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# Application of Ion Scattering Spectroscopy to Investigations of the Interaction between the Active Component and Carrier in Supported Catalysts

Low energy ion scattering spectroscopy (LEISS or ISS) can give information on the top layers of materials, and as a surface analysis technique it is showing an increasing importance (*1*). Several investigations on insulators, including supported catalysts, have been carried out recently (*2–9*), but we have not found any report as yet about the relationship between ion scattering peak positions and the chemical environment of surface atoms. In the low energy ISS technique the energy losses of the primary particles during the collisions are assumed to be completely kinetic, i.e., the energy transfer for electronic interaction is generally small and is neglected (*10, 11*). In this article we will show, however, that the electronic effect is measurable for Cu, Zn, and Na by the ISS technique, and we will use the concept of "effective mass" based upon a binary collision approach (*10*) to develop a method for the determination of the chemical shift in solid–solid surface interactions in catalyst systems. A series of Cu, Na, and Zn compounds, Al foil, and supported Cu and Zn catalysts have been investigated, and the $^4He^+$ scattering energy from the different atoms in the different compounds or catalysts has been determined. The "mass increments" in these samples are calculated from scattering peak shifts in the ion scattering spectra and the "mass increment" is used as a means to characterize interaction between surface atoms.

An ESCA LAB-5 (VG Ltd., UK) spectrometer with an AG 61 ion gun was used. The incident ion beam was $^4He^+$, operating within an energy range from 500 to 1500 eV and a beam current 8–15 nA. The diameter of the beam was about 1 mm and the scattering angle $\theta = 122.5°$. The residual pressure in the analytical chamber was $10^{-9}$ Torr (1 Torr = 133.3 N $m^{-2}$). The preparation method of $CuCl/\gamma\text{-}Al_2O_3$ powder catalyst samples has been described previously (*12*). $CuO/\gamma\text{-}Al_2O_3$, $ZnO/SiO_2$, $ZnO/TiO_2$, and $ZnO/\gamma\text{-}Al_2O_3$ powders were prepared by an impregnation method (*13, 14*). $Zn_2SiO_4$ and $ZnAl_2O_4$ were obtained by a calcination method, and phase determinations were made by X-ray diffraction (XRD). The rest of the samples were of analytical quality, obtained commercially.

The first important thing in the investigation of scattering peak positions is to measure the ion scattering energy accurately. Charging of solid insulators in ISS measurements has always been an awkward problem which strongly affects the scattering peak position. In our experiments, the powder samples were pressed onto Pb or In foil uniformly in order to avoid charge effects. A flood gun was used in the experiments to eliminate charge effects completely. The working conditions of the flood gun were different from sample to sample; we chose the operating condition of the flood gun at which scattering peak was not changed. Different areas of the same sample were examined repeatedly in order to reduce errors. The instrument was carefully calibrated using pure gold and copper before measurement (*15*) according to the basic equation of ISS as reduced by the binary collision approach,

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TABLE 1

The "Mass Increment" of Cu Series Samples ($E$ = 1476 eV)

| No. | Samples[a] | $^4He^+ \rightarrow Cu$ scattering peak position (eV) | "Mass increment" $\Delta M_2$[b] |
|---|---|---|---|
| 1 | Cu | 1216 | 0 |
| 2 | CuCl | 1222 | 1.61 |
| 3 | 0.11 g CuCl/g $\gamma$-$Al_2O_3$ | 1233 | 4.57 |
| 4 | CuO | 1226 | 2.69 |
| 5 | 0.13 g CuO/g $\gamma$-$Al_2O_3$ | 1230 | 3.76 |

[a] Specific surface area of $\gamma$-$Al_2O_3$ for CuCl/$\gamma$-$Al_2O_3$ sample is 343 $m^2 g^{-1}$, and for CuO/$\gamma$-$Al_2O_3$ sample is 250 $m^2 g^{-1}$.

[b] Relative to $^4He^+ \rightarrow Cu$ scattering peak position.

$$\frac{E_1}{E_0} = \left(1 + \frac{M_2}{M_1}\right)^{-2} \left\{\cos\theta + \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta\right]\Big]\right\}^2, \quad [1]$$

when $M_2 \geq M_1$ and where $E_0$ and $M_1$ are the energy and mass of the incident ion, $E_1$ is the energy of the scattering ion, $M_2$ is the mass of the element determined, and $\theta$ is the scattering angle. The experimental error is within $\pm 2$ eV. All data were recorded at room temperature.

