



Title	ABOUT THE SINTERING OF UNSUPPORTED POLYCRYSTALLINE COBALT CATALYST
Author(s)	HASSAN, Salah A.; ABDEL-KHALIK, Mohamed; HASSAN, Hamdi A.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 27(3), 157-166
Issue Date	1980-03
Doc URL	http://hdl.handle.net/2115/25068
Type	bulletin (article)
File Information	27(3)_P157-166.pdf



[Instructions for use](#)

ABOUT THE SINTERING OF UNSUPPORTED POLYCRYSTALLINE COBALT CATALYST

By

Salah, A. HASSAN^{*1}, Mohamed ABDEL-KHALIK^{*2}
and Hamdi A. HASSAN^{*3}

(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.¹⁾ During this study, it became necessary to investigate the behaviour of sintering of the unsupported polycrystalline cobalt catalyst which determines its industrial use.

Some work²⁻⁶⁾ 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.

* Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt.

Sintering of Unsupported Polycrystalline Cobalt Catalyst

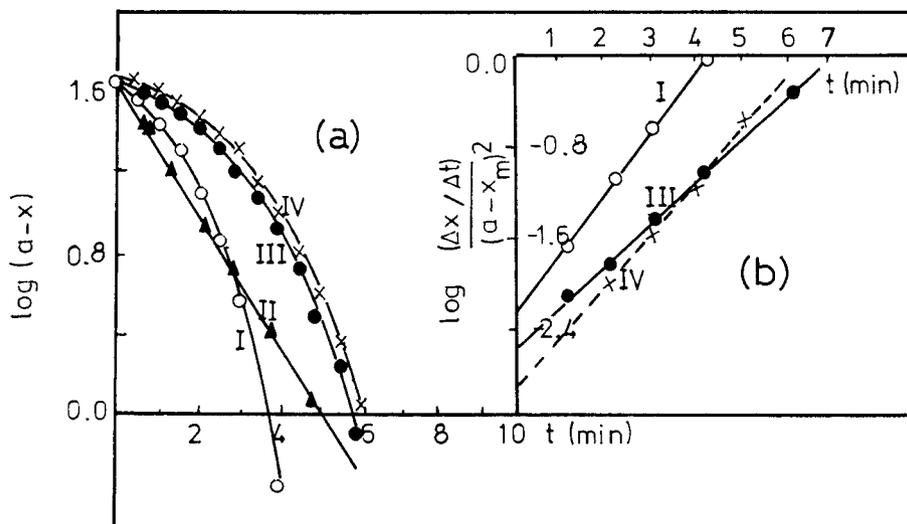


Fig. 1. (a) First-order plots of the decomposition of H_2O_2 over the surface of the fresh cobalt catalyst samples of different preparations: I) from NO_3^- , II) from oxalate, III) from OH^- , IV) from CO_3^{2-} .
 (b) Auto-catalytic plots for the catalyst samples: I, III and IV.

$[\text{X}]$ is an undefined surface intermediate compound which is accumulated during the reaction, and Co_nO_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

S. A. HASSAN, M. ABDEL-KHALIK and H. A. HASSAN

TABLE 1. Activity of various freshly prepared samples of unsupported cobalt catalyst in the decomposition of H_2O_2 (at 40°C)

Catalyst sample	k_0 (min^{-1})	k_1 (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°C in *vacuo* and in air

The behaviour of the sintering isotherms of the catalyst sample I at 350°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-

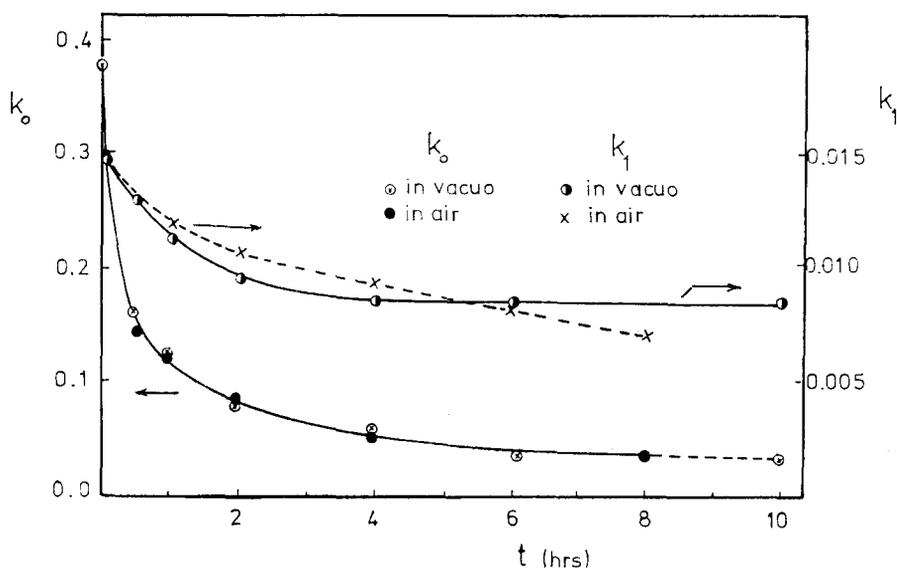


Fig. 2. Activity (k_0 and k_1) of unsupported cobalt catalyst as a function of time of sintering at 350°C in *vacuo* and in air.

