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Active Surface of γ-Al_2O_3–Supported Co_3O_4

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Samples of Co_3O_4 deposited on two types of γ-Al_2O_3 with different textures are investigated. A kinetic method employing reduction by hydrogen is used to provide a differential determination of the transition metal oxide surface, and magnetic and XPS measurements are also employed. It is found that, depending on the concentration of the impregnating solution, the value of the surface area of supported Co_3O_4 passes through a maximum. The concentration at which a maximum surface area of the active phase should be expected has been calculated, and a good correlation has been found with the experimental value. It is established that the differences in the support texture characteristics such as specific surface area, pore volume, and pore size distribution affect the active phase distribution on the support surface, and hence the interaction between the active phase and the support. It is concluded that the amount of the Co_3O_4 phase formed and its surface area depend not only on the impregnating solution concentration and the preparation temperature but also on the support texture. © 1994 Academic Press, Inc.

INTRODUCTION

Many investigations (1–20) have been dedicated to γ-Al_2O_3-supported cobalt oxide catalysts. The application of a combination of reliable modern methods has allowed important conclusions to be drawn on the nature of the Co phases formed on the support surface and their distribution in Co/Al_2O_3 catalysts. It is known that during the catalyst preparation the cobalt ions diffuse into the structure of Al_2O_3 occupying octahedral or tetrahedral positions. As a result, mainly two types of cobalt-containing phases are formed: (i) surface phases of Co bonded to the support, which are difficult to reduce and which prevail at low Co concentrations and a high calcination temperature, and (ii) an easily reducible Co_3O_4 phase appearing above a definite Co concentration (about 2 wt%). The relative amounts of the Co phases depend on the concentration of Co ions and the final calcination temperature. The difference between the reduction temperatures of Co_3O_4 and the other Co-containing phases is often used for their identification and quantitative estimation. The phase where Co ions occupy tetrahedral positions in the Al_2O_3 lattice is usually assumed to be $CoAl_2O_4$. There are different opinions concerning the existence of a Co_3O_4 phase, ranging from the assumption about initial saturation of the support surface with Co ions up to about 10% Co followed by formation of Co_3O_4 (10) to the assertion that almost the total amount of Co above 3–4% is included in the formation of Co_3O_4 (15–17). Obviously, the process is quite complicated and is affected not only by the concentration of Co and the calcination temperature but also by other factors such as the preparation method, and, probably, the support texture.

A series of our investigations deal with determination of the active surface of Co_3O_4 supported on silica gel. A kinetic method has been used for the differential determination of the transition metal oxide surface by measurement of the rate of its reduction with a gaseous reagent (21). The application of this method to copper oxide (22) and cobalt oxide (23, 24) catalysts deposited on silica gel has allowed investigation of the effect of the impregnating solution concentration and the texture characteristics of the support on the surface area of the supported oxide phase. Theoretical conclusions (25) have been drawn concerning the cases when formation of a large number of crystal nuclei and a maximum surface area of the supported active phase may be expected. These are the cases when (i) the crystallization of the active phase begins after evaporation of the liquid condensed in the capillaries of the support, i.e., in the adsorption layer, remaining on the support surface, and (ii) the support used is monoporous or has a narrow pore size distribution curve. Such a texture presupposes simultaneous crystallization in the whole bulk and formation of a large surface of the supported active phase. It is shown that using the nitrogen adsorption isotherm of the support it is possible to predict the optimum concentration of the impregnating solution for obtaining a maximum size surface of the active phase. A good agreement between the theoretically calculated and the experimentally obtained maxima in the size of the active surface is established.

Knowledge of the active surface of supported catalysts

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is of special importance due to the direct connection between the catalytic activity and the active phase surface. From this viewpoint, the kinetic method may be very useful for the choice of optimum preparation conditions of effective catalysts. Without determining the amount of the oxide, the method gives information on the surface area obtained under definite conditions. Thus, the increase in amount of the active phase above a certain concentration is associated with an increase in size of the crystallites and a decrease of the active surface, which is registered by the kinetic method.

