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Effect of Thermal Treatment on Catalytic and Surface Characteristics of a Diluted Supported Co/Al_2O_3 Catalyst

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The sintering of a diluted sample of Co/Al_2O_3 hydrocracking catalyst was investigated in the temperature range 300–450°C. Both activity (A) and metallic surface area (S_{Co}) measured through chemisorption of hydrogen showed essentially the same sintering trends: deactivation below 400°C and activation above this temperature. In the temperature region below 400°C, the activation energy of the sintering process, determined from both activity and chemisorption data, was found to be 14.70 kcal/mole. This is thought to be due mostly to surface diffusion. On the other hand, activation occurred at 450°C as a result of the increased migration of metal atoms on the support surface. This indicates that a solid solution with lowered melting point might be formed, and the sintering step becomes rate-determining in this temperature region. Changes in the total surface area and in the pore-size distribution of the support during the heat treatment were also studied.

INTRODUCTION

It is a known fact that solid catalysts are affected by thermal treatment to varying extents. In supported catalysts the extent to which sintering may take place is markedly dependent on the amount of active component supported on an inert carrier. With the increased commercial importance of supported catalysts of low metal concentrations, the physical structure of such catalysts has become of considerable interest.

Cobalt is one of the known catalysts which are normally used under high temperature conditions. Several investigations on supported cobalt catalysts have shown that cobalt deposited on an inactive carrier, e.g., asbestos, Cr_2O_3, and Al_2O_3, is more active than pure cobalt (*1*). Agronomov and Mischenko (*2*) studied cobalt–alumina catalysts containing various proportions of cobalt. They noticed that, in hydrogenation of cyclohexene, the most active catalyst was the one containing 36.6 mol% of cobalt while the catalysts containing 1.7, 3.5, and 8.3 mol% of cobalt were completely inactive. When the amount of cobalt was increased, especially from 36.6 to 100%, a strong decrease in the total adsorption capacity of the catalyst resulted. From the pore size distribution curves, it was found that the most active catalyst (36.6 mol% Co) had the widest pores.

According to Hiroshi and Etsurs (*3*), the chemical state of cobalt in the supported catalysts could be classified into two types: one in which cobalt is not combined with the carrier but remains free on its surface and another where cobalt forms a complex with the carrier and resists reduction by hydrogen. Specifically for the cobalt–

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alumina system, it was noticed (*4*) that during dehydration the adsorbed metal ions become incorporated into the alumina lattice forming the magnetically dilute δ-phase which was assumed to be formed at low metal concentrations. On the other hand, a β-phase consisting mainly of metal oxide was found to be formed during the dehydration and subsequent decomposition of the occluded solution of higher metal concentration.

The sintering of supported cobalt catalysts was also studied by several investigators. For example, in a recent study (*5*) on the sintering of cobalt supported on MoO films on Al_2O_3 carrier, the changes in the surface area during the heat treatment have been related to two processes: (1) surface diffusion occurring below 800°C and (2) volume diffusion occurring above this temperature. The activation energy for the process occurring below 800°C was 35 kcal/mole and for the process occurring above this temperature it was 85 kcal/mole. These results supported the previously published idea of Roberts (*6*) that the extent of sintering depends on the mechanism of diffusion. This extent was found also to depend on the ratio of the sintering temperature to the melting point of the oxide (*7*).

Similarly, the behavior of cobalt oxide was investigated during calcining a mixture of Al_2O_3 and CoO at 500–800°C (*8*). It was found that the formation of cobalt aluminate begins at temperatures higher than 850°C. At lower temperatures, oxidation and reduction of supported cobalt oxide occurs by the same process as that operating with bulk CoO.

A study of the effect of thermal treatment on the structure of cobalt catalysts, supported on a number of carriers, was carried out by Guyer *et al.* (*9*). This study has shown that the strongest stabilizing effect occurred by using wide-porous silica. Treatment of this catalyst up to 700°C did not lead to a measurable change in structure and surface area. In the case of microporous silica, the change in structure and the decrease in surface area were much more pronounced. Moreover, the same authors explained the stabilizing effect of the porous silica by the formation of a $Co–SiO_2$ complex, which prevents the thermal migration of cobalt atoms.

