NOTES

Apparent Surface Coverage Determination in NiO/γ-Al$_2$O$_3$ and CoO/γ-Al$_2$O$_3$ Systems

The relevance of NiO/γ-Al$_2$O$_3$ and CoO/ γ-Al$_2$O$_3$ systems is based on the importance of hydrodesulfurization catalysts used in the petroleum industry. Although these systems have often been studied in various works relating to hydrodesulfurization catalysts (*1–5*), there is not sufficient information about the nickel and cobalt coverage. It is known that both metals form spinels MeAl$_2$O$_4$ (Me = Ni or Co) (*3*) and that cobalt forms Co$_3$O$_4$ at CoO content above 2 wt% (*2*).

In a recent study (*6*) we made electrophoretic migration measurements in order to determine the "apparent surface coverage" (ASC) by molybdena in Mo/γ-Al$_2$O$_3$ catalyst. The results were in agreement with the values obtained by oxygen chemisorption (*7*). In the present work we compare the apparent surface coverage by nickel and cobalt in NiO/γ-Al$_2$O$_3$ and CoO/ γ-Al$_2$O$_3$ systems. In both series the metal content is expressed as grams of MeO (MeO = NiO or CoO) per 100 g of dry Al$_2$O$_3$. The maximum metal content was 9 wt%.

A commercial γ-Al$_2$O$_3$ (Girdler T-126) of specific surface area $S_{BET} = 188$ m^2 g^{-1} and pore volume = 0.39 cm^3 g^{-1} was used as support material. The samples with different metal content were prepared by the "wet" method (impregnation in excess of the pore volume). The support was impregnated with an aqueous solution containing the appropriate concentration of nickel or cobalt nitrate (Merck p.a.). The solvent was removed in a rotary evaporator at 80°C and 200 Torr. The samples were dried at 110°C for 1 hr and then calcined at 550°C for

4.5 hr. Metal contents were determined by atomic absorption spectroscopy.

NiAl$_2$O$_4$ and CoAl$_2$O$_4$ were prepared as reference compounds by heating a mixture of γ-Al$_2$O$_3$ and nickel or cobalt nitrate at 1100°C for 48 hr. Before the high temperature treatment, the mixtures were progressively heated at 100°C for 4 hr and then at 300°C for 14 hr, as described by Gajardo *et al.* (*8*). Co$_3$O$_4$ and NiO were prepared by calcination of nickel and cobalt nitrate at 550°C for 4.5 hr. X-Ray diffraction gave the expected spectra for these reference compounds.

Zeta-potential measurements were car-

TABLE 1

Composition, Zero Point Charge (ZPC), and "Apparent Surface Coverage" (ASC) of the Samples, and Isoelectric Point (IEP) of the Reference Compounds

Sample	MeO[a] (%)	IEP	ZPC	ASC (%)
γ-Al$_2$O$_3$	—	8.80	—	0
1-CoAl	0.6	—	8.30	13
2-CoAl	1.0	—	8.05	19
3-CoAl	1.6	—	7.65	29
4-CoAl	4.4	—	7.95	—
5-CoAl	5.9	—	8.05	—
CoAl$_2$O$_4$	—	2.65	—	—
Co$_3$O$_4$	—	7.30	—	—
1-NiAl	2.3	—	8.15	17
2-NiAl	4.5	—	8.00	21
3-NiAl	6.0	—	7.80	25
4-NiAl	9.0	—	7.60	30
NiAl$_2$O$_4$	—	2.65	—	—
NiO	—	8.30	—	—

[a] Weight per 100 g of dried Al$_2$O$_3$.

ried out in a Zeta-meter Inc. (Model ZM-77), using 200 mg of 2-μm samples particles ultrasonically suspended in 200 ml of 10^{-3} M KCl solution, as reported before (6). Electrolyte solutions were prepared by adjusting the pH value with 10^{-3} M KOH and HCl solutions. Zeta-potential and migration electrophoretic rate are related by the well-known Smoluchowski equation.