Taking into account the data in the literature on γ-Al_2O_3-supported cobalt oxide catalysts and the possibility of determining the surface area of supported Co_3O_4 by the kinetic method, it is of interest to check the formation of a Co_3O_4 phase during the synthesis of this kind of catalyst and to determine the surface area of this phase and the factors on which it depends. Simultaneously, the validity of the prediction concerning the concentration of the impregnating solution at which a maximum surface area of the supported phase is formed can be checked. Additional information on this problem is obtained by magnetic and XPS measurements.

EXPERIMENTAL

I. Supports

Two types of γ-Al_2O_3 were used: (a) extrudate (labelled as B) from the Higher Chemical Technological Institute in Bourgas, Bulgaria (26), and (b) γ-Al_2O_3 (Rhône Poulenc), denoted as RP.

II. Samples

Four series of samples were obtained by impregnation of the two types of Al_2O_3 (B and RP) with $Co(NO_3)_2 \cdot 6H_2O$ solutions. Concentrations of 2, 5, 7.5, 10, and 15 g Co in 100-ml solutions were used. The supports were granules and 0.3–0.6 mm fractions. The final calcination proceeded at 823 K for 3 h. Chemical analysis was carried out with a Pye Unicam SP 90 B atomic absorption spectrometer.

For the sake of simplicity, the samples with granulated supports are denoted B_g and RP_g, respectively, while the fractions are labelled B_f and RP_f, respectively. The figure after the symbol shows the concentration of the impregnating solution.

The standard Co_3O_4 for selective determination of the active surface was obtained from $Co(NO_3)_2 \cdot 6H_2O$ by decomposition at 823 K for 6 h.

III. Characterization of the Samples and the Supports

1. Determination of the texture characteristics. Nitrogen adsorption isotherms were obtained at 77 K and the specific surface areas were determined by the BET method. The total pore volume and the relative pressure at the beginning of hysteresis $(p/p_0)_h$ were also found. The pore size distribution was established by the Pierce method (27).

2. Active surface determination. The measurements were performed in a specially constructed static high-vacuum apparatus (28). The sample investigated was heated for 1 h under a vacuum of 3×10^{-5} Torr (1 Torr $= 133.3$ N m^{-2}) at 623 K. Hydrogen was used as a reducing gas. The reduction kinetics were determined at 623 K and a constant hydrogen pressure of 1.1×10^{-1} Torr in the reaction volume. The experimental conditions were chosen so as to ensure the required low reduction degree.

Inertness of the support towards the reducing gas and preservation of the active phase specificity during its deposition on the support are indispensable conditions needed for the application of the method. Inertness of Al_2O_3 with respect to hydrogen was checked and confirmed. The second requirement on which the method is based was checked by comparing the kinetic parameters (E_a, m, and n) in the reduction rate equation $V = k \cdot e^{-E_a/RT} S^m P^n$ for both supported and unsupported oxides (E_a, activation energy; S, Co_3O_4 surface area; P, pressure of the reducing gas; m and n, orders of magnitude with respect to surface and pressure). In certain cases we have obtained good agreement between the kinetic parameters of standard and supported Co_3O_4 [E_a standard = 71 kJ/mol, E_a supported = 73 kJ/mol; m standard = 1.1, m supported = 1.3; n standard = 0.4, n supported = 0.5], which permits assuming that the measurement of the surface area of supported Co_3O_4 is correct.

The "reduction rate–surface" calibration curve for standard Co_3O_4 was taken under the above experimental conditions. The specific surface area of the standard sample (5.0 m^2/g) was determined by the BET method. The surface area of supported Co_3O_4 was found from the experimental data on the reduction rate of the sample investigated using the linear calibration.

In the literature there are different opinions on the reduction of Co_3O_4 with hydrogen in Co/Al_2O_3 catalysts. Stranick *et al.* (17) have assumed that at 673–873 K only Co_3O_4 is reduced, while Arnoldy and Moulijn (6), using TPR, have established the reduction temperature as 600 K for Co_3O_4, 750 K for the Co^{3+} surface phase, and 900 K for the Co^{2+} surface phase. It is evident that at a temperature of 623 K, at which the active surface of the samples investigated is determined, only Co_3O_4 would be reduced.