Analysis of the literature data indicates that insufficient attention has been paid to the sintering of diluted supported cobalt catalysts, which undoubtedly is of considerable economic importance. The present study was thus undertaken to follow the changes in physical and textural parameters taking place during the sintering of a very diluted sample of a Co/Al_2O_3 hydrocracking catalyst and to study the kinetics of the sintering process itself. The sintering effects imparted to the catalyst involved determination of catalytic activity in a simple model reaction and measurement of specific surface area and degree of metal dispersion by means of gas adsorption techniques. The mechanisms of sintering, followed either from activity parameters or from surface changes, were supplemented by electron microscopic measurements.

EXPERIMENTAL METHODS

Catalyst. A very diluted sample corresponding to 0.453 wt% of cobalt was prepared by the impregnation, in conventional ways, of the γ-alumina support with the appropriate quantity of the decomposable cobalt nitrate solution, followed by stirring for 14 hr. The alumina support was previously heated at 650°C to eliminate any changes in its surface characteristics during the sintering study. After fiteration and drying for 24 hr at 110°C, the sample was reduced in flowing pure hydrogen for 20 hr at 300°C (*1*). This procedure resulted in good reproducibility of the adsorption and catalytic activity measurements.

The fractional degree of coverage of the support surface (α) was determined from

the knowledge of the specific surface area of the support and from the amount of cobalt adsorbed on the surface by using the following equation (*10*):

$$\alpha = \frac{\sigma_{Co} \cdot N_{Co}}{S},$$

where σ_{Co} is the cross-sectional area of one cobalt atom taken as 6.25×10^{-20} m^2 when atomic radius is assumed to be 1.25 Å, N_{Co} is the number of cobalt atoms adsorbed per gram of support, and S is the surface area of alumina support in square meters per gram. It was found that α in this case equals 0.017, i.e., only 1.7% of the total surface of the support was covered with cobalt atoms, assuming a monoatomic dispersion over the support.

Sintering technique. The sintering study was carried out *in vacuo* using a volumetric apparatus of a conventional design (*11*).

With the aim of stabilizing a freshly prepared catalyst, evacuation for 1.5 hr at 300°C in a hydrogen atmosphere was adopted as the standard pretreatment.

The pretreated catalyst was heated *in vacuo* for varying times, namely, 0.5, 1, 2, 4, and 6 hr at the required temperatures. The present study was carried out in the temperature range 300–450°C within which most of the industrial cobalt catalysts possess their maximum activity.

Determination of catalytic activity. The activity of the freshly prepared catalyst and of different sintered samples were tested with the aid of a simple model reaction, namely, liquid-phase decomposition of hydrogen peroxide.[2] The reaction was found to obey first-order kinetics. From the results of gasometric measurements of the volume of evolved oxygen, V_{O_2}, and the half-life, $t_{\frac{1}{2}}$, the rate constant (k) was evaluated. The rate constant ($k_{H_2O_2}$) was taken as a measure of the catalytic activity (A). It was occasionally preferred to use the specific activity parameter (a), which denotes the number of molecules of H_2O_2 decomposing per second per gram of catalyst (*13*).

Determination of specific surface area and pore-structure analysis. Adsorption–desorption isotherms of nitrogen were measured at −195°C using a conventional volumetric apparatus. Specific surface areas were calculated from the isotherms by applying the BET equation (*14*). The pore structure was analyzed by using the corrected modelless method (*15*).

Determination of metallic surface area and degree of metal dispersion. The degree of dispersion of cobalt, supported on the surface of alumina, was estimated by means of chemisorption of pure hydrogen at room temperature (*16*). The technique adopted is based on minimizing adsorption on the support and maximizing adsorption on the metal (*17*). This was achieved by measuring adsorption on a nonmetallized support and subtracting this from the total adsorption on the catalyst, giving the so-called "net adsorption." The net adsorption was simply converted into degrees of dispersion [H]/[Co], which is considered as the number of atoms of hydrogen adsorbed per cobalt atom. The specific surface area of supported cobalt could thus be calculated by the use of the following equation (*16*):

$$S_{Co} = \frac{N \cdot \sigma_{Co}}{A_k} \times \frac{[H]}{[Co]},$$

where N is Avogadro's number, A_k is the atomic weight of cobalt, σ_{Co} is the cross-sectional area of cobalt atom (6.25×10^{-20} m^2), and [H]/[Co] is the degree of dispersion.