The ISS results for the Cu series samples are shown in Table 1. The primary ion energy, $E_0$, is 1476 eV. It is clearly shown that the $^4He^+$ scattering peak positions of Cu vary due to the different compounds. If we differentiate with respect to Eq. [1], thus

$$\frac{\Delta E_1}{E_0} = -\frac{2\Delta M_2}{M_1}\left(1 + \frac{M_2}{M_1}\right)^{-3} \left\{\cos\theta + \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta\right]^{1/2}\right\}^2 + 2\Delta M_2 \frac{M_2}{M_1}\left(1 + \frac{M_2}{M_1}\right)^{-2} \left\{\cos\theta + \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta\right]^{1/2}\right\} \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta\right]^{-1/2},$$

$$\Delta M_2 = f(M_1, M_2, \theta)E_0^{-1}\Delta E_1, \quad [2]$$

where $f$ is constant, and we can obtain the $\Delta M_2$ for the surface atom in question from experimental $\Delta E_1$ values according to Eq. [2]. This $\Delta M_2$ is called the "mass increment" for the atom. The $^4He^+$ scattering peak position depends on the mass of the atom under the particular experimental condition; when the atom has a strong chemical bond with other atoms, the mass of this atom seems to be changed, causing a scattering peak position shift. In other words, the experimental $\Delta E_1$ values vary due to the different binding forces in the various compounds involving the same atom. The stronger the binding force, the larger the "mass increment" $\Delta M_2$. The strength of the interaction for the surface atoms in the different compounds can thus be assessed from the $\Delta M_2$ values.

It has been indicated by XRD, XPS, and SIMS (*16*) that CuCl (cuprous chloride, sample 3) is dispersed as a monolayer on the carrier. There is a fairly strong interaction between CuCl and $\gamma$-$Al_2O_3$, so its $\Delta M_2$ value is larger than that of pure CuCl (see Table 1). Similarly, when CuO is dispersed on the $\gamma$-$Al_2O_3$ surface the interaction between CuO and the carrier surface is strengthened. Therefore its $\Delta M_2$ (3.76) is larger than the $\Delta M_2$ (2.69) of CuO. The $\Delta M_2$ of Cu for CuO is larger than that of CuCl ($\Delta M_2$ = 1.61); this agrees with the fact that the binding energy of Cu to O in CuO is stronger than Cu to Cl in CuCl. Thus it can be seen that the interaction between the active component and the carrier in CuCl/$\gamma$-$Al_2O_3$ is stronger than that in CuO/$\gamma$-$Al_2O_3$.

First, it must be pointed out that the change in the Cu scattering peak position is not due to the sample charge; we used the flood gun under different conditions until the scattering peak was stable; i.e. the surface charges of the samples were neutralized completely. Second, no influence of the background subtraction was found; we have obtained the same results using Pb or In foil as a substrate.

The results for a series of samples containing Zn are given in Table 2. It is known that the electronegativity of fluorine is larger than that of oxygen. As a result, the interaction of surfaces Zn to F in $ZnF_2$ should be stronger than that in ZnO. This has been confirmed by our experimental results. In samples 4, 5 and 6, ZnO is dispersed on different carriers. Investigations by ISS (*17*) have demonstrated that ZnO is dispersed as a monolayer on the $TiO_2$ surface in ZnO/$TiO_2$. The compound $ZnAl_2O_4$ was found in ZnO/$\gamma$-$Al_2O_3$ by XRD determination and a stronger interaction between ZnO and $\gamma$-$Al_2O_3$ in a ZnO/$\gamma$-$Al_2O_3$ sample was demonstrated (*18*). Therefore, the $\Delta M_2$ of Zn in ZnO/$\gamma$-$Al_2O_3$ is larger than that in ZnO and approaches the $\Delta M_2$ of Zn in $ZnAl_2O_4$. No $\beta$-$Zn_2SiO_4$ was found in ZnO/$SiO_2$ by XRD, but the Zn binding energy in ZnO/$SiO_2$ is approximately equal to that in $\beta$-$Zn_2SiO_4$ (*18*). This supports the suggestion that a stronger chemical interaction occurs between ZnO and $SiO_2$ surfaces, and that is why the value of $\Delta M_2$ is larger and approaches the $\Delta M_2$ in the $\beta$-$Zn_2SiO_4$ sample. The value of $\Delta M_2$ in ZnO/$TiO_2$ (sample 4) approaches that of $\Delta M_2$ in ZnO in comparison to samples 5–8, which also suggests that there may be a weak interaction between ZnO and $TiO_2$. Hence we may suggest that the strength of the interaction between the ZnO and different carrier surfaces in the supported catalyst samples, in which ZnO is dispersed on the surface of the carrier, can be characterized by measuring $\Delta M$. Furthermore, according to the values of $\Delta M_2$ obtained from Table 2, we assume that the order of the interaction forces is Zn/Si $\cong$ Zn/Al > Zn/Ti for ZnO/$SiO_2$, ZnO/$\gamma$-$Al_2O_3$, and ZnO/$TiO_2$, respectively.

