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NOTE

On the Quantitative Analysis of XPS Intensity Data for Supported Catalysts with Partial Surface Segregation

In a recent paper (*1*) we have reported an extension of the models derived by Kerkhof and Moulijn (*2*) and Defossé *et al.* (*3*) for the quantitative description of XPS intensity ratios of supported catalysts.

This extension takes into consideration the segregation of a fraction of the supported phase (the promoter p) at the external surface of the support particle, a phenomenon which occurs quite frequently during the preparation of supported catalysts.

The model is based on a sheet-stacking representation of the support as described in Fig. 1. In its simplified version the XPS intensity ratio was expressed as[1]

$$\left(\frac{I_\mathrm{p}}{I_\mathrm{s}}\right)_\mathrm{XPS} = \frac{K_\mathrm{p}}{K_\mathrm{s}}\left[\frac{(1 - P_1P_2^2)}{(1 - P_1)P_3} - 1\right], \qquad (1)$$

where p and s represent the dispersed phase (the promoter) and the support, respectively. P_1, P_2, and P_3 are probabilities for photoelectrons to cross various sections of the model solid represented in Fig. 1. These probabilities are written (see Ref. (*1*)) as explicit functions of three independent adjustable parameters; for example, C_1 and x_1 are the crystallite size and weight percent of the well-dispersed fraction, and C_2 is the crystallite size of the segregated fraction (the loading of which can be calculated from the bulk loading $x_\mathrm{B} = x_1 + x_2$). As a consequence the experimental XPS intensity ratio $I_\mathrm{p}/I_\mathrm{s}$ is not sufficient information to determine the parameters of the model. In our previous paper the use of this model was demonstrated for a series of RuO_2/ZSM-5 catalysts. An arbitrary value was assumed for C_1 and an additional equation was introduced yielding an independent estimation of x_1 from the determination of the percentage of the Brønsted acid sites of the support which disappeared upon introduction of the supported phase[1]:

$$x_1 = (x_1)_\mathrm{ref.}\,\frac{(\%\mathrm{H_{ex}})}{(\%\mathrm{H_{ex}})_\mathrm{ref.}}. \qquad (2)$$

This approach necessitates experimental determinations of the Brønsted acid sites' concentrations of the support and the catalyst, and an arbitrary choice has to be made for the reference sample and its value of $(x_1)_\mathrm{ref.}$.

We wish to report in the present note an alternative procedure which replaces Eq. (2) by a new equation we derived for the representation of the XPS intensity ratios of the catalyst obtained after a thorough grinding of the sample. In the model of the ground catalyst it was assumed that the sizes C_1 and C_2 of the microcrystallites are not affected by the grinding process. In a ground catalyst the particles of size C_2 seen by the ESCA analyzer are not all exposed on the top surface of the powder but are covered with layers of the support. In our calculations we have assumed that the distribution function for the thickness of these layers can be represented by a uniform distribution if the grinding and mixing of the support particles is thorough enough. The sheet-stacking model lends itself perfectly to the representation of such a distribution: a quasi-uniform distribution of thicknesses can be generated by distributing uniformly the population of crystallites (C_2, x_2) over the surfaces of the sheets which represent

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[1] Equations (1) and (2) are identical with Eqs. (17) and (18) of Ref. (*1*).

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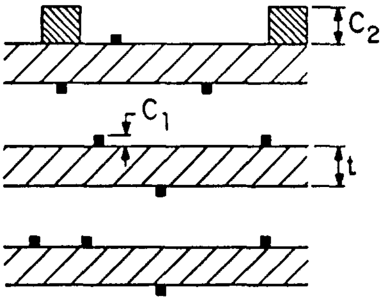

FIG. 1. Model for the catalyst particle (unground catalyst).

the support as shown in Fig. 2. Of course as C_2 is rather large the distances between sheets may have to be higher compared to the model of the unground catalyst, but this is of no consequence as these distances do not affect the values of ESCA intensity ratios calculated from the model.

Assuming that the total surface area S_0 of the support is not affected by grinding, the fraction of this area covered by the particles of size C_2, in the model of both the ground and the unground catalyst is expressed as

$$f_3 = \frac{x_2}{S_0(1 - x_B)\rho_p C_2} \tag{3}$$

and the probabilities for photoelectrons from the support and the promoter to cross the outer discontinuous layer of the supported phase are

$$P_{sp2} = 1 - f_1 - f_3 + f_1 e^{-\alpha_2} + f_3 e^{-\gamma_2} \tag{4}$$

$$P_{pp2} = 1 - f_1 - f_3 + f_1 e^{-\alpha_1} + f_3 e^{-\gamma_1}. \tag{5}$$

Under these conditions the equation derived for the XPS intensity ratio of the ground catalyst is similar to Eq. (16) of Ref. (*1*):

$$\left(\frac{I_p}{I_s}\right)_G = \frac{K_p}{K_s}\frac{(1 - P_{pp2})}{(1 - P_{ss})} \frac{(1 - P_{ss}P_{sp2}^2)}{(1 - P_{ps}P_{pp2}^2)}\left[\frac{1 + P_{ps}P_{pp2}}{P_{sp2}}\right]. \tag{6}$$