Sintering of Unsupported Polycrystalline Cobalt Catalyst

TABLE 2. Activation energies of the decomposition of H_2O_2 over the surface of the cobalt catalyst samples sintered at 350°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.*, ~ 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°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 authors⁹ was used and the activity parameter (A) was adopted by converting k_0 values according to the equation described elsewhere.¹⁰ 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).¹⁰ 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 classification¹² 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.

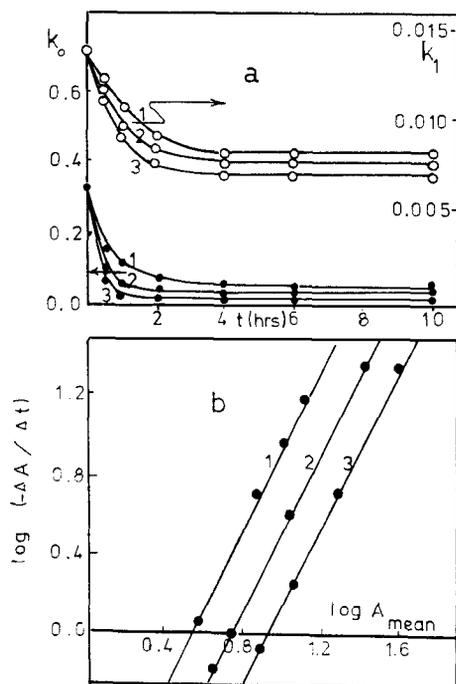


Fig. 3. (a) Sintering isotherms (k_0 and k_1 vs t_{sint}) for the unsupported cobalt catalyst at: 1-350°C, 2-400°C and 3-450°C.

(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.

Sintering of Unsupported Polycrystalline Cobalt Catalyst

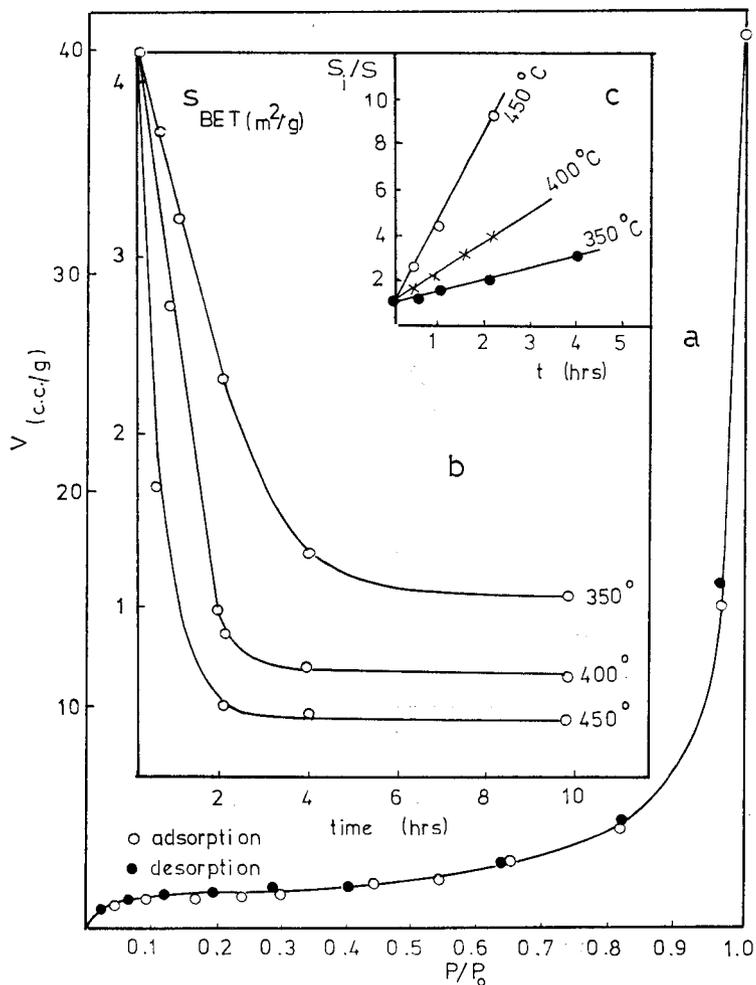


Fig. 4. (a) Adsorption-desorption isotherm of N_2 at $-196^\circ C$ for the freshly prepared cobalt catalyst (I).
 (b) Specific surface area of unsupported cobalt catalyst as a function of time of sintering at 350, 400 and $450^\circ C$.
 (c) Validity of the second-order equation (S_i/S vs t_{sint}).