TABLE 2

The "Mass Increment" for Zn Series Samples ($E$ = 1476 eV)

| No. | Sample | $^4He^+ \rightarrow$ Zn scattering peak position (eV) | $\Delta M_2$[a] |
|---|---|---|---|
| 1 | Zn | 1221 | 0 |
| 2 | ZnO | 1223 | 0.56 |
| 3 | $ZnF_2$ | 1226 | 1.41 |
| 4 | ZnO/$TiO_2$ | 1225 | 1.13 |
| 5 | ZnO/$\gamma$-$Al_2O_3$ | 1231 | 2.82 |
| 6 | ZnO/$SiO_2$ | 1232 | 3.11 |
| 7 | $ZnAl_2O_4$ | 1229 | 2.26 |
| 8 | $\beta$-$Zn_2SiO_4$ | 1230 | 2.54 |

[a] Relative to $^4He^+ \rightarrow$ Zn scattering peak position.

TABLE 3

The "Mass Increment" of Na Series Samples ($E$ = 1476 eV)

| Sample | $^4He^+ \rightarrow$ Na scattering peak position (eV) | $\Delta M_2$[a] |
|---|---|---|
| Na | 835 | 0 |
| NaF | 848 | 0.63 |
| NaCl | 842 | 0.34 |
| NaBr | 838 | 0.15 |

[a] Relative to $^4He^+ \rightarrow$ Na scattering peak position.

The binary compounds NaF, NaCl, and NaBr are all of NaCl structure, and the electronegativities of F, Cl, and Br are 3.98, 3.16 and 2.96, respectively. The binding energy between Na and the negative ions in NaF, NaCl, and NaBr decreases in that order. We have found that the scattering peak position for $^4He^+ \rightarrow$ Na decreases in that order also (see Table 3), and this reflects the difference of interaction between Na and the different negative ions in NaF, NaCl, and NaBr.

In addition, we have found that the $^4He^+ \rightarrow Al$ scattering peak position drifts away more from the theoretical value (the value observed for the scattering energy is decreased) due to the inelastic energy loss in the Al foil sample. This agrees with the inelastic energy loss of $^{20}Ne^+ \rightarrow Al$ found by Miller (*15*) and MacDonald and O'Connor (*19*).

A larger shift has been found for the $^4He^+ \rightarrow Al$ scattering peak position in the case of adsorbed oxygen on Al foil. When oxygen is adsorbed on Al foil, the $^4He^+ \rightarrow Al$ scattering peak is decreased in energy by 8 eV corresponding to no adsorbed oxygen on the Al foil surface. Similar results have been obtained for $^4He^+ \rightarrow Ta$ and V scattering peaks due to adsorbed oxygen on Ta and V surfaces, respectively (*20, 21*). We have also observed that the $^4He^+ \rightarrow Cl$ and $^4He^+ \rightarrow Br$ scattering peak positions drift toward the lower kinetic energy end when there is Na on the topmost layer of the NaCl and NaBr surfaces. Thus it can be seen that the peak position of the element in question may also be shifted when oxygen or other elements cover its surface. The reason for the inelastic energy loss is that some interaction has occurred between the $^4He^+$ ions and other elements on the surface during the scattering processes causing a lowering of the kinetic energy. Recent papers (*22, 23*) have also reported that the inelastic energy losses occur from clean sample surfaces when $He^+$ and $Ar^+$ are used. The authors consider that the inelastic energy losses are mainly related to a charge exchange mechanism leading to the reionization of the scattered particles. However, it is very important to note whether there is a deposit on the surface of the element to be determined which can cause an inelastic energy loss (peak shifts to lower energy). The $\Delta M$ of the same sample should be a constant over a certain $E_0$ range; we obtained much the same result using $E_0 = 1000$ eV. At lower $E_0$, for example <200 eV, there will be a deviation from binary collision theory.

In the case of complete elastic collisions of incident ions and surface atoms without energy loss of inelastic collision we can obtain $\Delta M$ according to a peak position shift of the element in oxides, halides, and supported catalysts and it may be used to assess the strength of the interaction between the atoms in the surface. If the peak position is shifted toward the lower end of the kinetic energy scale there is probably some other element present on the surface. Therefore, low energy ISS is a useful tool not only for the elemental analysis of the surface but also, probably, is an effective probe for the determination of chemical information on surface species.

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