To establish the possible effect of the presence of $CoAl_2O_4$ on the reduction rate of Co_3O_4 in the supported samples, we performed a test: reduction of $CoAl_2O_4$ synthesized from stoichiometric amounts of Al_2O_3 and

$Co(NO_3)_2$ using a solid phase reaction at 1473 K. The results obtained confirmed the data from the literature according to which the reduction of $CoAl_2O_4$ proceeds at a temperature much higher than that of Co_3O_4 reduction, on the basis of which it may be assumed that the presence of $CoAl_2O_4$ in the samples investigated would not affect the reduction rate of supported Co_3O_4.

3. Magnetic measurements. The magnetic measurements were made in a Faraday-type apparatus. The specific magnetic susceptibility was studied from liquid-nitrogen temperature to 573 K.

4. XPS measurements. XPS measurements were carried out in a UHV chamber with an ESCALAB II electron spectrometer at a residual gas pressure of 7.5×10^{-11} Torr. An Mg K_α radiation source was used. The resolution of the instrument was 1.1 eV. The powder samples were pressed in stainless-steel holders and the tablets obtained had a diameter of 12 mm and a thickness of 0.5–1 mm. The C 1*s* peak corresponding to an energy of 285.0 eV was used for calibration of the binding energy of the other photoelectron peaks. Due to their low intensity, the Co $2p_{3/2}$ spectra have been smoothed by a procedure including spline approximation. The Al/Co atomic ratio was calculated from the areas of the Co $2p_{3/2}$ and Al 2*p* peaks corrected by the corresponding photoionization cross sections (29). Samples from the two series B_f – 7.5, B_f – 15, and RP_f – 7.5, RP_f – 15 were investigated.

5. Determination of the impregnating solution concentration at which a maximum active surface area should be expected. According to the method proposed (25), a maximum active surface area should be expected at an impregnating solution concentration C_M determined from the formula

$$C_M = \frac{C_n \cdot V_{ads}}{V_p},$$

where C_n is the saturation concentration of the impregnating solution at about 373 K, V_{ads} denotes the adsorbed amount of the liquid at the beginning of hysteresis, and V_p, the total pore volume of the support. V_{ads} depends on the specific surface area of the support S_0 and the thickness of the adsorption layer at the beginning of hysteresis t_{ads}, where $V_{ads} = S_0 \cdot t_{ads}$. The determination of t_{ads} is performed using the standard *t*-curve (30, 31) after finding experimentally the relative pressure of the beginning of hysteresis in the nitrogen adsorption isotherm $(p/p_0)_hN_2$. The correlation between $(p/p_0)_hN_2$ and $(p/p_0)_hH_2O$ is utilized for establishing the relative pressure at the beginning of hysteresis in the water vapour adsorption isotherm.

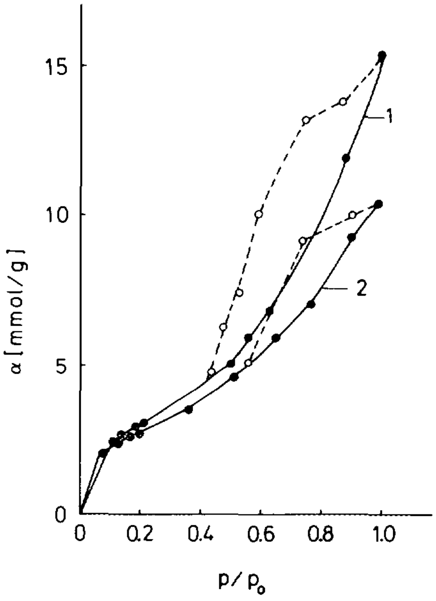

FIG. 1. Nitrogen adsorption isotherms of the supports used: (1) γ-Al_2O_3 (B) and (2) γ-Al_2O_3 (RP).

RESULTS

1. Texture Characteristics

The main results in Figs. 1 and 2 (curves 1 and 2) and Table 1 exhibit certain differences in texture for the two types of Al_2O_3. Support B has a much larger specific surface area and total pore volume than does support RP. Irrespective of the fact that both supports can be characterized as polydisperse, the pore size distribution curve for Al_2O_3 (RP) has a much narrower maximum.

