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IS THERE A DIFFERENCE BETWEEN SURFACE AND BULK OXIDATION LEVELS IN PARTIALLY REDUCED METAL OXIDE CATALYSTS? EVIDENCE FROM METHANE OXIDATIVE COUPLING KINETICS

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From the dependence of the rate of oxidative coupling of methane by a mixed manganese-magnesium oxide on the degree of reduction, we infer that even at equilibrium the surface remains more reduced that the bulk, and estimate the magnitude of the difference.

According to the Mars-van Krevelen mechanism for selective oxidation over metal oxide catalysts, the active sites are surface lattice oxide positions, which are consumed in substrate oxidation and subsequently regenerated by gas-phase dioxygen [1]. This amounts to (at least) microscopic reduction of the metal oxide, and a detailed understanding of this process will be needed in order to extend mechanistic understanding of such catalytic reactions to the molecular level. Kung has recently commented that the surface stoichiometry of a metal oxide catalyst (as well as the structure) may differ from that of the bulk, though little information on this issue is currently available [2]. A conceptually straightforward approach would utilize a technique such as XPS to probe the surface of a partially reduced metal oxide; however, both the sensitivity to oxidation state and the degree of surface-specificity of such techniques are questionable.

The oxidative coupling of methane, a process of considerable current interest, is particularly relevant to this question: it may be carried out either in "normal" mode, where methane and dioxygen are cofed; or in "redox" mode, where methane and dioxygen are fed separately and alternatively [3]. In the latter case, extensive reduction of the "catalyst" (actually used as a recycling stoichiometric reagent) is clearly a vital feature. We have previously reported detailed kinetics studies on the redox mode oxidative coupling of methane over a mixed manganese-magnesium oxide [4], and propose here that the results may be

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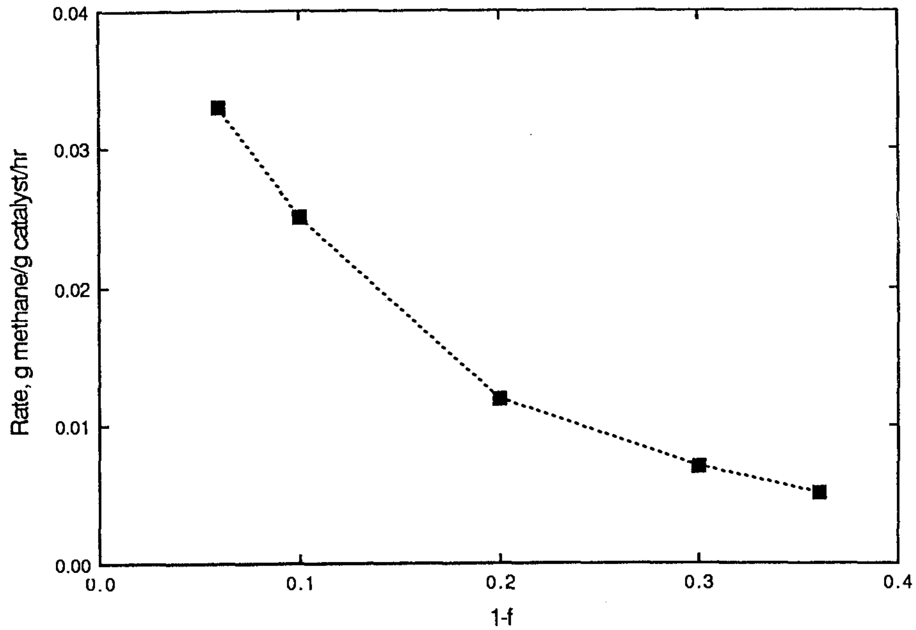

Fig. 1. Rate of methane conversion vs. fractional reduction of catalyst. (Catalyst: 10% $NaMnO_4/MgO$; methane pressure = 0.2 atm; $T = 825\,^\circ C$.)

extended to infer a significant surface-bulk difference with a thermodynamic origin.

