THE CATALYTIC ACTIVITY AND DEFECT STRUCTURE OF ZINC CHROMATE

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Computer simulation techniques are used to develop defect models for the non-stoichiometric spinel with composition $Zn_{1+x}Cr_{2-x}O_4$ system. The results are used to provide an interpretation of the variation with composition of the catalytic activity of the monophasic material. We suggest that the increase in the catalytic activity with the Zn/Cr ratio is associated with an increased concentration of oxygen vacancies.

Keywords: Computer modelling, non-stoichiometry, oxide catalysis

1. Introduction

It has long been recognized that the degree of non-stoichiometry of a solid oxide is often a concomitant of catalytic activity. Several decades ago Stone [1], Emmett [2] and Parravano [3] and their coworkers examined this phenomenon especially with respect to variously doped nickel oxides. Ref. [4] contains a review of all relevant early work on this topic. Until comparatively recently it was difficult to establish conclusively using experimental techniques, that the operating solid catalyst was monophasic; nor were there the theoretical procedures for ascertaining which of the various possible types of non-stoichiometry was likely to dominate under different regimes of composition and temperature.

Recently Trifiro and Vaccari [5] have demonstrated that *monophasic* zinc chromate of composition $Zn_{1-x}Cr_{2-x}O_4$ exhibits interesting variations in catalytic activity for the hydrogenation of carbon monoxide to methanol. The dramatic effect of non-stoichiometry is shown in fig. 1. This clearly demonstrates how deviation from the stoichiometric composition of the spinel-structured material (in which the Zn/Cr ratio is 1/2) greatly increases the activity of the material. This observation naturally provokes the question of whether the observed change in catalytic activity can be understood in terms of structural modifications accompanying the variation in stoichiometry. It is known [5] that the material is monophasic with the spinel structure for compositions ranging from the stoichio-
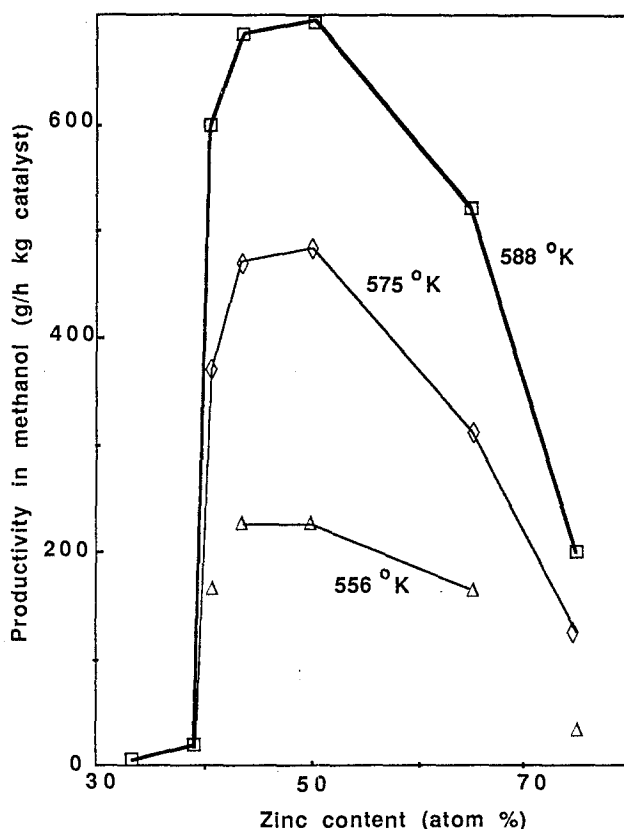
Fig. 1. Methanol productivity as a function of catalyst composition (after ref. [5]).

metric to the 50 : 50 Zn/Cr ratio. The variation in composition is therefore accommodated by defect formation. In this paper we explore by computer simulation possible defect models for the material, with a view to shedding light on the catalytic activity of the materials.

2. Methods

We have calculated the energies of several plausible types of defect using standard Mott-Littleton methodologies [6], which have been extensively and successfully applied to simulating the defect properties of ionic and semi-ionic solids [7–9]. The basis of the methodology is simple; the defect is embedded in a region of crystal (containing typically 200–300 ions) which, using specified interatomic potentials, is relaxed to equilibrium. The response of the remainder of the crystal is calculated analytically using macroscopic dielectric theory. There is now abundant evidence [7–9] that given adequate interatomic potentials and a sufficiently large size of the inner region, these methods can yield accurate values

for defect formation, migration and interaction energies. In the present calculations an inner region of ca 200 atoms was used.

The interatomic potentials employed were of the ionic, Born-model type with analytical short-range pair potentials and a shell model treatment of polarisability. The parameters, which are reported in the Appendix were taken from separate studies of Cr_2O_3 and ZnO and were shown by Cormack et al. [10] to reproduce satisfactorily the structural properties of $ZnCr_2O_4$.