The deposition of the active phase affects the support texture, producing a decrease in total surface area and pore volume (Table 1) and a change in the shape of the

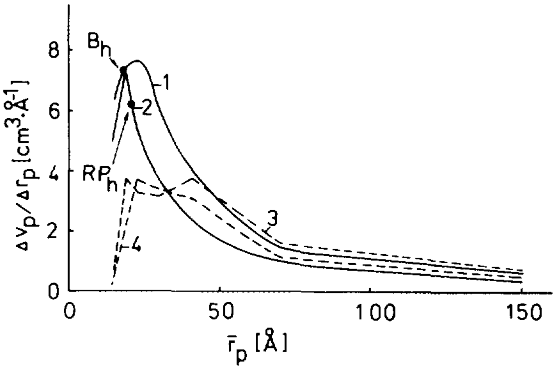

FIG. 2. Pore size distribution of the supports and the supported samples: (1) γ-Al_2O_3 (B), (2) γ-Al_2O_3 (RP), (3) B_f-15; and (4) RP_f-15. B_h, RP_h—beginning of the adsorption hysteresis.

TABLE 1

Texture Characteristics of Supports and Catalysts

Sample	C^a (g Co/100 ml)	Co (wt%)	S_{BET} (m^2/g)	V_p^b (cm^3/g)	ΔV_p (cm^3/g)
B	—	—	262	0.52	—
B_g-2	2	2.0	198	0.49	0.03
B_g-15	15	9.2	180	0.47	0.05
RP	—	—	226	0.40	—
RP_g-2	2	1.8	188	0.38	0.02
RP_g-15	15	7.0	160	0.35	0.05

[a] Impregnating solution concentration.
[b] Total pore volume.

pore size distribution curves (Fig. 2). Deposition of the cobalt is seen to be associated with a substantial decrease in contribution of the pores with radii ranging from 15 to 30 Å. The change in pore volume after deposition of the active phase obtained from the adsorption isotherms exceeds the theoretical values of the volume of the supported phase (e.g., Co_3O_4) by one order of magnitude. Therefore, in addition to the filling of pores by the active phase, a large part of their volume may be blocked. This is also observed, although to a lower degree, at the highest concentration of supported cobalt.

II. Deposition of the Active Phase Depending on the Texture of the Support

It should be pointed out that (i) the Co amount deposited on B is larger than on RP, which is obviously due to the larger pore volume of the support B, and (ii) the amount deposited on granulated supports is smaller than on fractions, which can be attributed to the irregular impregnation of the granules due to diffusion. This is especially pronounced with samples obtained by impregnation of RP granules with high Co concentrations. It is clear that not only the pore volume but also the support texture considerably affects the amount of deposited Co. The pore size distribution in the case of the support B favours a more uniform impregnation of the granules. The diffusion due to the texture of the RP support is the reason for the reduced amount of deposited Co especially at high impregnating solution concentrations.

III. Active Surface

Experiments aimed at determination of the active surface area S_a of supported samples have shown that even at the lowest concentration of supported cobalt (1.8 wt%), reduction of the samples takes place, i.e., there is a Co_3O_4 phase. It is known (6) that at T = 623 K, at which the active surface is determined, only Co_3O_4 is reduced. Taking into account that the final heating temperature (823 K) is the reason for the presence, in the surface layers of the supported samples, of other cobalt-containing phases in addition to Co_3O_4, one should present the measured Co_3O_4 surface area per gram of supported Co and per gram of sample.

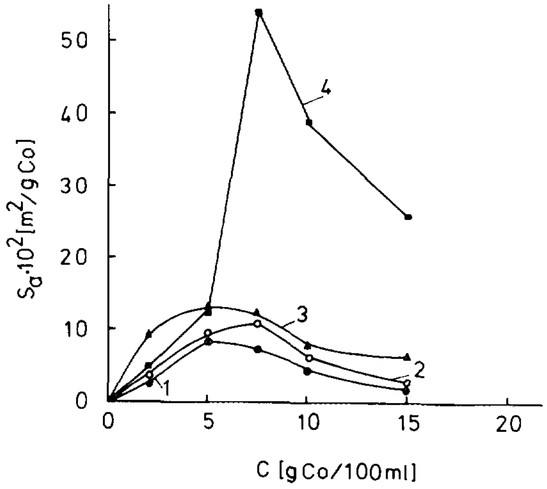

FIG. 3. Dependence of the active phase surface (S_a, m^2/g supported Co) on the concentration of the impregnating solution (C, g Co/100 ml). Samples deposited on (1) B_f, (2) RP_f, (3) B_g, and (4) RP_g.