From the first approximation that all cobalt crystallites are ideal cubes of uniform size with one face in contact with the support and the remaining five faces exposed, the average size of cobalt particles

[2] Although this reaction is not a typical one for cobalt catalysts, its simplicity was required in correlating the catalytic activity with other surface and textural parameters (*12*).

could be determined by the use of the following equation (*18*):

$$a_e = \frac{5}{S_{Co} \cdot \rho_{Co}},$$

where a_e is the particle size, ρ_{Co} is the density of cobalt, and S_{Co} is the surface area of supported cobalt, calculated from chemisorption of hydrogen.

Electron microscopic studies. The microstructural changes of the various catalyst samples were investigated using an electron microscope, Type JEM-6C, manufactured in Japan, applying the suspension technique. The maximum original magnification power was 20,000 ×.

RESULTS AND DISCUSSION

(a) *Catalytic Activity as a Function of Time and Temperature of Sintering*

The sintering isotherms represented in Fig. 1 show the changes of catalytic activity, expressed as a first-order velocity constant ($k_{H_2O_2}$), with time of sintering at 350, 400, and 450°C. It is clear that at a given temperature, the activity decreases with time of sintering, achieving certain constant values characteristic for the stationary state at this temperature. The isothermal stationary activity at 450°C is much higher than that obtained either at 350 or at 400°C, indicating that some sort of activation takes place at this temperature. The phenomenon of activation has been observed previously in the case of supported Pt–Al_2O_3 (*19*), Ag–SiO_2 (*20*), and Pt–SiO_2 (*21*).

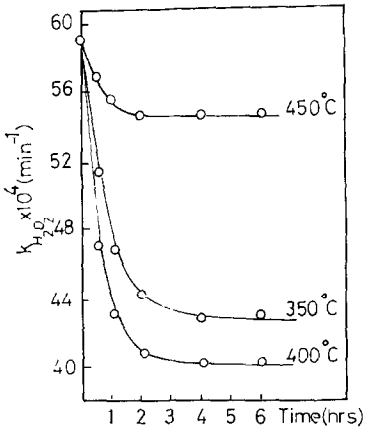

FIG. 1. The catalytic activity of a diluted Co/Al_2O_3 catalyst, measured in H_2O_2 decomposition reaction, as a function of time of sintering at different temperatures (sintering isotherms).

The kinetic results of the deactivation process, taking place in the temperature region below 400°C, were treated following the method previously described by Hassan *et al.* (*19*). This treatment showed that the process of sintering, in the present case, follows an unrealistic higher order mechanism ($n_{sint.} > 7$).[3]

The calculated activation energy of the sintering process, assuming that the Arrhenius equation can be applied, was found to be 14.70 kcal/mole.

From the obtained results, two regions of activity seemed to exist: (a) deactivation or sintering region, below 400°C, and (b) activation region, occurring above this temperature. Moreover, it seems that the high-order mechanism of sintering is dependent on some factors connected with the pore system, the metal dispersion, and the nature of the controlling reaction. The activation phenomenon itself may be interpreted in view of surface migration of the supported cobalt atoms, which increases with the increase of temperature of treatment.

(b) *Specific Surface Area as a Function of Time and Temperature of Sintering*

The soaked alumina support used in this investigation was prepared by applying the same technique utilized for the preparation of the parent Co/Al_2O_3 catalyst, i.e., by impregnation in bidistilled water of the same pH as that of cobalt solution, followed

[3] Similar previous studies (*19, 20, 21*) showed that the sintering process follows a second-order mechanism.