Diffuse reflectance spectra of samples were recorded with a Pye Unicam SP-1800 spectrophotometer with a SP-890 diffuse reflectance accessory. The support γ-Al$_2$O$_3$ was used as reference.

Table 1 shows the composition, zero point charge (ZPC), and apparent surface coverage (ASC) of the samples, and the isoelectric points (IEP) of the reference compounds. Both the zero point charge and the isoelectric point are used according to the definitions of Parks (9). The ASC were calculated in accordance with our Eq. (1) (6) where the subscripts "S" and

$$ASC = \frac{(IEP_s - ZPC)M_S^{-1}}{(M_M^{-1} - M_S^{-1})(ZPC - IEP_S) + (IEP_S - IEP_M)M_M^{-1}} \times 100 \qquad (1)$$

"M" represent the support and supported species, respectively, and M corresponds to the molecular weights.

Diffuse reflectance spectra are shown in Figs. 1 and 2. The Ni/γ-Al$_2$O$_3$ spectra (Fig. 1) show that on increasing the nickel content, a doublet between 550 and 650 nm and an absorption band in the 350–450 nm region both increased. These bands have

been assigned, respectively, to Ni^{2+} ions in tetrahedral and octahedral coordination (4, 10–12). Although the spectra do not show characteristic NiO bands, we cannot discount the possibility that a small amount could be present (the spectrum of 4-NiAl sample shows a small shoulder near 700 nm, which is assigned to NiO absorption).

Samples of Co/γ-Al$_2$O$_3$ at low Co content (Fig. 2) show a broad triplet band situated between 500 and 650 nm which has been

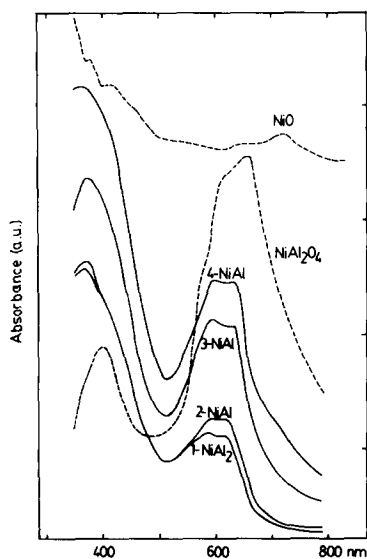

FIG. 1. Diffuse reflectance spectra of oxidic Ni/γ-Al$_2$O$_3$ samples and of model compounds.

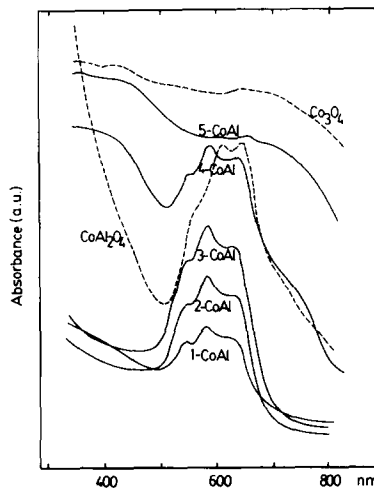FIG. 2. Diffuse reflectance spectra of oxidic Co/γ-Al$_2$O$_3$ samples and of model compounds.

assigned to ligand field transitions of tetra-hedral Co^{2+} coordination (2, 8, 13, 14). The intensity of this band increases with the cobalt loading. However, at the highest cobalt contents studied (4-CoAl and 5-CoAl) the spectra show an obscuring effect (8) due to the presence of Co_3O_4.

The spectral behavior of both our series are as expected. It was known that the greater reactivity of nickel oxide with alumina (1, 3) leads mainly to the formation of $NiAl_2O_4$ even at high nickel content, but in cobalt samples $CoAl_2O_4$ is only present alone at low cobalt content.

