Analytical Methods

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Acidity Scale for Metal Oxides and Sanderson's Electronegativities of Lanthanide Elements**

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Metal oxides are widely used in industry and academia.[1,2] As their electron-acceptor or acidic strengths play vital roles in their applications, there needs to be a general scale that can quantitatively compare their relative acidic strengths. Conventionally, calorimetric heat measurements during adsorption of probe molecules,[3] infrared spectroscopic analyses of adsorbed bases or acids,[5,6] application of indicator dyes,[4] and temperature-programmed desorption of the pre-adsorbed bases are standard methods for the analyses of their acidic strengths.[6–8] However, these methods are not suitable for a quantitative comparison. Thus, unlike metal ions in solution,[9] no such scales have been available for metal oxides.

One of the important types of interaction between adsorbates and metal oxides is the formation of coordinate covalent bonding between adsorbates and the surface metal ions. For instance, in the case of TiO_2, those compounds that have enediol,[10–14] carboxylate,[15–18] and nitrile[19,20] groups have been shown to form coordinate covalent bonding with the surface Ti^{4+} ions. In this type of interaction, the adsorbate-to-metal charge-transfer interaction is often the lowest-energy electronic transition. However, in the case of alizarin (Figure 1 a, inset) on TiO_2, a theoretical study has suggested that the intramolecular charge-transfer (IMCT) band from the catechol moiety to the entire ring system is the lowest-energy transition.[11]

Electronegativity (EN) is one of the most important fundamental properties of an atom, which represents "the power of an atom in a compound to attract electrons to itself".[21,22] Among various EN scales that have been developed,[21–35] Sanderson's scale and the associated EN equalization principle[31–35] are successful in calculating the bond energies of various compounds[32–36], elucidating the acidic and basic properties of zeolites,[37,38] and establishing the relationship between the reactivity and the composition of the zeolite that served as the guideline for the preparation of optimum zeolite catalysts.[39] These methods have also been used for various other purposes.[40–44] However, owing to a lack of experimental data, Sanderson's EN scale has not been extended to lanthanides (Ln) during the last five decades, despite the fact that lanthanide-containing compounds are widely used.

Herein, we report that the IMCT transition of alizarin is still the lowest-energy transition when it is adsorbed on various metal oxides and sulfides, regardless of the nature of the metal ion. The charge-transfer transition serves as a highly sensitive and accurate probe for the quantitative comparison of the acidic strengths of the metal oxides and sulfides. We also report the factors that govern the surface acidity, which allows us to assign for the first time the important Sanderson's EN values of Ln^{3+} ions ($S_{Ln^{3+}}$) and Ce^{4+}.

To experimentally verify the IMCT nature of the lowest-energy electronic transition from the catechol moiety to the entire ring,[11] we also synthesized 4-methoxyalizarin (Figure 1 a, inset; Supporting Information, SI-1). The UV/Vis spectra of the two compounds (Figure 1 a) show that the lowest-energy transition (2.856 eV) shifts to the lower energy region (2.617 eV) upon introducing a methoxy group at the 4 position; that is, upon increasing the donor strength of the catechol moiety, which verifies the IMCT nature of the transition.

The IMCT bands of alizarin and 4-methoxyalizarin adsorbed on various metal oxides and sulfides are shown in Figure 1 b, with the order of energy increasing from bottom to top. The IMCT bands appear at 2.322–2.713 eV for alizarin and 2.288–2.536 eV for 4-methoxyalizarin (Supporting Information, Table SI-2). The red-shift from alizarin to 4-methoxyalizarin also suggests that the lowest-energy transition of the adsorbed alizarin is IMCT. Furthermore, the IMCT bands of alizarin and 4-methoxyalizarin are red-shifted when they are adsorbed onto oxides and sulfides. Such coordination-induced redshifts were also observed in solution. The IMCT band of alizarin (2.398 eV) red-shifts upon coordinating to Mg^{2+} in ethanol relative to its uncoordinated state (2.856 eV; Supporting Information, Figure SI-3). We attribute the red shift to a decrease in the degree of electron withdrawal of the two phenoxide groups as a result of the replacement of the two strongly electron-withdrawing protons by a less strongly electron-withdrawing metal cation (Figure 1 d, inset). In this context, the gradual blue shift of the IMCT band of the adsorbed alizarin and 4-methoxyalizarin on going from MgO to Ta_2O_5 is attributed to the increase in the degree of electron withdrawal from the two phenoxide ligands to a surface metal ion in the following order: $MgO < PbO < Y_2O_3 < ZnO < ZnS < HfO_2 < Ga_2O_3 < ZrO_2 < TiO_2 < SnO_2 < Ta_2O_5$.