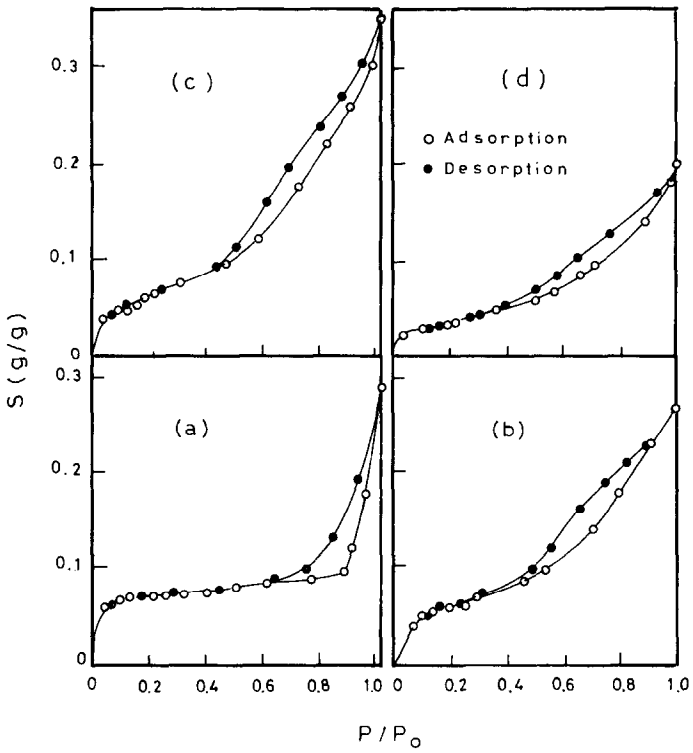

FIG. 2. Typical adsorption–desorption isotherms of N_2 on the surface of (a) original soaked alumina support; (b) γ-alumina, heated at 650°C; (c) a freshly prepared Co/Al_2O_3 catalyst sample; and (d) a Co/Al_2O_3 catalyst sample, sintered for 2 hr at 350°C.

by drying, calcination, and reduction in a stream of hydrogen. Typical adsorption–desorption isotherms of nitrogen on the surface of some selected samples, namely, the alumina support (soaked and heated at 650°C), freshly prepared Co/Al_2O_3 catalyst, and one sintered sample, are illustrated in Fig. 2. All the isotherms seem to belong to type II of Brunauer and Emmett's classification (*22*) forming closed hysteresis loops in all cases.

The adsorption data for all the samples under investigation are summarized in Table 1, including the BET-C constants and the specific surface areas (S_{BET}) calculated by applying the BET equation and the total pore volumes (V_p) estimated from the saturation values of the adsorption isotherms.

In Fig. 3, the calculated specific surface area (S_{BET}) is plotted versus time of sintering at different temperatures. It is evident from this figure that at each temperature a decrease in surface area takes place during the first few hours of sintering. In each case, this decrease is followed by a subsequent increase in the surface area. However, this decrease reaches its maximum value at a characteristic time of sintering. The time required to reach the minimum surface area is lowered as the temperature of thermal treatment is increased.

(c) *Pore-Structure Analysis of Freshly Prepared and Sintered Catalyst Samples*

Several investigators offered reference *t*-curves for the adsorption of nitrogen, e.g., Mikhail *et al.* (*23*), de Boer *et al.* (*24*), Sing *et al.* (*25*) and Cranston and Inkley (*26*). The appropriate *t*-curves adopted for the adsorption of nitrogen on the studied

samples were chosen on the basis of BET-C constants, which in each case should be of the same order in both the reference t-curve and the catalyst sample under investigation.

The experimental adsorption curves were plotted as a function of the t-values; hence $V = f(t)$ instead of $V = f(p/p_0)$. In any normal case of multimolecular adsorption, the experimental points should, therefore, fall on a straight line passing through the origin. The slope of this line gives the surface area, S_t, according to the following equation $S_t = 10^4(V_e/t)$, where V_e is the volume of nitrogen adsorbed in milliliters per gram, and t is the statistical thickness in angstrom units. The agreement between S_{BET} and S_t is the main criterion for the correct choice of the t-curve used in the analysis (Table 2).

The pore analysis of all the samples under study (except the original soaked alumina) was carried out using the corrected modelless method (*15*), since only mesopores were detected. It was decided that the parallel plate model can reasonably describe the shape of pores, for which the suffix (pp) was used.