On the other hand, it was assumed by Huttig¹³ 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,

S. A. HASSAN, M. ABDEL-KHALIK and H. A. HASSAN

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

where ΔE_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

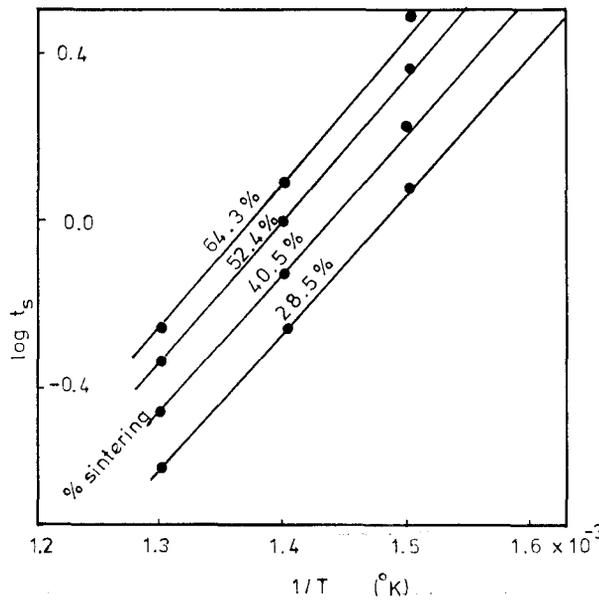


Fig. 5. Plots of $\log t_s$ vs $1/T$ ($^{\circ}\text{K}$) for different percentages of sintering.

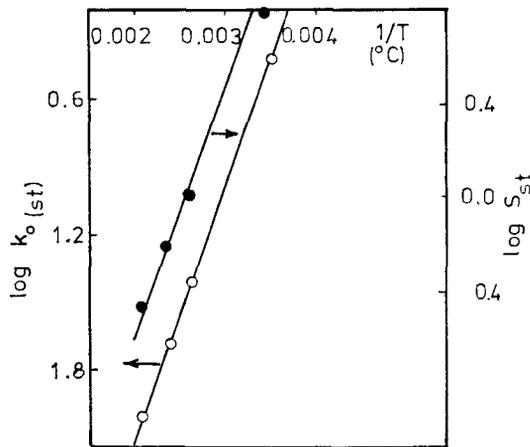


Fig. 6. Logarithmic relationship of the stationary values of activity (k_0, st) and surface area (S_{st}) with $1/T$ ($^{\circ}\text{C}$).

Sintering of Unsupported Polycrystalline Cobalt Catalyst

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).¹⁴⁾ 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°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 platinum⁹⁾ and the unsupported copper.¹⁵⁾ 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.

References

- 1) S. A. Hassan, M. Abdel-Khalik and H. A. Hassan, *J. Catal.*, **52**, 261 (1978).
- 2) H. E. Ries, Jr. and M. F. L. Johnson, *J. Phys. Chem.*, **57**, 865 (1953).
- 3) R. F. Laurentovich, M. T. Pusov and Yu. N. Artyukh, *Kinetika i Kataliz*, **7** (2) 254 (1966).

S. A. HASSAN, M. ABDEL-KHALIK and H. A. HASSAN

- 4) L. V. Milton and J. F. Reddy, *J. Catal.*, **7**(1), 76 (1967).
- 5) M. Kalina and J. Paseck, *Kinetika i Kataliz*, **10**(3), 574 (1969).
- 6) H. R. Akhmedli, *Zh. Obsh. Khim. (J. Gen. Chem. USSR)*, **19**, 462 (1949).
- 7) Ya. I. Gerasimov, V. P. Lebedev and V. P. Vendillo, *Practical Work in Physical Chemistry, Part II-Kinetika i Kataliz*, Moscow State University, Moscow, p. 78 (1963).
- 8) S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, **60**, 309 (1938).
- 9) S. A. Hassan, S. G. Fedorkina, G. I. Emelyanova and V. P. Lebedev, *Zh. Fiz. Khim. (USSR)*, **42**, 2507 (1968).
- 10) S. A. Hassan, F. H. Khalil and F. G. El-Gamal, *J. Catal.*, **44**, 5 (1976).
- 11) S. A. Hassan, *J. Appl. Biotechnol.*, **24**, 497 (1974).
- 12) S. Brunauer, P. H. Emmett, *J. Amer. Chem. Soc.*, **57**, 1745 (1935).
- 13) G. F. Huttig, *Kolloid Z.*, **99**, 262 (1942).
- 14) A. J. Dekker, *Solid State Physics*, 10th Ed., Macmillan Press, London, p. 73 (1975).
- 15) S. A. Hassan, *Bull. Sc. Ain Shams University, Cairo*, **16**, 251 (1972).