The dependence of the surface area of the supported Co_3O_4 on the impregnating solution concentration is given in Figs. 3 and 4. The curves for both types of Al_2O_3 pass through a maximum. A similar shape of the dependence has been obtained in previous investigations for silica-gel-supported Co_3O_4 and CuO samples, where the presence of a maximum has been associated with the existence of a concentration of the impregnating solution at which a maximum active surface is obtained. To elucidate how

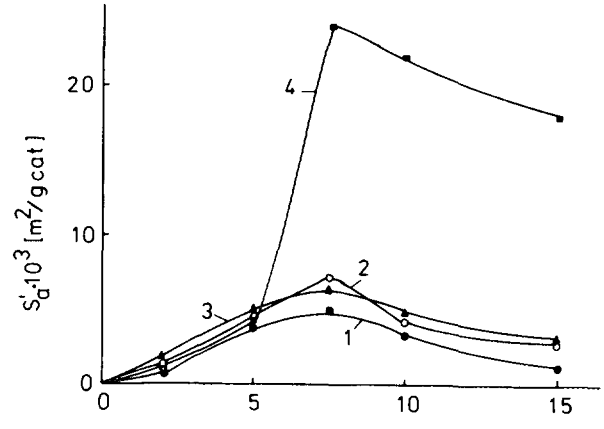

FIG. 4. Dependence of the active surface of supported samples (S'_a, m^2/g sample) on the concentration of the impregnating solution (C, g Co/100 ml). Samples deposited on (1) B_f, (2) RP_f, (3) B_g, and (4) RP_g.

TABLE 2

Data from Determination of the Impregnating Solution Concentration at which a Maximum Active Surface Area Occurs

Support	$(p/p_0)_h N_2^a$	$t_{ads} N_2^b$ (Å)	$(p/p_0)_h H_2O^c$	$t_{ads} H_2O^d$ (Å)	V_{ads} (cm^3/g)	C_M^{theor} (wt%)	C_M^{exp} (g Co/100 ml)
B	0.43	5.94	0.40	4.68	0.12	5.9	5.0
RP	0.50	6.50	0.46	5.02	0.11	7.1	7.5

[a] Relative pressure at the beginning of hysteresis of the nitrogen adsorption isotherm.

[b] Thickness of the adsorption layer at $(p/p_0)_h N_2$.

[c] Relative pressure at the beginning of hysteresis of the water vapour adsorption isotherm.

[d] Thickness of the adsorption layer at $(p/p_0)_h H_2O$.

far the maxima observed here can be ascribed to earlier conclusions (25), t_{ads}, V_{ads}, and C_M have been calculated. The data are presented in Table 2. Comparison of the theoretically calculated concentration C_M with the impregnating solution concentration, at which a maximum surface area of the supported Co_3O_4 is experimentally observed (Fig. 3), reveals good agreement for the two series of samples (Table 2, columns 7 and 8). It is obvious that for RP-supported samples with impregnating solution concentrations above 7 g Co/100 ml solution, the initial concentration exceeds C_M, which leads to a decrease in the surface of the supported active phase at the expense of an increase in size of the Co_3O_4 crystallites. The same concerns B-supported samples obtained at an impregnating solution concentration higher than 6 g/100 ml solution.

Figures 3 and 4 also show that larger active phase surfaces are obtained on RP regardless of the lower concentration of supported Co. However, curve 4 for samples on RP granules has a quite different shape. At an impregnating solution concentration of 7.5 g Co/100 ml, the active phase surface strongly increases.

Nevertheless, it should be noted that the Co_3O_4 surface area is very small. It is only 0.5–8% of the surface area of standard Co_3O_4. The fact that above 773 K a strong diffusion of Co ions into the lattice of Al_2O_3 begins (6, 14), and part of the supported Co is bonded to the support during the final heating of the samples, explains the small surface area of Co_3O_4 formed under these synthesis conditions. Evidently, another reason for the formation of a small active surface area is the blocking of a large part of the active phase in the pores of the support.