The IMCT energies do not correlate with Sanderson's partial charges of the metal ions (δ_M) in metal oxides and sulfides (Figure 1 c), which are expressed by Equation (1) for metal chalcogenides M_xCh_y (Ch = chalcogen):[32]

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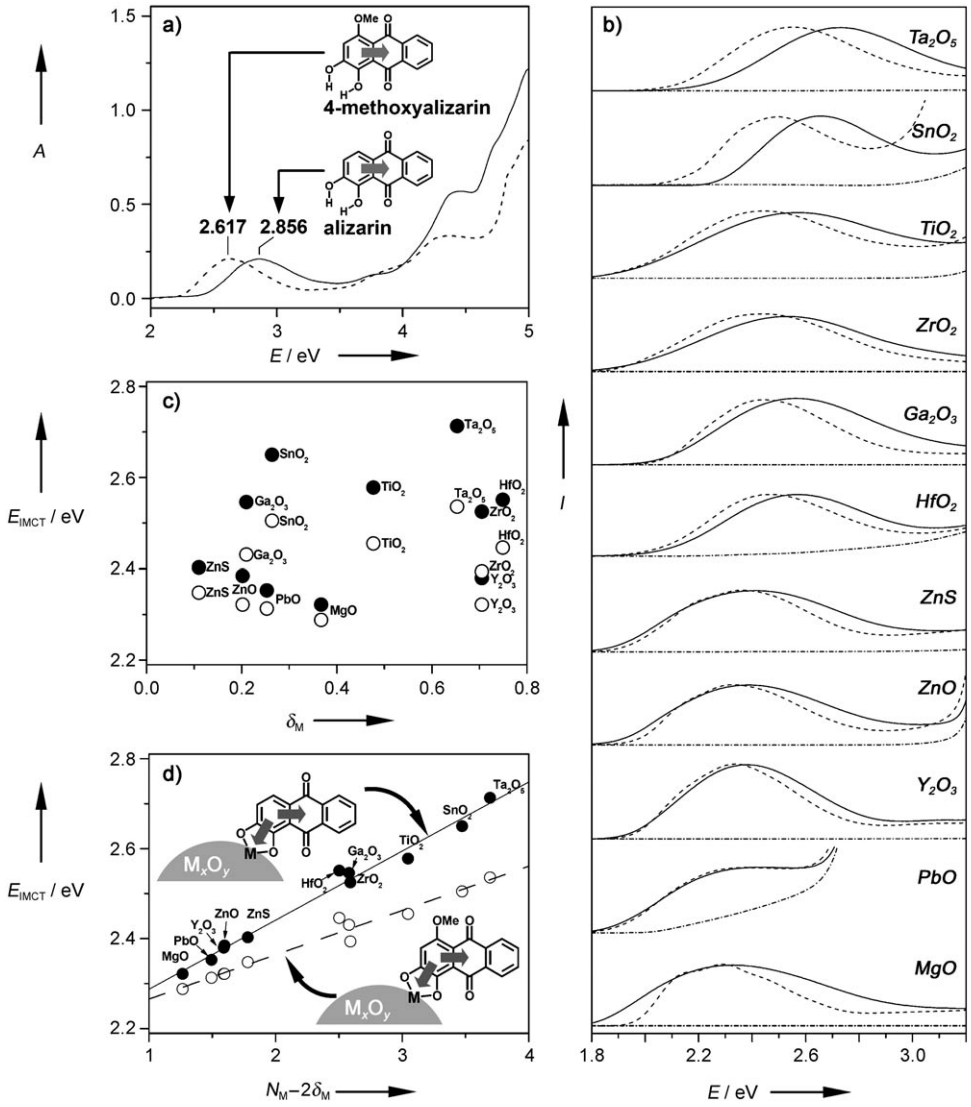