In soaked alumina, both meso- and micropores were detected. In this case the

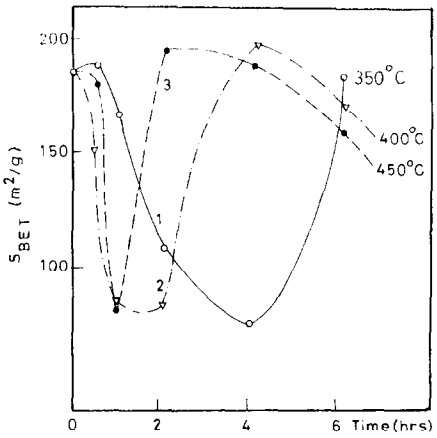

FIG. 3. Variation of BET-specific surface area of Co/Al_2O_3 catalyst during heat treatment at different temperatures.

TABLE 1

Adsorption Data of Nitrogen on the Surfaces of Alumina Support and Different Samples of Co/Al_2O_3 Catalyst

Temperature of sintering (°C)	Time of sintering (hr)	BET-C constant	S_{BET} (m^2/g)	V_p (ml/g)
Original (soaked) alumina		67	204.0	0.323
—	—			
γ-Alumina, heated at 650°C		171	171.0	0.371
—	—			
—	—			
Freshly prepared Co/Al_2O_3 catalyst		125	187.3	0.439
—	—			
Sintered catalyst				
350	0.5	61	190.8	1.144
	1	104	168.0	0.392
	2	53	110.0	0.208
	4	59	78.8	0.235
	6	94	186.3	0.618
400	0.5	113	153.7	0.409
	1	67	86.9	0.238
	2	138	84.5	0.278
	4	58	192.8	0.562
	6	81	172.3	0.562
450	0.5	75	181.5	0.547
	1	206	84.6	0.262
	2	89	197.0	0.759
	4	61	190.6	0.634
	6	87	160.0	0.429

TABLE 2

Characteristics of Pore Structure of γ-Alumina Support and Different Samples of Co/Al_2O_3 Catalyst

Temperature of sintering (°C)	Time of sintering (hr)	S_t (m^2/g)	$S_{cum.pp}$ (m^2/g)	$V_{cum.pp}$ (ml/g)
Original (soaked) alumina[a]		204.0	205.8	0.347
—	—			
γ-Alumina, heated at 650°C		166.0	160.3	0.365
—	—			
Freshly prepared Co/Al_2O_3 catalyst		191.0	189.9	0.442
—	—			
Sintered catalyst				
350	0.5	194.8	190.2	1.123
	1	168.0	171.8	0.408
	2	107.0	109.4	0.218
	4	72.0	66.5	0.225
	6	185.0	180.8	0.598
400	0.5	153.0	160.0	0.409
	1	81.0	86.6	0.234
	2	85.0	82.1	0.274
	4	190.0	188.5	0.559
	6	172.5	169.9	0.559
450	0.5	181.0	180.3	0.540
	1	88.0	80.2	0.259
	2	198.0	198.9	0.749
	4	191.0	189.3	0.634
	6	160.0	158.4	0.429

[a] S_n = 171.7 m^2/g; $S_{w^{pp}}$ = 34.1 m^2/g; V_n = 0.0676 ml/g; and $V_{w^{pp}}$ = 0.0356 ml/g.