The relationship between zeta-potential and pH (Fig. 3) shows that the isoelectric points of both $NiAl_2O_4$ and $CoAl_2O_4$ are equal. This is in agreement with IEP values of other nickel and cobalt compounds, such as NiO and CoO whose IEP are equal (15) or $Ni(OH)_2$ and $Co(OH)_2$ which are very similar (16). The IEP of Al_2O_3, Co_3O_4, and NiO (Fig. 3) are in agreement with reported values (15).

The information obtained from reflectance spectra are in agreement with the ZPC behavior as shown in Table 1: the ZPC of NiAl samples decrease with increase of nickel content. This behavior indicates an increase in quantity of some surface compound with an IEP less than 8.80 (which corresponds to γ-Al_2O_3 support). Based on

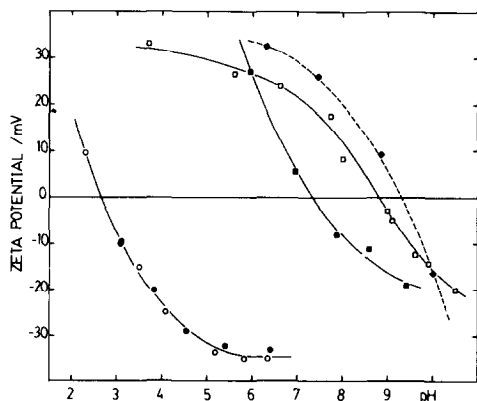the reflectance spectra of these samples this compound must be surface spinel $NiAl_2O_4$. A similar behavior is observed for CoAl samples, but only at low content. At high cobalt loading the ZPC increases from 7.65 to 7.95 for 3-CoAl and 4-CoAl, respectively. This suggests the formation of Co_3O_4 over the surface spinel $CoAl_2O_4$. If Co_3O_4 were to be formed over Al_2O_3, the IEP of these samples should decrease for increasing cobalt content, since the Co_3O_4 IEP is also lower than the support.

We now consider the coverage. The apparent surface coverage of a sample may be determined by electrophoretic migration measurements using Eq. (1) only if the support surface is covered by one species (6). Therefore, in CoAl samples with higher cobalt content, the ASC cannot be calculated by Eq. (1) because there are two species ($CoAl_2O_4$ and Co_3O_4).

The ASC of NiAl and CoAl samples, plotted versus metal content in Fig. 4, show that for samples with equal metal content the coverage is clearly larger in cobalt samples. However, at high nickel content the coverage reaches similar values to cobalt. At 2 CoO wt% the coverage is about 33% but at 2 NiO wt% it is 14%, although at 9 NiO wt% the ASC is about 30%.

This different behavior is due to the larger reactivity of nickel with the alumina (1, 3). In the nickel samples, under the surface spinel $NiAl_2O_4$, a bulk $NiAl_2O_4$ (3) is formed. In cobalt samples no bulk $CoAl_2O_4$ is formed because cobalt is less reactive with the alumina. Thus, in these last sam-
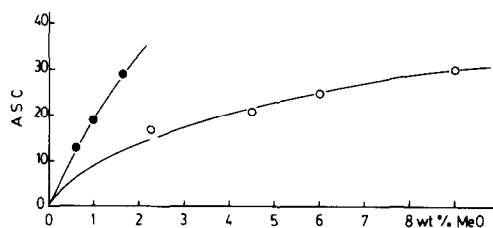

FIG. 3. Zeta-potential at 22.5°C as a function of suspension pH of (○) $NiAl_2O_4$, (●) $CoAl_2O_4$, (■) Co_3O_4, (□) Al_2O_3, and (♦) NiO.

FIG. 4. "Apparent surface coverage" (ASC) of (●) oxidic Co/γ-Al_2O_3 and (○) oxidic Ni/γ-Al_2O_3 systems, versus metal content.

ples, at low cobalt content a surface spinel $CoAl_2O_4$ is formed covering a large part of the Al_2O_3 surface.

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