Figure 1. a) UV/vis spectra of alizarin (0.2 mM, ——) and 4-methoxyalizarin (0.2 mM, -----) in ethanol. b) The diffuse-reflectance spectra of alizarin (——) and 4-methoxyalizarin (-----) adsorbed on various metal oxides and sulfide. The –•–• curves represent the spectra of the metal oxides before adsorption of dyes. c) Plot of IMCT bands of alizarin (●) and 4-methoxyalizarin (○) with respect to the partial charge of the metal (δ_M) in the metal oxide and sulfide. d) The linear relationships between the IMCT energy and $N_M-2\delta_M$ for alizarin (top) and 4-methoxyalizarin (bottom).

$$\delta_M = \frac{\sqrt[(x+y)]{(S_{M^{n+}})^x (S_{Ch})^y} - S_{M^{n+}}}{\sqrt[2.08]{S_{M^{n+}}}} \quad (1)$$

where $S_{M^{n+}}$ and S_{Ch} represent Sanderson's EN of the metal in the oxidation state of $n+$ and Sanderson's EN of the chalcogen, respectively. However, IMCT energies show an excellent linear relationship with respect to the values of $N_M-2\delta_M$ of the metal oxides and sulfides according to [Eqs. (2) and (3), Figure 1 d; Supporting Information, Table SI-2],

$$h\nu_{CT}\ (\text{alizarin}) = 0.153\ (N_M-2\delta_M)\ +\ 2.134 \quad (2)$$

$$h\nu_{CT}\ (\text{4-methoxyalizarin}) = 0.098\ (N_M-2\delta_M)\ +\ 2.167 \quad (3)$$

where N_M represents the formal oxidation state of the metal in a compound. This result shows the remarkable phenomenon of the electron withdrawal from the two phenoxide groups by a surface metal ion. This effect thus represents the (Lewis) acidic strength of the oxide being governed by the interplay of N_M and $2\delta_M$. This effect is valid regardless of the metal being a main group (Mg, Pb, Ga, Sn), or a transition-metal (Y, Zn, Hf, Zr, Ti, and Ta) element, and regardless of the period (3rd: Mg; 4th: Ti, Zn, Ga; 5th: Y, Zr, Sn; 6th: Pb, Hf, Ta). The above result thus underscores the fact that the $N_M-2\delta_M$ values, which can be readily derived from their stoichiometries and the Sanderson's EN values of the component elements, can serve as a scale for surface acidities of various metal oxides and sulfides. This opens an unprecedented opportunity to scale the surface acidities of all the metal oxides and metal sulfides (or metal chalcogenides in general) based on their stoichiometries and the Sanderson's EN values of the component elements.

The above linear relationship [Eqs. (2) and (3)] further provides another valuable opportunity to obtain δ_M values from Ln_2O_3 compounds, which eventually leads to the determination of the unknown $S_{Ln^{3+}}$ values from Equation (1). Using alizarin as the probe, we obtained the IMCT bands of alizarin from the Ln_2O_3 compounds, which do not have strong intrinsic colors to obscure the IMCT bands of alizarin (Figure 2 a; Supporting Information, Table SI-4). By fitting the obtained IMCT energies to Equation (2), we could deduce $S_{Ln^{3+}}$ values for La^{3+} (0.154), Sm^{3+} (0.370), Eu^{3+} (0.405), Gd^{3+} (0.469), Dy^{3+} (0.565), Tm^{3+} (0.698), and Lu^{3+} (0.773).