IV. Magnetic Measurements

Magnetic measurements provide information on the phases appearing during the deposition of cobalt oxides. If only a normal Co_3O_4 spinel is formed, the magnetic moment can be determined from the relationship

$$\mu_{eff}^2 = \mu_{eff}^2(Co^{2+})_{T_d} + 2\mu_{eff}^2(Co^{3+})_{O_h},$$

or $\mu_{eff}^2 = \mu_{eff}^2(Co^{2+})_{T_d}$ since $\mu_{eff}(Co^{3+})_{O_h} = 0$. It is known that $\mu_{eff}(Co^{2+})_{T_d} = 4.48$ BM (32). However, if two phases are formed, e.g., Co_3O_4 and $CoAl_2O_4$, the magnetic moment should increase, since part of $(Co^{3+})_{O_h}$ has passed into $(Co^{2+})_{T_d}$. The effective magnetic moment can be calculated if the Curie–Weiss law is observed, because in this case the necessary condition is $\theta(Co_3O_4) \approx \theta(CoAl_2O_4)$, where θ is the Weiss constant, or the presence of only a negligible amount of one of the phases. Our experiments have shown that for samples with a Co content up to 8 wt% the Curie–Weiss law is not valid. Above this value the law holds good. Table 3 shows the results obtained. If one assumes that the sample is two-phase ($\alpha Co_3O_4 + \beta CoAl_2O_4 = 1$), and the magnetic moments are calculated from the formula weight for Co_3O_4, then the following relationships will be valid:

$$\mu_{eff}^2(\exp) = (\alpha + \beta)\,\mu_{eff}^2(Co^{2+})_{T_d} + \gamma\,\mu_{eff}^2(Co^{3+})_{O_h}$$

$$\gamma/\alpha = 2 \quad \text{and} \quad \alpha + \beta + \gamma = 3.$$

Then $\alpha = 1.5 - \mu_{eff}^2(\exp)/40.14$. When $\alpha = 1$, $\mu_{eff} = 4.48$ BM, and when $\alpha = 0$, $\mu_{eff} = 7.76$ BM.

Obviously, with rising cobalt concentration, the magnetic moment decreases, which indicates that the relative content of Co_3O_4 also increases. In samples with a lower concentration of Co, the latter is present mainly as $CoAl_2O_4$ or another phase differing from Co_3O_4. The data on μ_{eff} indicate that the RP-15 sample contains the largest amount of Co_3O_4.

V. XPS Measurements

Figure 5 shows the Co $2p_{3/2}$ spectra of the supported samples. The binding energies of the main peaks are given in Table 3 where data from the literature on Co^{3+} and Co^{2+} ions and on Co_3O_4 are given for the sake of comparison. The Co^{3+} ions have a lower binding energy than that of Co^{2+} and a much lower intensity than the satellite peak which is situated at a larger distance from the main peak. It is evident that the Co $2p_{3/2}$ line of the samples (except

TABLE 3

Magnetic Moment (μ_{eff}), Weiss Constant (θ), and XPS Data

Sample	Co (wt%)	μ_{eff} (BM)	θ (K)	Co $2p_{3/2}$ BE (eV)	Al/Co atomic ratio	
					Theoretical	Experimental
B_f-7.5	7.1			781.2	14.8	67
B_f-10	8.5	6.60	−163			
B_f-15	12.4	5.88	−91	781.2	7.7	77
RP_f-7.5	6.7			781.5	15.6	68
RP_f-10	8.3	6.41	−109			
RP_f-15	12.0	4.85	−60	780.7	8.1	61
CoO				781.1		
Co_3O_4				780.6		
CoOOH				780.65		