The experimental procedure was described previously [4]: mass spectrometric sampling permits continuous determination of methane conversion, product selectivities, and degree of catalyst reduction throughout the reaction. Figure 1 shows a typical plot of activity vs. degree of reduction. If the surface stoichiometry were *identical* to that of the bulk, one would expect a linear dependence, which is clearly not observed. An explanation based upon kinetics could be offered: reduced surface sites must be replenished by bulk-to-surface diffusion, and if the latter process is slow relative to methane oxidation, the surface will remain more reduced than the bulk. However, we previously showed that the following two-step model can account accurately for the dependence of rate upon both methane pressure and metal loading [5]:

$$MO_s + CH_4 \xrightarrow{k_1} M_s + H_2O + C_xH_y \tag{1}$$

$$M_s + MO_b \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} MO_s + M_b \tag{2}$$

where MO and M are oxidized and reduced sites, and subscripts s and b indicate surface and bulk, respectively. At low (< 0.5 atm) partial pressures of methane rates are first-order in methane, which implies that bulk-to-surface diffusion is

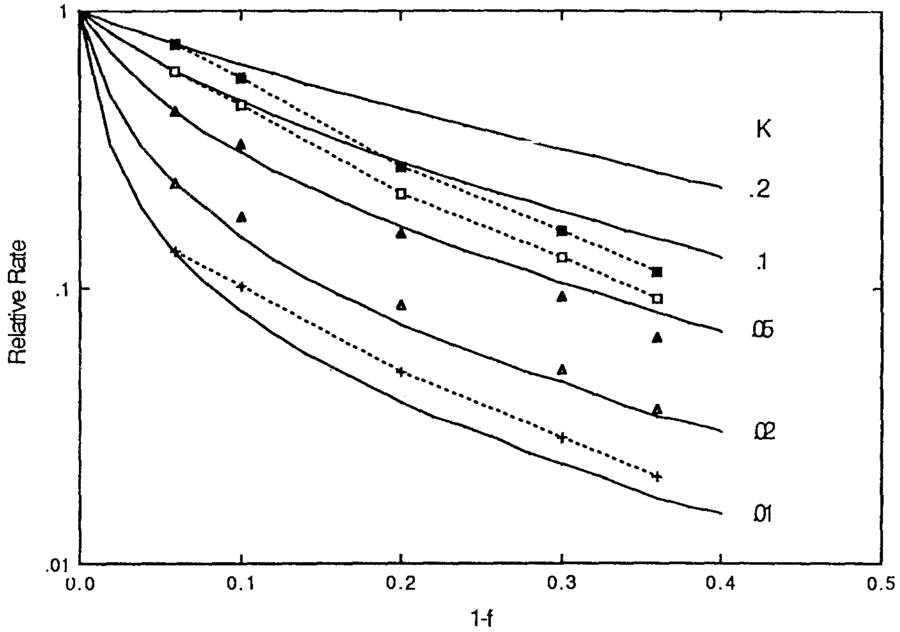

Fig. 2. Comparison of calculated and observed variation of rate with fractional reduction, for different values of K. (Vertical axis displayed logarithmically in order to show differences more clearly.)

fast relative to methane oxidation and that an interpretation based upon kinetic control of surface oxidation level is not viable.

In that case, we may write an equilibrium expression:

$$K \equiv k_2/k_{-2} = (\mathrm{MO_s})(\mathrm{M_b})/(\mathrm{M_s})(\mathrm{MO_b}). \tag{3}$$

As before [5], we let M = total concentration of sites, f = fraction of total sites oxidized, and S = fraction of sites on the surface. Since S is small, $(\mathrm{MO_b}) \approx \mathrm{M}f$, $(\mathrm{M_b}) \approx \mathrm{M}(1-f)$; also $(\mathrm{M_s}) = \mathrm{M}S - (\mathrm{MO_s})$. Substituting in eq. (3) and solving for $(\mathrm{MO_s})$ gives

$$(\mathrm{MO_s}) = \mathrm{M}SK\frac{f}{1-f(1-K)}. \tag{4}$$

But the rate $v = k_1(\mathrm{CH_4})(\mathrm{MO_s})$; if $v_{\max} \equiv$ the rate for a fully-oxidized sample ($f = 1$), then

$$v_{\mathrm{rel}} \equiv v/v_{\max} = \frac{fK}{1-f(1-K)}. \tag{5}$$

Figure 2 shows v_{rel} vs. K curves calculated from eq. (5) for several trial values of K. Superimposed are the data from fig. 1, transformed to v_{rel} and then renormalized to match each curve at the first data point. The best fit is obtained for a value of K around 0.02–0.05; values of K outside this range give signifi-