The obtained $S_{Ln^{3+}}$ values showed an excellent linear relationship with the electron densities (total number of electrons divided by the volume) of the ions (Figure 2 b),[45] regardless of the degree of f-orbital filling (half, less than half, or more than half). Likewise, the Sanderson's EN values of

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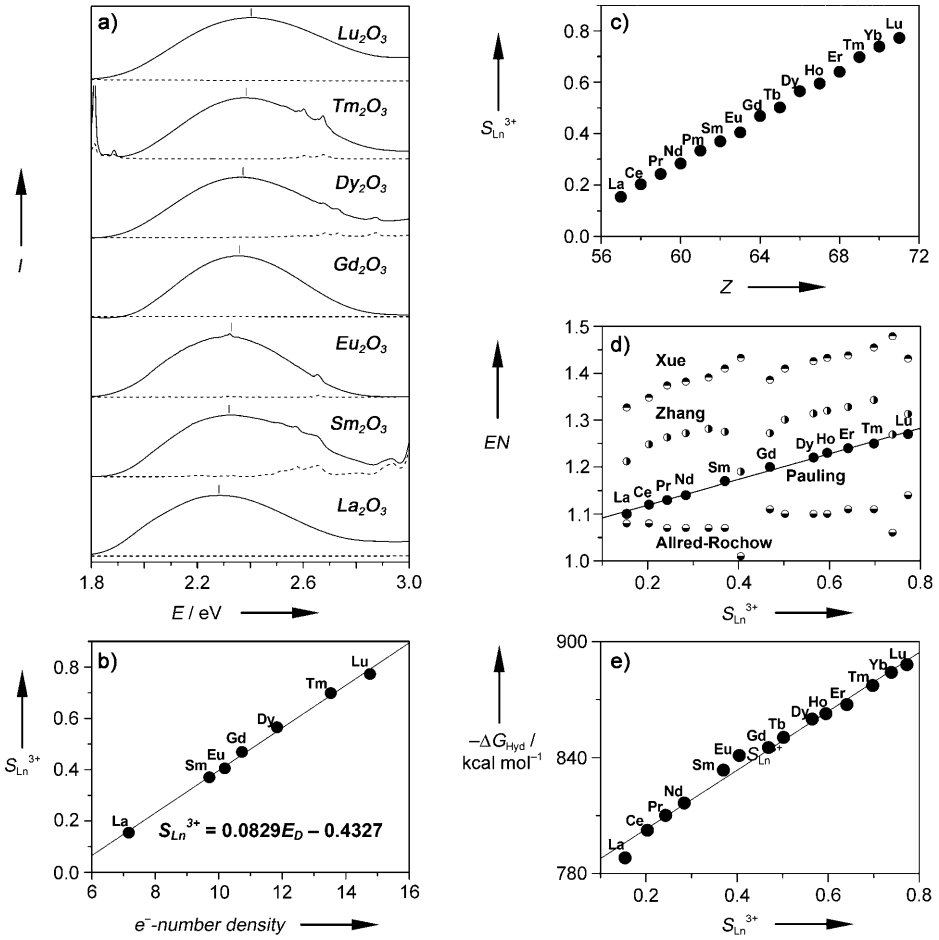

Figure 2. a) The IMCT bands of alizarin adsorbed on several Ln_2O_3 compounds. The ----- curves represent the spectra of the metal oxides before adsorption of dyes b) The linear relationship between the electron number density (total number of electrons divided by the volume) and the assigned Sanderson's EN in Ln^{3+} ions. c) The linear relationship between the atomic number (Z) and the assigned Sanderson's EN in Ln^{3+} ions. d) Plots of various EN values of Ln^{3+} ions with respect to the newly obtained Sanderson's values. e) The plot of the hydration energy with respect to the assigned Sanderson's EN values for Ln^{3+} ions.

