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A Comparison of the Water–Gas Shift Reaction on Chromia-Promoted Magnetite and on Supported Copper Catalysts

In this note we shall show that the water–gas shift reaction proceeds in closely similar ways on the two commercial catalysts commonly used, viz. chromia-promoted magnetite and $Cu/ZnO/Al_2O_3$, even though the catalysts have no component in common and the active phase in one is an oxide (Fe_3O_4) and in the other, a metal (Cu). Mechanisms proposed for the water–gas shift reaction fall into two categories: associative mechanisms, Eqs. (1) and (2), where the reagents form an intermediate, *I*, on the catalyst surface,

$$CO + H_2O \rightleftharpoons I \tag{1}$$

$$I \rightleftharpoons CO_2 + H_2 \tag{2}$$

and regenerative mechanisms, Eqs. (3) and (4), in which oxygen on the catalyst surface participates,

$$H_2O \rightleftharpoons H_2 + O_{(a)} \tag{3}$$

$$CO + O_{(a)} \rightleftharpoons CO_2 \tag{4}$$

Recent work has shown that the regenerative mechanism is dominant on the low-temperature catalysts (copper/zinc oxide/alumina) (*1*, *2*) and on the high-temperature catalysts (magnetite/chromia) (*3*, *4*). The associative mechanism, especially with adsorbed formate as the intermediate *I*, for the water–gas shift reaction has been found (*3*) on various oxides, but as a slower reaction. If surface oxygen formation and removal are facile, as they are on copper metal (*1*) and on magnetite (by the Fe^{II}/Fe^{III} ions in octahedral holes in the lattice (*3*)), then presumably the simplicity of reactions (3) and (4) makes the regenerative mechanism the faster, preferred route.

In a previous paper Chinchen *et al.* (*1*) used *in situ* measurements of copper area to determine coverages of adsorbed oxygen, and thereby calculated the free energy of formation of $O_{(a)}$ to be ca. -240 kJ mol^{-1} at 513 K. This can be compared with the free energy of formation of cuprous oxide at the same temperture, -130.5 kJ mol^{-1}. Thus the compound formed by the adsorption of oxygen on a copper metal surface, at a coverage of less than one-half monolayer, is some 110 kJ mol^{-1} more stable than cuprous oxide. Reactions (3) and (4) with copper metal are not possible with conversion to cuprous oxide, but they do occur with surface oxygen formation (*1*). The activity of magnetite/chromia catalysts for the water–gas shift reaction is proportional to total surface area, even after ageing (*5*), so a constant fraction of the surface is the active phase. A similar approach can therefore be used.

Kubsh and Dumesic (*4*) studied oxygen addition to and removal from a commercial magnetite/chromia catalyst as a function of gas composition, so it is possible to use their data to calculate a comparable value of ΔG° for this catalyst. They presented their results as a semilog plot (Ref. (*4*, Fig. 3), but interpretation in terms of the equilibrium constant of reaction (5) is more useful here. In this context

$$CO + O_{(a)} \rightleftharpoons CO_2 + \square \tag{5}$$

where $O_{(a)}$ is a removable oxide ion in the magnetite surface and $\square$ is an anion vacancy in the magnetite surface. Kubsh and Dumesic's results fit Eq. (5) better than Eq. (4), used for the copper metal surface. The equilibrium constant of reaction (5) is given by Eq. (6), where, following Kubsh and Dumesic,

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TABLE I

Calculated Parameters for Magnetite and Copper Catalysts

Catalyst	Magnetite	Copper
Maximum coverage of adsorbed oxygen	0.087 monolayer	0.50 monolayer
Free energy of formation of $O_{(a)}$	-210 kJ mol^{-1} at 637 K	-240 kJ mol^{-1} at 513 K
Coverage of available sites at $[CO_2]/[CO] = 1$	~6% at 637 K	~60% at 513 K

$$K_5 = \frac{[CO_2]\,[\Box]}{[CO]\,[O_{(a)}]} = \frac{[CO_2]\theta_v}{[CO]\theta_{(o)}}, \qquad (6)$$

θ_v is the coverage of vacant anion sites and θ_o the coverage of removal oxygen, both relative to the total BET area. The limiting value (*4*) of θ_o ($\theta_o = 0.087$, maximum value; $\theta_o = 0.052$ at $[CO_2]/[CO] = 10.8$), with values for oxygen removal, relative to that at $[CO_2]/[CO] = 10.8$, from Ref. (*4*, Fig. 3, were used to calculate pairs of values of θ_v and θ_o for varying $[CO_2]/[CO]$ ratios from 2 to 20. The equilibrium constant, K_5, was then calculated from Eq. (6) for each set of values, to give a mean value $K_5 = 15.1 \pm 1.7$.