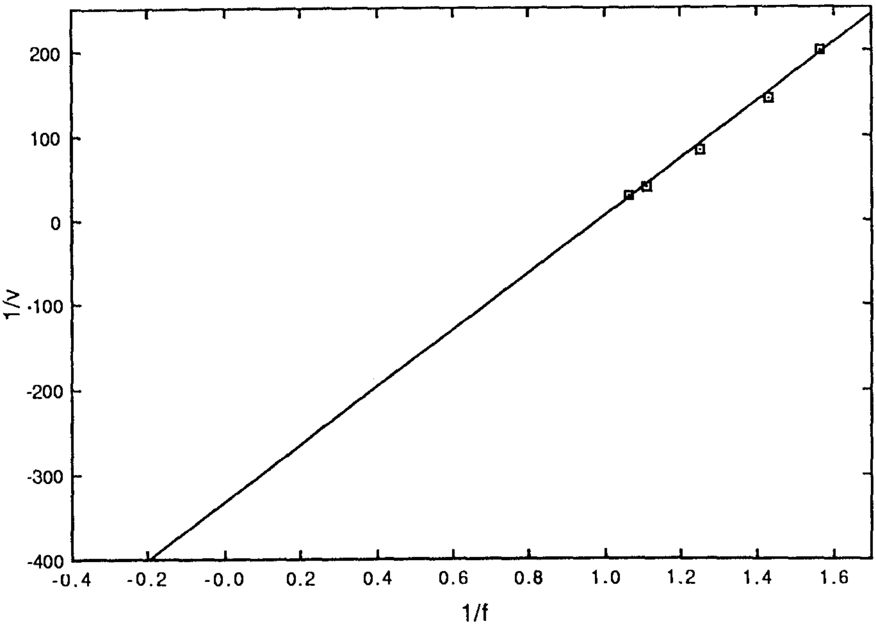

Fig. 3. Double-reciprocal plot of data from fig. 1.

cantly poorer agreement. Alternatively, K can be determined analytically from the same data and the rearranged equation:

$$1/v = 1/fKv_{\max} - (1-K)/Kv_{\max} \tag{6}$$

so that K may be determined from the ratio of intercept to slope in a plot of $1/v$ vs. $1/f$. Such a plot is shown in fig. 3, and gives $K = 0.025 \pm 0.02$ [6].

Although this calculation employs several assumptions and approximations that may be open to some question, it is possible to obtain an independent estimate of K by comparing rates measured for the same catalyst under redox and cofeed conditions (assuming that the mechanisms for the two cases are essentially the same, differing only by the means of regenerating active surface sites). In cofeed mode, the surface oxidation level is determined kinetically by the competition of site reduction and reoxidation, and may be calculated from the fit of experimental data to the Mars-van Krevelen model. Taking data obtained in cofeed mode on the same catalyst [7], we choose conditions that give a calculated surface oxidation level $f^* \approx 90\%$, and find a rate of conversion approximately 3.8 times higher than that measured in the redox mode for *bulk* oxidation level $f \approx 90\%$ and the same methane pressure. In the above model the cofeed rate is simply the rate for a fully oxidized surface times the fractional surface oxidation level, or $v_{\max}$ times f^*, so

$$v_{\text{cofeed}}/v_{\text{redox}} = f^*/\{fK/(1-f(1-K))\} = 0.9/\{0.9K/(1-0.9(1-K))\} = 3.8 \tag{7}$$

from which K is calculated to be 0.035 ± 0.015, in excellent agreement with the value obtained from redox data alone.

These calculations suggest that there is indeed a thermodynamic difference between bulk and surface oxidation levels; the preference for placing an oxygen ion in the bulk and a vacancy at the surface rather than vice-versa has an apparent $\Delta G^0 \approx -7$ kcal mol^{-1} at 825 °C. Physically, this result seems reasonable from the simplest point of view: there are more favorable Coulombic interactions for this arrangement. It should be noted that the catalyst used in this study features a close structural resemblance between the oxidized (Mg_6MnO_8) and reduced (Mg, Mn)O solid solution) forms [5], so the conclusion may not be generally applicable; but the shapes of the rate vs. f curves are qualitatively similar for other catalysts as well. Possible theoretical approaches to this issue are under exploration [8].

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