transition metal ions in the 3+ and 4+ oxidation states also show linear relationships with their electron densities when they belong to the same period (Supporting Information, Figure SI-5). Based on the above discussion, we deduced the $S_{Ln^{3+}}$ values for the remaining eight Ln^{3+} ions by fitting their electron densities into the linear relationship obtained from Figure 2b (Supporting Information, Figure SI-6). Thus, the $S_{Ln^{3+}}$ values obtained are: Ce^{3+} 0.203, Pr^{3+} 0.243, Nd^{3+} 0.284, Pm^{3+} 0.334, Tb^{3+} 0.502, Ho^{3+} 0.595, Er^{3+} 0.641, and Yb^{3+} 0.739. We also assigned Sanderson's EN values to Ce^{4+} (0.410) by measuring the IMCT band ($h\nu_{max} = 2.436$ eV) of alizarin on CeO_2.

Interestingly, the $S_{Ln^{3+}}$ values linearly correlate to the atomic numbers (Z) (Figure 2c). Among four other EN scales that have been assigned to Ln^{3+} (Supporting Information, Table SI-7), only that of Pauling shows a linear correlation with the obtained $S_{Ln^{3+}}$ values, and thus to Z (Figure 2d). The linear relationship between $S_{Ln^{3+}}$ values and the Pauling's values further allows us to assign the missing Pauling EN values for Pm (1.155), Eu (1.174), Tb (1.201), and Yb (1.265). The $S_{Ln^{3+}}$ values also show a good linear relationship with the heats of hydration of Ln^{3+} ions (Figure 2e),[46] which allows us to estimate the unavailable heat of hydration for Pm^{3+} to be 823.4 kcal mol^{-1}. The assigned $S_{Ln^{3+}}$ values (0.154–0.773) are lower than those of Allred–Rochow (1.08–1.14), Pauling (1.10–1.27), Zhang (1.190–1.343), and Xue (1.327–1.479). However, the $S_{Ln^{3+}}$ values show highest sensitivity to Z. We believe that this methodology can be extended to assign Sanderson's EN values to other elements.

In Figure 1d, the IMCT band of alizarin on HfO_2 deviated from the linear relationship. We attribute the deviation to the imprecise Sanderson's EN value for Hf^{4+} (0.810). Based on this argument, the $N_M - 2\delta_M$ value for HfO_2 was adjusted to fit into the line by increasing $S_{Hf^{4+}}$ to 0.956. The newly assigned $S_{Hf^{4+}}$ then becomes significantly larger than that of Zr^{4+} (0.900) despite Hf being an element from the 5th period, and Zr being in the 4th period. Consistent with our observation, the recently assigned theoretical EN values for Hf^{4+} are substantially larger than those of Zr^{4+} (Xue: 1.706 vs 1.610, and Zhang: 1.568 vs 1.476).[19,20] We conclude that the linear relationship between the IMCT band of alizarin and $N_M - 2\delta_M$ is sensitive and accurate to use for the readjustment of the existing Sanderson's EN values. The new Sanderson's EN values are listed in the Supporting Information (Table SI-8).

By generalizing Equation 2, we scaled the acidities of 101 metal oxides with known Sanderson's EN values based on their $N_M - 2\delta_M$ values (Figure 3; Supporting Information, Table SI-9). Consistent with our scale, the order of acidities of some metal oxides reported in the literature[5,7] was BaO < SrO < CaO ≤ MgO < $ZrO_2 \approx TiO_2 < SnO_2 \approx Ta_2O_5$. However, there are no relative quantitative acidity scales and the differences between CaO and MgO, between ZrO_2 and TiO_2, and between SnO_2 and Ta_2O_5 have not been clear. Our acidity scales for the above eight metal oxides were BaO (0.938) < SrO (0.978) < CaO (1.099) < MgO (1.266) < ZrO_2 (2.591) < TiO_2 (3.046) < SnO_2 (3.473) < Ta_2O_5 (3.694), giving rise to clear distinction.