RP_f-15) has characteristics close to those of Co^{2+} with respect to both binding energy and intensity of the satellite, regardless of the fact that the latter is not well resolved. Since the samples have been stored in air and CoO passes into Co_3O_4 under such conditions, it can be assumed that the spectra observed correspond to $CoAl_2O_4$ species. The only exception is the RP_f-15 sample whose binding energy is closer to that of Co_3O_4. For all samples the Co $2p_{3/2}$ line intensity is much weaker than expected. Comparison of the photoelectron peak intensities reflecting the concentrations of Al and Co in the layer under consideration allows a qualitative analysis of the surface state of the samples to be made. In addition, it is worth noting that the Al/Co ratio does not change proportionally to the weight content of Co in the different samples, i.e., to efficient Co coverage on Al_2O_3. This shows that probably a large part of the Co oxide is blocked in the Al_2O_3 pores or is present as large crystallites (at higher Co concentrations) and only part of the atoms on the surface under investigation are registered during the analysis. The results obtained are in good agreement with the data from XPS given by Chin and Hercules (10), who have investigated Co/Al_2O_3 samples calcined at 600°C. The binding energy (781.2 eV) for the Co $2p_{3/2}$ line of a sample with a Co concentration of 12% (i.e., a concentration close to the maximum concentration of our samples) is characteristic of $CoAl_2O_4$. On the basis of XPS data and reduction with hydrogen, the authors have concluded that a high percentage of Co in tetrahedral coordination is also present when the concentration of supported Co is high. A similar conclusion has been arrived at by Greegor *et al.* (7), who have used the EXAFS method.

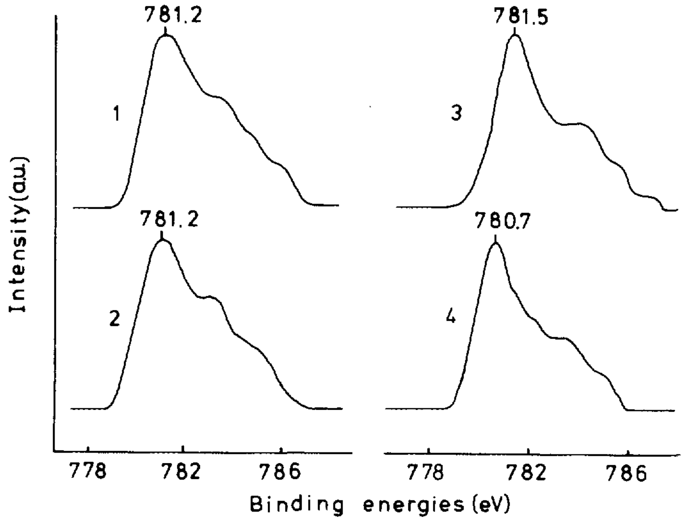

FIG. 5. Co $2p_{3/2}$ XPS of samples of Co deposited on γ-Al_2O_3, types B and RP: (1) B_f-7.5, (2) B_f-15, (3) RP_f-7.5, and (4) RP_f-15.

We are of the opinion that the XPS data are especially suitable for comparison with the results obtained by the kinetic method since they indicate the state of the active phase surface. In this respect, the publication of Stranick *et al.* (17) is of special interest. It contains a quantitative estimation of the distribution of Co-containing phases in Co/Al_2O_3 catalysts. The introduction of a correction for eliminating the crystallite size of Co_3O_4 (Kerkhof and Moulijn's model (33)) essentially changes the distribution of Co. However, we are interested in the results obtained without a correction of the model of Kerkhof and Moulijn because they are appropriate for comparison with our data, the more so that our purpose is not a quantitative determination of Co_3O_4, but measurement of the surface area of the Co_3O_4 obtained. We believe that there is very good agreement between the results of the two papers. As in our case, the Co/Al ratio in the paper of Stranick *et al.* (17) remains constant with rising Co concentrations (the same result being obtained by Grimblot *et al.* (13) during XPS studies of Co/Al_2O_3 catalysts), while the distribution of the Co-containing phases shows, depending on the Co concentration, a low percentage of the Co_3O_4 formed (about 30% at a 10% Co concentration). Comparison of the results of Stranick et al obtained with and without a correction of the particle size reflects, in our opinion, the correlation between the surface area and the amount of Co_3O_4, i.e., the effect of factors such as dispersion and blocking of the active phase in the support pores during the formation of the Co/Al_2O_3 catalysts.

DISCUSSION

Comparison of the results obtained by the various methods employed in this work allow some conclusions to be drawn on the formation of Co_3O_4 on the γ-Al_2O_3 supports. At the preparation temperature of 823 K, a large part of the supported Co is present as $CoAl_2O_4$ or other cobalt-containing phases. Nevertheless, already at the lowest concentration of supported Co, a Co_3O_4 phase is registered by the kinetic method. In addition, it is confirmed that there is an impregnating solution concentration at which a maximum specific surface area of the active oxide is formed, thereby reflecting optimum distribution of the supported active phase.