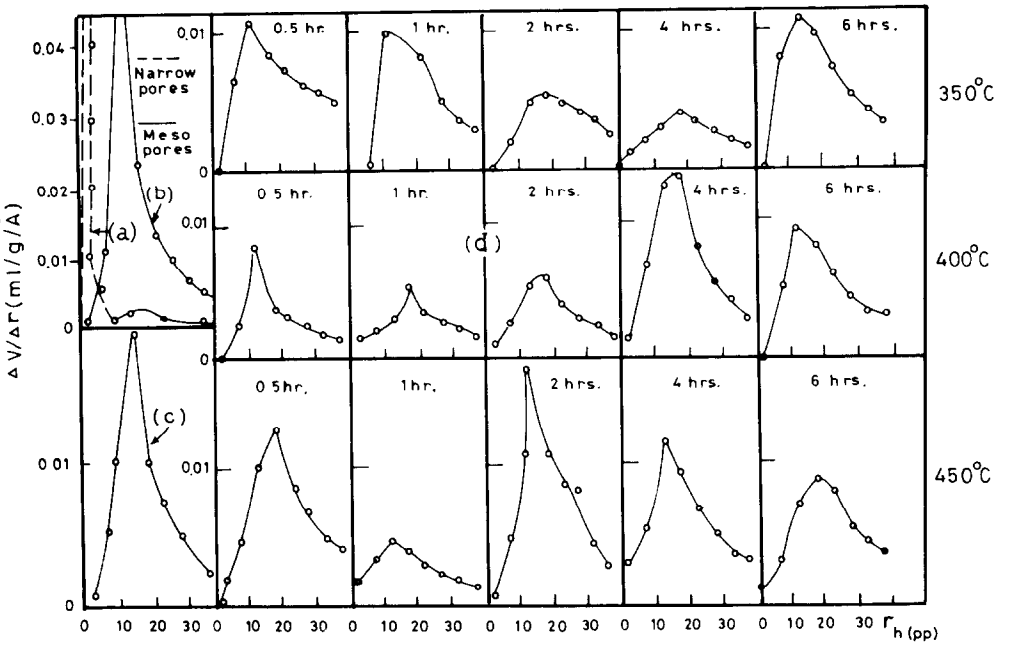

FIG. 4. Pore-size distribution curves for (a) original soaked alumina; (b) γ-alumina, heated at 650°C; (c) freshly prepared Co/Al_2O_3 catalyst; and (d) various samples of Co/Al_2O_3 catalyst, sintered for different times at 350, 400, and 450°C.

micropores were analyzed by the use of the MP method (*23*).

The pore-volume distribution curves for the various samples are shown in Fig. 4, representing the distribution of pore volumes ($\Delta V/\Delta r$ in milliliters per angstrom) as a function of the mean hydraulic radius ($\bar{r}_{h(pp)}$ in angstroms), assuming a parallel plate model. The collected data of pore structure analysis are also given in Table 2, where S_n and V_n represent the surfaces and the volumes associated with micropores whose shape has no effect on the results of the analysis and $S_w{}^{pp}$ and $V_w{}^{pp}$ represent the surfaces and the volumes associated with mesopores.

The results of pore-structure analysis showed that in soaked alumina, the micropores are characterized by a most frequent hydraulic radius of 3.5–4.0 Å. If these pores are considered to be parallel plates, as in the case of mesopores, then the width of these plates can be taken as 7–8 Å. In the alumina support initially treated at 650°C, as well as in the different samples of Co/Al_2O_3 catalyst, the micropores disappear and only the mesopores, characterized by a most frequent hydraulic radius of 13–15 Å, exist. By increasing the time of sintering at each temperature, the number of these mesopores undergoes the same changes occurring with the specific surface area.

It is to be noted that 2-hr treatment reflects the optimum sintering conditions, where both activity and surface area show parallel trends. This treatment is very similar to that reported recently for a Pt/Al_2O_3 catalyst (*13*).

From the foregoing discussion, it is clear that the sintering trends, judged from activity parameter and from surface area measurements, are widely different except with respect to the coincidence of the time of achievement of stationary activity with the time of maximum reduction in surface area.

TABLE 3

Chemisorption Data of Hydrogen on the Surface of Different Samples of Co/Al_2O_3 Catalyst

Temperature of sintering (°C)	Time of sintering (hr)	Net adsorption (ml/g_{Co})	H:Co ratio	Av particle size, a_e (Å)
Freshly prepared sample	—	0.524	0.306	29
Sintered catalyst				
350	0.5	0.386	0.225	39
	1	0.279	0.163	54
	2	0.181	0.106	84
	4	0.144	0.084	105
	6	0.090	0.053	168
400	0.5	0.336	0.196	45
	1	0.237	0.138	64
	2	0.154	0.090	98
	4	0.099	0.058	153
	6	0.058	0.034	262
450	0.5	0.443	0.258	34
	1	0.319	0.186	47
	2	0.210	0.123	72
	4	0.147	0.086	103
	6	0.112	0.066	135

(d) The Change of Degree of Metal Dispersion and Metallic Surface Area during Heat Treatment

Since the metal crystallite size in the catalyst under study is too small to be measured by the X-ray technique, it seems that chemisorption is the only approach to measure the metal dispersion.

The adsorption of hydrogen was measured at room temperature and was followed up to a pressure of 200 mm Hg.[4] The difference between the total adsorption on the catalyst and the adsorption on the corresponding support, under identical conditions, was taken as the net adsorption on the supported metal.