In the case where $\lambda_{pp} = \lambda_{sp} = \lambda_p$ and $\lambda_{ss} = \lambda_{ps} = \lambda_s$, Eq. (6) becomes

$$\left(\frac{I_p}{I_s}\right)_G = \frac{K_p}{K_s}\frac{(1 - P_4)}{(1 - P_1)}\left[\frac{1 + P_1 P_4}{P_4}\right], \tag{7}$$

where $P_{sp2} = P_{pp2} = P_4$.

The new procedure we propose here for the quantitative treatment of XPS intensity ratios involves the simultaneous resolution of Eq. (1), where $(I_p/I_s)_{XPS}$ is the experimental ratio obtained for an unground catalyst, and Eq. (7), where $(I_p/I_s)_G$ is the experimental ratio determined for the same catalyst after a thorough grinding.

This procedure was applied to two Fe_2O_3/ZSM-5 catalysts which were designated in our recent paper (*4*) as 4.6Fe/HZ-1 and 4.6FeDBZ/HZ-1. These two solids prepared by calcination of the support in the presence of ferrocene and dibenzoylferrocene, respectively, are known to have very different structural features even though their iron loadings are almost identical. The results for the analysis of $I_{Fe_{3p}}/I_{Si_{2p}}$ determined at various grinding times are reported in Table 1.

In the calculations the following parameter values have been utilized: $\rho_s = \rho_{SiO_2} = 2.40$ g/cm^3; $\rho_p = \rho_{Fe_2O_3} = 5.24$ g/cm^3; $S_0 = 350$ m^2/g; $A_0 = 10$ m^2/g; $\lambda_s = 23.7$ Å and $\lambda_{Fe_{3p}} = 24.3$ Å are the escape depths calculated from equations taken from Vulli and Stark (*5*) and Penn (*6*); $\sigma_{Si_{2p}} = 0.817$ and $\sigma_{Fe_{3p}} = 1.669$ are the values calculated by Scofield (*7*); n_{Fe}/n_{Si} was calculated as 0.819 from the atomic densities of Fe in Fe_2O_3 and Si in SiO_2, respectively; D_p/D_s was esti-

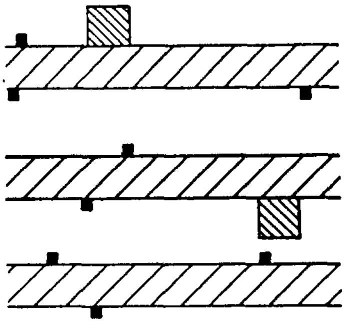

FIG. 2. Model for the ground catalyst.

TABLE 1

Determination of Crystallite Sizes and Loadings of the Dispersed and Segregated Fractions of Fe_2O_3 Supported on ZSM-5

Catalyst	Grinding time (min)	$\frac{I_{Fe_{3p}}}{I_{Si_{2p}}}$	x_B (wt% Fe)	x_1 (wt% Fe)	C_1 (Å)	x_2 (wt% Fe)	C_2 (Å)
4.6Fe/HZ-1	0	0.095	4.58				
	5	0.079	—	6.54	3	−1.96	−0.018
	20	0.068	—	5.57	3	−0.99	−0.001
	30	0.054	—	4.34	3	0.24	8.7
	40	0.054	—	4.34	3	0.24	8.7
4.6FeDBZ/HZ-1	0	0.035	4.62				
	5	0.026	—	2.15	3	2.47	1302
	20	0.027	—	2.24	3	2.36	1411
	30	0.020	—	1.61	3	3.01	950
	40	0.020	—	1.61	3	3.01	950

mated as $(E_{kp}/E_{ks})^{-1/2}$ with E_{kp} = 1431 eV and E_{ks} = 1384 eV. The value of C_1 was arbitrarily fixed at 3 Å as the small crystallites must fit into the ZSM-5 pores and as the calculated results for C_2 and x_1 are not sensitive to this parameter up to values exceeding 10 Å.

From Table 1 it may be seen that the I_{Fe}/I_{Si} ratio decreases with increased grinding time which corresponds to a change in the distribution of the thickness of covering support layers. The results in Table 1 also indicate that at low grinding times the solutions of Eqs. (1) and (7) yield results with no physical meaning (negative values for x_2 and C_2) for catalyst 4.6Fe/HZ-1. A necessary condition for Eq. (7) to apply is that the distribution of the large particles of promoter over the various layers of the model solid represented in Fig. 2 reaches a stable configuration. As found with many other catalysts supported on ZSM-5 zeolites synthesized in the same conditions as the support of the catalysts shown in Table 1, XPS intensity ratios reach stable values when the grinding time in our particular grinder reaches 25–30 min. As shown in Table 1, only after 30 min of grinding time do the calculated results for C_2, x_1, and x_2 reach values in general agreement with the known structural features of these catalysts discussed in our previous paper (*4*). Indeed sample 4.6Fe/HZ-1 has less segregated phase with crystallites smaller than 10 Å, whereas the segregated crystallites in 4.6FeDBZ/HZ-1 have very large sizes of the order of 1000 Å.

