Determination of Fe–O Bond Energy in Water-gas Shift Catalyst

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Synopsis. Oxygen catalyst bond energy may play an important role in determining the catalytic activity in water-gas shift reaction. In the present investigation a method for determining this parameter from electrical conductivity has been suggested.

In view of the fact that water-gas shift reaction in iron(III) oxide catalysts is a typical oxidation-reduction reaction, it is quite obvious that there should exist some correlation between the oxygen catalyst bond energy and shift reaction activity. In case of redox reaction in presence of oxygen this bond energy has been measured by various techniques.1,2) But in case of reactions taking place under reducing conditions *e.g.*, water-gas shift reactions, the only reported method is that of Rachkovsky and Yurjeva3) who studied the isotope exchange between hydrogen and deuterium oxide on spinels to estimate the oxygen-catalyst bond energy under reducing conditions. In the present investigation a simple method has been suggested to measure this bond energy from electrical conductivity of iron oxide catalyst.

Experimental

The samples A to E were all shift catalysts of commercial variety containing different type of iron(III) oxides promoted with 7—10% chromium(III) oxide. Sample F is pure iron oxide prepared by precipitation from iron(II) sulfate solution with ammonium carbonate followed by curing in air at 500 °C.

The conductivity cell and the circuit used for measurement have been described in detail in an earlier communication.4) Prior to measurement the catalyst was heated to 200 °C in a flow of N_2+steam in the ratio of 1:5. At 200 °C nitrogen was replaced by hydrogen and the temperature was slowly raised to 350±10 °C. The catalyst was finally stabilized at 460±10 °C. The stabilization was indicated by a constant value of the potential drop. The temperature was slowly brought down to 250 °C and the potential drop was measured at different temperatures after stabilization. Both heating and cooling cycles gave good reproducibility of conductivity values.

Results and Discussion

On reduction with H_2+H_2O mixture the iron oxide catalysts are all reduced to Fe_3O_4. In the present investigation it has been observed that all catalysts show good conductivity which means conduction takes place through Fe_3O_4 phase only irrespective of the presence of chromium(III) oxide. Following Suenaga5) and Parravano6) the Fe_3O_4 phase can be assumed to be in oxygen excess nonstoichiometric form which can be represented as:

$$Fe^{3+}[\square_{\delta}Fe^{2+}_{1-3\delta}\ Fe^{3+}_{1+2\delta}]O_4, \tag{1}$$

where $\square$ is the cation vacancy and δ is the mole fraction of cation vacancies and is a measure of the degree of nonstoichiometry. The conductivity (σ) at any temperature T (in K) can then be written as7)

$$\sigma = C[1-3\delta][1+2\delta]\exp(-E/RT), \tag{2}$$

where C is constant and E is activation energy of conduction. Since δ is very small,

$$\sigma = C[1-\delta]\exp(-E/RT). \tag{3}$$

Therefore,

$$\log\sigma = \log C + \log(1-\delta) - \frac{E}{2.303RT}. \tag{4}$$

Let δ_i, δ, and σ_i, σ are the degree of nonstoichiometry and conductivities at temperature T_i and T respectively,

Then

$$\log\frac{\sigma_i}{\sigma} = \log\frac{(1-\delta_i)}{(1-\delta)} + \frac{E}{2.303R}\left(\frac{1}{T}-\frac{1}{T_i}\right). \tag{5}$$

If the catalyst is stoichiometric (δ=0) at the temperature T,

$$\log\frac{\sigma_i}{\sigma} = \log(1-\delta_i) + \frac{E}{2.303R}\left(\frac{1}{T}-\frac{1}{T_i}\right). \tag{6}$$

From Fig. 1 it can be seen that the plot of log (σ_i/σ) *vs.* $(1/T-1/T_i)$ where T_i is the maximum temperature of measurement *i.e.*, 460±10 °C consists of two parts-linear at lower temperature and nonlinear at higher temperature for all catalysts. The general nature of the conductivity temperature plot obtained for different catalysts is presented in Fig. 2. This shows that the catalyst exhibits variable nonstoichiometry only when $T>T_s$. Thus Eq. 5 is obeyed for $T>T_s$ and Eq. 6 for $T\leqslant T_s$. If the catalyst does not show any variation in stoichiometry throughout the temperature range studied the conductivity temperature relationship can be represented by extrapolating the linear portion corresponding to lower temperature part

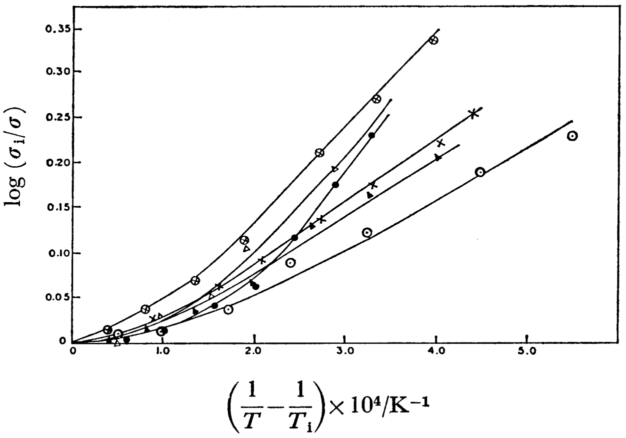

Fig. 1. Variation of resistance of the catalyst with temperature.
Sample A: —△—△—, Sample B: —⊗—⊗—, Sample C: —×—×—, Sample D: —●—●—, Sample E: —▲—▲—, Sample F: —⊙—⊙—.