With standard data for carbon monoxide and carbon dioxide, the equilibrium constant (K_7) of reaction (7),

$$\tfrac{1}{2}O_{2(g)} + \Box \rightleftharpoons O_{(a)} \qquad (7)$$

can be calculated to be 3×10^{17} $bar^{-\frac{1}{2}}$ and the standard free energy of reaction (7) is ca. -210 kJ mol^{-1} at 673 K. This is fairly close to the value of ΔG_f° for $O_{(a)}$ on copper at 513 K, but any more detailed comparison would require better thermodynamic data (*1*). For $[CO_2]/[CO] = 1$, the coverages of *available* sites can be calculated to be ca. 60% for the $Cu/ZnO/Al_2O_3$ catalysts at 513 K (*1*) and ca. 6% for the Fe_3O_4/Cr_2O_3 catalyst at 637 K. The higher coverage on the copper catalyst may reflect in part the role of adsorbed oxygen as promoter on copper. See Table 1.

The reaction steps above have been written, as in much previous literature, as Eley–Rideal reaction steps. Recently Tinkle and Dumesic (*3*) have shown that CO/CO_2 conversion on magnetite/chromia catalysts takes place through chemisorbed species, while still via a regenerative mechanism, and they suggest reactions (8) and (9) for the two stages (Fig. 1).

There is a close formal resemblance between reactions (8) and (9) and the mechanism put forward by Chinchen *et al.* (*1*) for the water–gas shift reaction over supported copper catalysts. On copper, adsorbed oxygen acts as a promoter as well as a reaction intermediate, facilitating the chemisorption, and subsequent dissociation, of both water (via hydroxyls) and carbon dioxide. Carbon dioxide forms strongly bonded chemisorbed states on partially oxidised copper, whereas physisorbed states only are observed on clean copper (*1, 6*). Au and Roberts (*7–9*) and Bange *et al.* (*10*) have shown that water is adsorbed and subsequently desorbed without dissociation on clean Cu (110) and (111) faces but that dissociative chemisorption to give hydroxyls occurs when adsorbed oxygen is present. Both forward and reverse water–gas shift reactions are therefore accelerated by a decrease in the activation energy for dissociation. If *M* in reactions (8) and (9) is now taken to be a surface ensemble of copper atoms rather than Fe^{II}/Fe^{III} atoms,

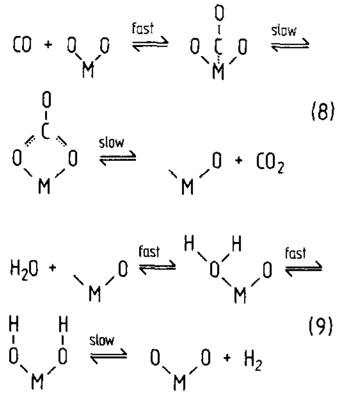

FIG. 1. Regenerative mechanism for the water–gas shift reaction over magnetite catalysts, proposed by Tinkle and Dumesic (*3*).

then these reactions are in accord with the proposals of Chinchen *et al.* (*1*), except that too little is yet known to be able to define fast and slow steps. The same lack of knowledge prevents any understanding of the reasons for the much higher activity of copper catalysts over magnetite catalysts. It is possible that the dissociative chemisorption and desorption of hydrogen, relatively fast on copper (*1, 11*) but slow on magnetite (*3*), may be a key factor.

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G. C. CHINCHEN
M. S. SPENCER

Billingham Catalysis Centre
Research and Technology Department
ICI Chemicals and Polymers Ltd.
Billingham, Cleveland TS23 1LB, England

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