The presence of a promoter-enriched zone at the outer surface of a supported catalyst (surface segregation) is indeed a very common feature of these systems. This feature is often quite detrimental to the surface area of the active phase. The practice of comparing XPS intensity ratios of a sample before and after grinding has been used in the past as a qualitative means of detection of surface segregation. It is proposed in this note that this practice can be used in a quantitative manner by solving simultaneously Eqs. (1) and (7). This procedure appears simple and very generally applicable compared to the one proposed in our previous paper (*1*). It cannot yet be considered as fully demonstrated and will require systematic studies of the precision of the quantitative estimates of parameters. The significance of the calculated values of C_2 and x_1 is indeed restricted both by the oversimplifying assumptions made in the model and by the lack of precision on the values of nonadjustable parameters (A_0, λ_i, . . .) in Eqs. (1) and (7). Results like the ones reported in Table 1 make us however reasonably confident in the validity of the structural description of supported catalysts reached by this approach.

APPENDIX: LIST OF SYMBOLS

Latin Letters

A_0	Specific external surface area of the support
C	Cube size length of crystallites for uniformly dispersed population (C_1) and surface-segregated population (C_2) (see Fig. 1).
D	Photoelectron detection efficiency of the analyzer
E_k	Photoelectron kinetic energy
f	Fraction of a surface of the support covered with promoter crystallites
f_1	Fraction of total surface S_0 covered with uniformly dispersed population
f_2	Fraction of external surface A_0 covered with surface segregated population
f_3	Fraction of total surface S_0 covered with both populations
$\%H_{ex}$	Percentage of exchanged Brønsted acid sites
I	XPS intensity or peak surface area
K	A constant parameter in Eq. (12) of Ref. (*1*): $$\frac{K_p}{K_s} = \frac{n_p}{n_s}\frac{\sigma_p}{\sigma_s}\frac{\lambda_p}{\lambda_s}\frac{D_p}{D_s}$$
n	Atomic density
P	Probability of photoelectrons to cross a given layer
P_{ss}, P_{ps}	Probability of photoelectrons from support (s) and promoter (P) to cross a continuous layer of support of thickness t (if $\lambda_{ss} = \lambda_{ps} = \lambda_s$, $P_{ss} = P_{ps} = P_1$)
P_{sp}, P_{pp}	Probability of photoelectrons from support (s) and promoter (p) to cross a discontinuous layer of promoter of thickness C_1 and occupied fraction f_1 (if $\lambda_{sp} = \lambda_{pp} = \lambda_p$, $P_{sp} = P_{pp} = P_2$)
P_{sp1}, P_{pp1}	Probability of photoelectrons from support (s) and promoter (p) to cross a discontinuous layer of promoter having both occupied fractions and thicknesses (C_1, f_1) and (C_2, f_2) (if $\lambda_{sp} = \lambda_{pp} = \lambda_p$, $P_{sp1} = P_{pp1} = P_3$)
P_{sp2}, P_{pp2}	Probability of photoelectrons from support (s) and promoter (p) to cross a discontinuous layer of promoter having both occupied fractions and thicknesses (C_1, f_1) and (C_2, f_3) (if $\lambda_{sp} = \lambda_{pp} = \lambda_p$, $P_{sp2} = P_{pp2} = P_4$)
S_0	Specific total surface area of the support
t	Thickness of the support layer, $t = 2/\rho_s S_0$ (see Fig. 1)
x	Weight percent of promoter, bulk value (x_B), uniformly dispersed (x_1) and surface-segregated (x_2) populations

Greek Letters

α	Adimensional length: $\alpha_1 = C_1/\lambda_{pp}$, $\alpha_2 = C_1/\lambda_{sp}$
β	Adimensional length: $\beta_1 = t/\lambda_{ss}$, $\beta_2 = t/\lambda_{ps}$
γ	Adimensional length: $\gamma_1 = C_2/\lambda_{pp}$, $\gamma_2 = C_2/\lambda_{sp}$
λ	Photoelectron mean free path, λ_{ij} for photoelectron originating from phase i and moving in phase j with i representing s, p and j representing s, p
ρ	Specific mass
σ	Photoelectric cross section

Indexes

G	Ground
p	Promoter
s	Support

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S. KALIAGUINE
A. ADNOT
G. LEMAY
L. RODRIGO

Department of Chemical Engineering and GRAPS
Université Laval
Ste-Foy, Quebec, Canada G1K 7P4

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