The results of chemisorption are summarized in Table 3, from which it is evident that at a given temperature the degree of metal dispersion of supported cobalt decreases by increasing the time of heating, whereas the average particle size increases continuously.

The change of calculated metallic surface area (S_{Co}) with time of sintering at different temperatures is shown in Fig. 5a. The data obtained at 450°C are higher than those obtained at other temperatures. The analysis of the data at 350 and 400°C showed that the rate of reduction of metallic surface area follows the second-order equation. By applying the Arrhenius equation in this case, the energy of activation of the sintering process was found to be 14.72 kcal/mole. This is in excellent agreement with the value obtained from activity data (viz., 14.70 kcal/mole).

The second-order mechanism can be interpreted along the same lines mentioned before in literature (*13, 27–29*). However,

[4] Adsorption of hydrogen at liquid nitrogen temperature gave much higher results, which seemed to be due to the marked contribution of physisorption at this temperature.

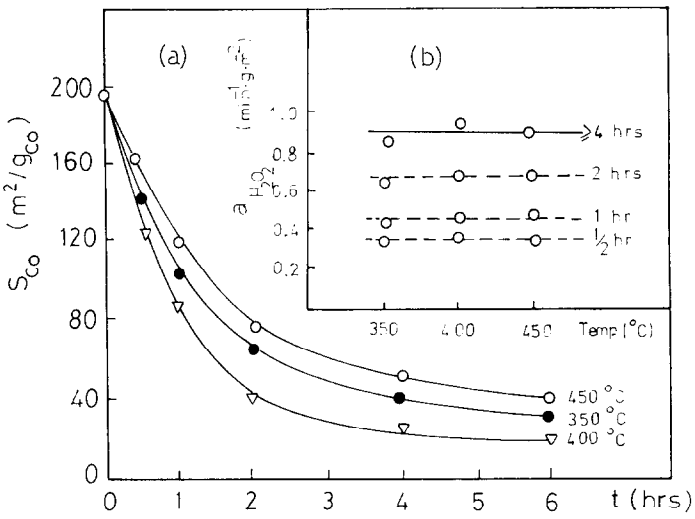

FIG. 5. (a) Specific surface area of supported cobalt (S_{Co}), as a function of time of sintering at different temperatures. (b) Variation of specific activity ($a_{H_2O_2}$) with sintering temperature.

the high order of sintering, obtained from the activity data, supports the idea of Ruckenstein and Pulvermacher (*30*), namely, that the sintering process in this temperature region (i.e., <400°C) is almost diffusion controlled.

From the change of chemisorption data with sintering temperature, it may be concluded that the sintering takes place only in the temperature region below 400°C, where both metallic surface area and degree of metal dispersion decrease and the average particle size shows a marked increase (viz., from 29 to 260 Å). At 450°C a marked decrease in the particle size is observed (viz., from 260 to 130 Å), which indicates dissociation of the already formed metal crystallites.

The variation of specific activity with temperature of sintering is illustrated in Fig. 5b. The specific activity ($a_{H_2O_2}$) is taken as the ratio between the activity ($k_{H_2O_2}$) measured in H_2O_2 decomposition and the metallic surface area (S_{Co}). It is evident that different specific activities are obtained depending on the time of sintering. The dashed lines show the nonequilibrium values of specific activity, obtained at times less than 4 hr. These nonequilibrium values indicate that when the time is increased, the reduction in surface area becomes much more pronounced than the loss in activity. However, at times >4 hr, the specific activity remains almost constant regardless of time and temperature of treatment. This seems to be due to attaining equilibrium values of activity and surface area (Figs. 1 and 5b).

The constancy of specific activity upon heating the catalyst for the same time at different temperatures indicates a good parallelism between the rates of reduction of surface area and loss of activity.

(e) *Electron Microscopic Study of the Investigated Samples*

It was reported previously (*7*) that three processes might occur during the sintering process: (1) adhesion, whereby separate particles become fritted together at points of contact; (2) surface diffusion, which is caused by movement of ions or atoms along the surface to form aggregates; and (3) lattice diffusion (or volume diffusion), building up a more or less perfect crystal lattice as a result of three-dimensional migration.