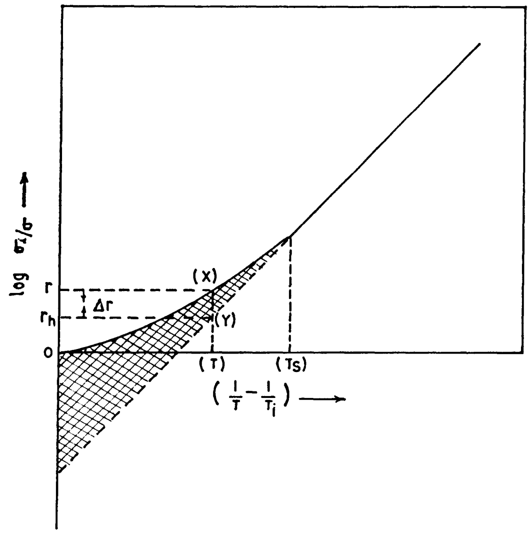

Fig. 2. Change in log (conductivity) *vs.* (temperature)$^{-1}$ plot due to variation in degree of nonstoichiometry.

to higher temperature as shown by the dotted line in Fig. 2. Let σ and σ_h be the conductivities at temperature T corresponding to points X and Y on the actual curve and on the hypothetical extrapolated line respectively. Since Eq. 5 holds for point X and Eq. 6 for point Y respectively then combining both Eqs. 5 and 6,

$$\log\frac{\sigma_h}{\sigma} = \log\frac{\sigma_1}{\sigma} - \log\frac{\sigma_1}{\sigma_h} = r - r_h = \Delta r$$
$$= -\log(1-\delta), \qquad (7)$$

if E is assumed to be independent of the degree of nonstoichiometry. Such an assumption can be justified on the basis of the reported value of E for Fe_3O_4 and γ-Fe_2O_3.[8,9]

The degree of nonstoichiometry (δ) of an oxide catalyst can be expressed by the following empirical equation.

$$1-\delta = \left[\exp\left\{-\frac{\Delta H}{R}\left(\frac{1}{T_s}-\frac{1}{T}\right)\right\}\right]\left(\frac{p^s_{O_2}}{p_{O_2}}\right)^{1/2}, \qquad (8)$$

where ΔH is enthalpy of vacancy formation/mol, $p^s_{O_2}$, p_{O_2} are the equilibrium partial pressure of oxygen at temperatures T_s and T respectively. When $T=T_s$, $p_{O_2}=p^s_{O_2}$, and $\delta=0$. Since in the present case the partial pressure of oxygen at different temperatures is determined by the dissociation of steam ($H_2O \rightleftharpoons H_2+\frac{1}{2}O_2$) we can write

$$\frac{1}{2}\log\left(\frac{p^s_{O_2}}{p_{O_2}}\right) = -\frac{\Delta H_w}{2.303R}\left(\frac{1}{T_s}-\frac{1}{T}\right), \qquad (9)$$

where ΔH_w is the enthalpy of dissociation of steam. Combining Eqs. 7, 8, and 9 and putting $T=T_i$

$$\Delta r = \frac{1}{2.303R}\left(\frac{1}{T_s}-\frac{1}{T_i}\right)(\Delta H+\Delta H_w). \qquad (10)$$

Table 1. Calculation of oxygen catalyst bond energy(ΔH)
ΔH_w = 59.3 kcal/mol, T_i = 460 ± 10 °C.

	Sample					
	A	B	C	D	E	F
Δr	0.157	0.077	0.053	0.205	0.050	0.100
$\frac{(1/T_s-1/T_i)}{10^{-4}\,K}$	2.9	1.675	1.675	2.475	1.75	4.25
ΔH/kcal mol^{-1}	61.7	61.0	60.7	63.0	60.5	60.3

ΔH for different catalysts has been calculated from Eq .10 utilizing the values of Δr and $(1/T_s-1/T_i)$ from Fig. 1 and are presented in Table 1. The average value of oxygen catalyst bond energy is 61.6±2.4 kcal/mol. Since the adsorption/desorption of each oxygen atom results in formation/rupture of two Fe–O bond, average energy per bond is 30.8±1.2 kcal which is good agreement with that calculated by Vijh.[10]

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