The above result shows that the surface acidity of a metal chalcogenide is eventually a function of N_M, $S_{M^{n+}}$, and S_{Ch}. The

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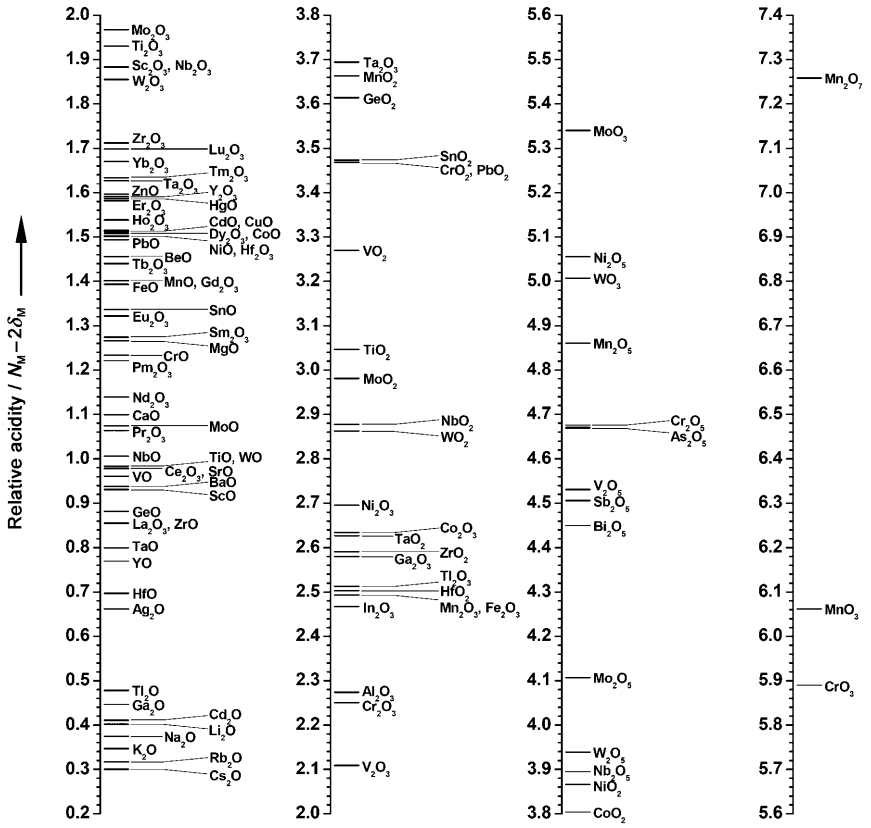

Figure 3. Comparison of the relative acidity of various oxides.

plots of N_M-$2\delta_M$ with respect to $S_{M^{n+}}$ and S_{Ch} for $N_M = 2$–5 predict that the acidity increases as $S_{M^{n+}}$ increases (Supporting Information, Figure SI-10a). The sensitivity of $N_M - 2\delta_M$ to $S_{M^{n+}}$ is higher in the smaller $S_{M^{n+}}$ region and for larger N_M values, although acidity decreases as S_{Ch} increases (Supporting Information, Figure SI-10b). This phenomenon is rather surprising. Indeed, the IMCT band of ZnO appears in the lower energy region than that of ZnS for both alizarin and 4-methoxyalizarin (Figure 1b,d; Supporting Information, Figure SI-10c).

Overall, this is the first work on the general (Lewis) acidity scale for metal oxides and sulfides. The work presented herein addresses factors governing the acidity of oxides and sulfides and proposes novel methods to 1) predict the acidity of a metal oxide and 2) assign Sanderson's EN values to the metal ions in various oxidation states. Furthermore, Sanderson's EN values of Ln^{3+} ions and Ce^{4+} (Figure SI-8), new Sanderson's EN values of Hf^{4+}, Pauling's EN values of Pm, Eu, Tb, and Yb, and the hydration energy of Pm^{3+} are presented. These findings will serve as important guides in the applications of metal chalcogenides and lanthanide elements.

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