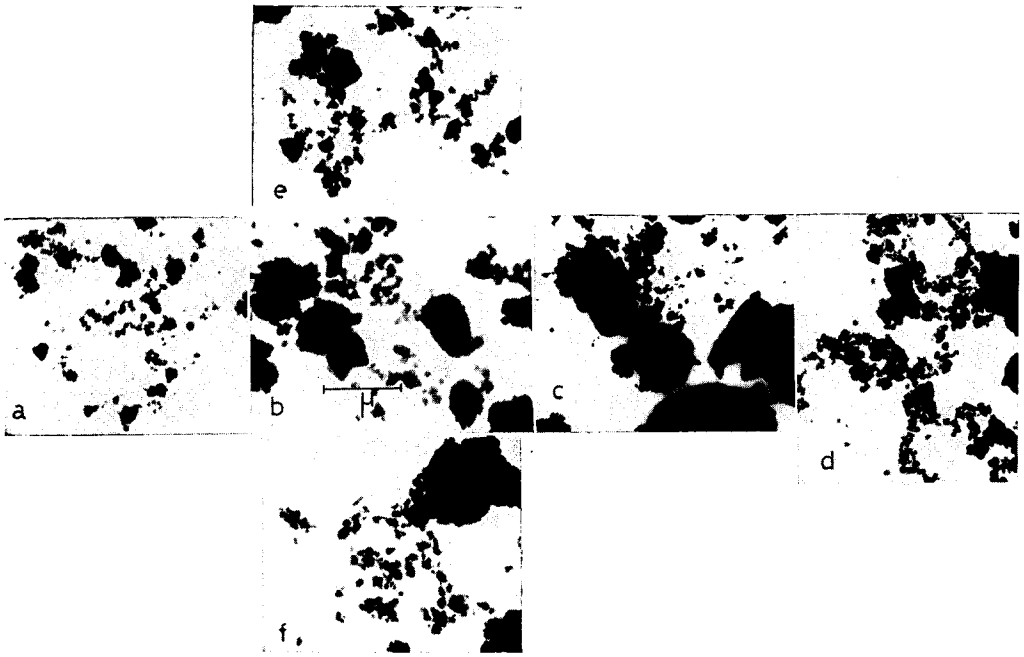

FIG. 6. Electron micrographs of Co/Al_2O_3 catalyst samples, sintered for (b) 2 hr at 350°C, (c) 2 hr at 400°C, (d) 2 hr at 450°C, (e) 0.5 hr at 350°C, and (f) 4 hr at 350°C. Electron micrograph (a) represents the microstructure of the freshly prepared catalyst sample.

In the same report it was also found that when the ratio of sintering temperature (T) to melting temperature (T_m) of a supported metal oxide equals 0.33–0.45, sintering proceeds via surface diffusion, whereas above Tamman's temperature (i.e., $> T/T_m = 0.45$), the operative mechanism is that of volume diffusion.

The electron micrographs of some selected samples shown in Fig. 6 indicate that by increasing the time of sintering at 350°C, the rate of recrystallization increases. These micrographs also show that the particle size increases when the catalyst is treated for 2 hr at 350 and 400°C, while it decreases, under the same conditions, at 450°C.

In conclusion, it is clear that below 400°C ($T/T_m < 0.42$) the activation energy of the sintering process, as judged from both activity and surface parameters, shows the same value, viz., 14.70 kcal/mole, indicating mainly surface diffusion, which causes the formation and the growth of cobalt crystallites (a_e) and, consequently, a decay of the exposed surface area of the metal (S_{Co}).

On the other hand, at 450°C, near Tamman's temperature ($T/T_m = 0.48$), activation took place as a result of the increased migration of supported cobalt atoms on the surface of the support. This may provide further support to the previously published idea of Dollimore and Rickett (*5*) which postulates that although this distinct change in activity and surface area is to be expected at $T/T_m > 0.5$, it appears that a small addition of an active component to the alumina surface causes this surface to behave as if it were a solid solution with a lowered melting point, leading to a consequent readjustment of the parameters relating to sintering. From the above, it seems that in this high temperature region (>400°C), the sintering step becomes, most probably, rate-determining.

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