Interesting conclusions concerning the texture peculiarities of the supports used can be drawn from Figs. 2–4. Two factors influence the amount of the Co_3O_4 phase formed: (i) the position and width of the maximum in the pore size distribution curve, which strongly affects the uniform impregnation of the support, and (ii) the position of the beginning of hysteresis on the pore size distribution curve, which reflects the distribution of the active phase between the adsorbed layer and the filled pores. On the basis of these factors, the lower active surface area value for the samples on support B (in comparison with the RP-supported samples) can be associated with the larger surface area of the support and the broader maximum of the pores in the pore size distribution curve, which is shifted to the region of larger pores. This texture not only presupposes a more uniform distribution of the active phase on the support, but also favours a more intense interaction of the support with the deposited cobalt. As a result, the amount of Co_3O_4 on the support, i.e., the surface area of Co_3O_4, decreases.

In Fig. 2, the beginning of adsorption hysteresis, denoted as B_h and RP_h, is marked on the distribution curves of the initial supports. After attaining the impregnating solution concentration C_M, only 15% of the total pore volume of the support B is filled, while in the case of RP the amount is about 35%. Thus the crystallization of the active phase on support B proceeds mainly in the adsorption layer, where the strongest interaction of the active phase with the support occurs, whereas with RP a large part of the active phase crystallizes in the bulk of pores with radii of 20 Å and below. According to Ref. (25), simultaneous crystallization in a large number of pores with almost the same sizes leads to the formation of a large number of crystal nuclei, i.e., a large active phase surface. This model, which in our opinion is valid for support RP, presupposes a smaller number of contacts between the support and the crystallized active phase, and hence, interaction of a smaller amount of Co_3O_4 with Al_2O_3. The effect of the texture should be more pronounced on granulated supports. The texture characteristics of the RP support should provoke diffusion and nonuniform distribution of the active phase in the interior of the granules. This would lead to increasing Co concentration at the periphery of the granules and an enhanced contribution of Co (as Co_3O_4) that has not reacted with the support. This should be observed above a certain Co concentration since at low concentrations, where crystallites which are relatively small in number and size appear, the interaction between Al_2O_3 and Co is obviously predominating. This is the explanation of the high maximum in the surface area value of sample RP_g-7.5. With rising concentration of the impregnating solution, the Co_3O_4 crystallites become larger and this results in a relatively weak decrease of the active phase surface. A similar decrease in the dispersion of the active phase with the increase of its concentration was also noted by Bartholomew and Farrauto (34).

Some of our concepts are confirmed in the work of Declerck-Grimée *et al.* (4) where a large specific surface area of the support is considered to promote the formation of a surface aluminate. These authors proposed that the increase of the support surface area induces the formation of small-sized cobalt aggregates which can interact with the support. A similar idea about preferential diffusion of the small Co_3O_4 particles into the support lattice accompanied by formation of a surface spinel was also advanced by Chin and Hercules (10).

The magnetic studies and the XPS spectra of samples RP-15 and B-15 confirm indirectly the differences in the quantitative interaction of Co with the support depending on the support texture.

On the basis of the foregoing, sample RP-15 should contain a larger amount of Co_3O_4 than is the case of sample B-15 irrespective of the lower concentration of supported Co.

Table 3 shows that the magnetic moment of sample RP-15 is quite close to the magnetic moment of Co_3O_4, while the magnetic moment of B-15 indicates the presence of larger amounts of $CoAl_2O_4$ or other Co-containing phases.

The XPS results can also be attributed to a larger amount of Co_3O_4 in sample RP-15. The main peak in the spectrum of RP-15 has a binding energy very close to that of Co_3O_4. The profile of the peak accompanied by a satellite is characteristic of Co^{2+}. However, since significant amounts of $CoAl_2O_4$ are formed at all Co concentrations, it can be assumed that the spectrum recorded represents a sum of the signals of Co_3O_4 and $CoAl_2O_4$.

Thus, in addition to the calcination temperature and the impregnating solution concentration, the amount of Co_3O_4 formed and its surface area are strongly affected by the texture of the support used. The specific surface area of the support and its pore size distribution play an important role with respect to the amount of cobalt bonded to Al_2O_3.

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