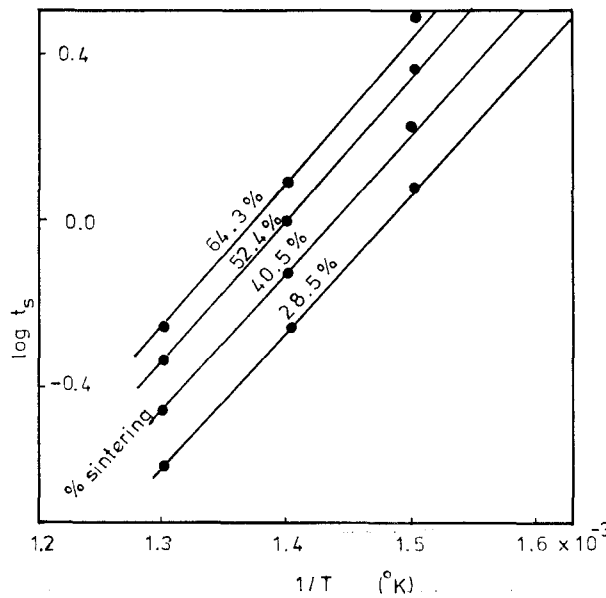


Fig. 5. Plots of  $\log t_s$  vs  $1/T$  ( $^{\circ}\text{K}$ ) for different percentages of sintering.

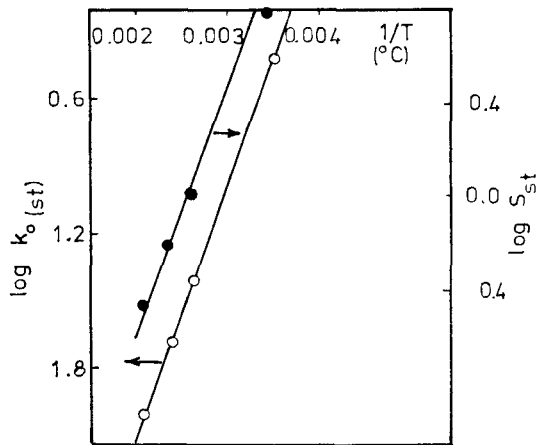


Fig. 6. Logarithmic relationship of the stationary values of activity ( $k_0, st$ ) and surface area ( $S_{st}$ ) with  $1/T$  ( $^{\circ}\text{C}$ ).

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of the sintering process was found to be 15.7 kcal/mole. This value is fairly consistent with that found for the activation energy of the diffusion of the interstitial cobalt atoms in the solid lattice (14~15 kcal/mole).<sup>14)</sup> This may also provide an interpretation for the same value obtained from activity data.

The exponential behaviour of the sintering isotherms (Figs. 3, 4) could be better expressed in linear logarithmic relationship shown in Fig. 6 indicating the following :

- a) A good parallelism between stationary values of activity and surface area. It is to be mentioned that reporting the rates per unit surface area could remove the necessity of discussing the change in activity with sintering, but the special nature of the test reaction dictated such study. In addition, the calculated  $k_0/S$  was found to be  $0.095 \text{ min}^{-1} \text{ g m}^{-2}$  for all the samples sintered at different conditions, which certainly needs much for deducing its significance.
- b) The results may fit the empirical equation of the form ;

$$\log S = \log S_{st} + \log S_i/S_{st} \left[ \frac{T_0}{T_{st} - T_0} (T_{st}/T - 1) \right]$$

where  $S$  is the surface area of the catalyst sintered at a given temperature  $T$ ,  $S_i$  is the surface area of the freshly prepared catalyst ( $T_0$  is the preparation temperature which equals  $300^\circ\text{C}$  in the present study),  $S_{st}$  is the isothermal stationary surface area at a known temperature  $T_{st}$  which is higher than the initial preparation temperature  $T_0$ .

For catalytic activity a very similar equation could be postulated. This equation is widely different from those suggested before by one of the authors for the unsupported platinum<sup>9)</sup> and the unsupported copper.<sup>15)</sup> The difference seems most likely to lie in the behaviour of the sintering process, *i. e.*, the rates of the elimination of active centers or the diffusion of interstitial atoms are different in the studied systems although the process follows the second order mechanism in all cases.

#### Acknowledgement

The authors are greatly indebted to Professor Dr. R. Sh. Mikhail for numerous helpful discussions.

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