3. Defect models

The following models may be proposed for the incorporation of excess ZnO into $ZnCr_2O_4$.

(i) Chromium vacancy formation, which using Kröger-Vink [10] notation may be written as:

$$'ZnO' \rightarrow 2V_{Cr}''' + 3V_{\ddot{O}} + 'ZnCr_2O_4'$$
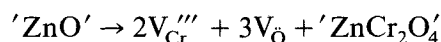
(ii) Substitution of Zn at the Cr site.

$$'ZnO' \rightarrow \tfrac{2}{3}Zn_{Cr}' + \tfrac{1}{3}V_{\ddot{O}} + \tfrac{1}{3}'ZnCr_2O_4' \tag{2}$$

(iii) Zn interstitial formation with oxygen interstitial compensation

$$'ZnO' \rightarrow Zn_i + O_i'' \tag{3}$$

(iv) Zn interstitial formation with chromium vacancy compensation

$$'ZnO' \rightarrow \tfrac{3}{4}Zn_i + \tfrac{1}{2}V_{Cr}''' + \tfrac{1}{4}'ZnCr_2O_4'. \tag{4}$$

The relevant defect and lattice energies are reported in table 1, from them we can obtain the energies for reactions [1–4] given in table 2. Reaction [2] is clearly preferred.

Table 1
Calculated defect and lattice energies

a) Defect energies	
Defect	Calculated energy (eV)
Oxygen vacancy (V_O''	24.22
Chromium vacancy V_{Cr}'''	53.92
Zinc interstitial (Zn_i'')	−14.71
Oxygen interstitial (O_i'')	−7.37
Zinc substitutional (Zn_i')	29.24
Chromium 4 + substitutional (Cr_{Cr}')	−42.13

b) Lattice energies	
Structure	Energy per formula unit (eV)
ZnO	−39.27
$ZnCr_2O_4$	−193.25

Table 2
Calculated solution energies

Solution reaction	Energy cell
1	25.28
2	2.18
3	17.19
4	6.71

Note: Calculated energies used the value of 49.1 eV for the 4th ionisation energy of Cr.

Next we investigated the effects of redox processes. The non-stoichiometric material can be oxidised by the following reaction:

$$V_O'' + \tfrac{1}{2}O_2 \rightarrow O_O + 2Cr;$$ (5)

where Cr indicates an oxidised Cr^{4+} ion.

The energy of this reaction can be written as:

$$E_{OX} = -E_{VO} + \tfrac{1}{2}D_{(O2)} + E_O + E_{Cr'}$$ (6)

where E_{VO} is the oxygen vacancy formation energy, $D_{(O2)}$ is the dissociation energy of oxygen, E_O is the sum of the 1st and 2nd electron affinities of oxygen and $E_{Cr'}$ is the energy to create a Cr^{4+} from a Cr^{3+} ion at the Cr lattice site. We equate this to the difference between the 4th ionisation potential of Cr (I_4^{Cr}) and the Cr^{4+} substitutional energy reported in table 1. The resulting value for E_{OX} is -0.96 eV.

4. Discussion and conclusions

The small energy for E_{OX} indicates that the equilibrium described by eq. (5) could easily be displaced by changes in the total defect concentration and charge compensation by oxygen partial pressure. The calculated energy of E_{OX} would indicate that, at low deviations from stoichiometry, holes (Cr^{4+} ions) are likely to predominate. As the defect concentration increases, repulsions between the holes may displace the equilibrium to the left leading to oxygen vacancies which we postulate to be implicated in the active site in this catalyst. This increase in the oxygen vacancy population would explain the rapid enhancement in the catalytic activity of the material with deviation from stoichiometry as shown in fig. 1.

If our hypothesis is correct we would expect increase in the oxygen partial pressure, which will suppress oxygen vacancies, to lead to a decrease in catalytic activity. It would be of great interest to test this prediction experimentally.

Acknowledgements

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Appendix

INTERATOMIC POTENTIALS

Integral ionic charges were used. Short range potential were represented by the Buckingham function:

$$V(r) = A\,e^{-r/p} - Cr^{-6}$$

with the following parameters:

Interaction	A (eV)	p (Å)	C (eVÅ^6)
Zn...O	488.11	0.3639	0.0
Cr...O	1734.1	0.3010	0.0
O...O	22764.3	0.1490	27.88

Other short range potentials were ignored. A shell model treatment of polarisability is employed with the following parameters:

$$Y = -2.869\,|e|; \quad K = 74.92\ \text{eVÅ}^2$$

The cations are unpolarisable.