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# Methanol Synthesis Activity of Au/$CeO_2$ Catalysts Derived from a $CeAu_2$ Alloy Precursor: Do Schottky Barriers Matter?

A metal/oxide junction effect theory of methanol synthesis catalysts has recently been proposed (*1*) according to which all the catalytic chemistry occurs over a (metal-promoted) oxide phase; the active sites are considered to be doubly ionised oxygen vacancies. It is suggested that the mode of action of such catalysts involves metal promotion of the oxide productivity by enhancement of the equilibrium concentration of oxygen vacancies. A large contribution to the enthalpy of formation of an oxygen vacancy in an oxide comes from the energy required to raise two electrons to the oxide conduction band. Any metal which forms a Schottky junction with a given oxide can give rise to an active catalyst because in such cases the conduction band edge lies higher in energy than the metal Fermi level. The enthalpy of formation of a doubly ionised vacancy is reduced by allowing electrons to move to the metal Fermi level. This scheme predicts that catalyst productivity is dependent on metal/oxide contact area. Hence, catalyst microstructure determines the absolute activity. However, the junction effect theory is not without controversy.

In light of the junction effect hypothesis, we reported earlier on an investigation of the activity and microstructure of Ag/$CeO_2$ systems derived from binary Ce–Ag alloys (*2*). Here we should recall that *Cu*/$CeO_2$ catalysts derived from Ce–*Cu* alloys (*3*) exhibit remarkably high activity for methanol synthesis, even at low temperatures (*4*). These catalysts are comprised of small metal particles in contact with very poorly crystalline cerium oxide (*5–7*). The Cu visible in XRD had a particle size of ~80 Å. However, approximately 60% of the Cu was not seen in the XRD measurements; EXAFS subsequently revealed that these particles had an average size of ~25 Å. However, despite producing Ag/$CeO_2$ systems characterised by extensive interaction between oxide and silver, no methanol synthesis activity was observed at any temperature below 300°C.

To form a Schottky junction with an oxide, the work function of the metal must be sufficiently high. The work function of Ag is ~0.4 eV *below* that of Cu (*8*), so the Fermi level of Ag might actually lie above the lower edge of the cerium oxide conduction band: this could then rationalise the lack of methanol synthesis activity exhibited by such Ag/$CeO_2$ systems in terms of the junction effect theory (*1*). On the other hand, the work function of polycrystalline Au is ~0.4 eV *higher* than that of copper; if a Schottky junction *is* created when Cu is placed in contact with a given oxide, then, a fortiori, Au in contact with the same oxide *must* give rise to a junction with a larger Schottky barrier.

We have therefore extended our earlier studies (*2, 3, 5–7*) to examine the methanol synthesis activity of Au/$CeO_2$ catalysts derived by the oxidative activation of $CeAu_2$.

The $CeAu_2$ sample was prepared by radiofrequency induction heating of the constituent elements. Au (99.99%) was obtained from Johnson Matthey; the total metal impurity level was 100 ppm. Ce was obtained from Rare Earth Products (Cu, 30 ppm; Fe, 20 ppm; Si, Mn, Mg, Cr, Ca, Al, 1–10 ppm) as was the $CeO_2$ (99.99%; Cu, 3 ppm; Fe, 5 ppm; Si, 10 ppm; Mg, Al, Ca, <1 ppm). XRD confirmed that the starting material consisted of ~95% $CeAu_2$ with a small amount of $CeAu_3$. Catalyst testing was car-

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ried out in a fixed-bed microreactor incorporating continuous mass spectrometric analysis; details have been reported elsewhere (*9*). Alloy samples of ~0.6 g were ground to 50–250 μm and diluted with glass beads to accommodate the expansion that occurs on activation (due to the transformation of $CeAu_2$ into $Au/CeO_2$). *Ex situ* XRD analyses of discharged catalyst samples were also performed. In each case the exposure of the catalyst to ambient air was minimised by discharging the catalyst into a glove box and then placing a sample of it onto an XRD slide and recording the pattern. The total exposure time, from its removal from the glove box to the end of the XRD run, was approximately 1 h. The gases used (He, CP grade ≥99.999% purity; $H_2$, CP grade ≥99.999% purity; CO, $H_2$ 33:67; impurities $O_2$, 5 ppm; $H_2O$, 2 ppm; and $CO_2$, 20 ppm and premixed $N_2O$ (2.6%) in He; impurities $O_2$, 6 ppm; $CO_2$, 3 ppm; and $H_2O$, 3 ppm) were obtained from BOC Special Gases Ltd. Helium was further purified by passage through a molecular sieve at ambient temperature; all other gases were used without additional purification.

First of all, the transformation of $CeAu_2$ in 20 bar $CO/H_2$ was investigated. No methanol production was detected at any temperature up to 250°C at a flow rate of 50 standard cubic centimetres per minute (sccm). XRD revealed that the alloy was only partially transformed.

Previous work in this laboratory (*5*) has shown that the methanol synthesis activity of similar Cu alloy-derived catalysts is significantly increased by a hydrogen pretreatment. In the present case, pretreating the alloy with 15-bar hydrogen at 250°C, prior to exposure to 20 bar $CO/H_2$ at 250–350°C, did not induce any methanol synthesis activity. However, following this 350°C treatment XRD showed that the starting alloy had completely transformed into elemental Au and poorly crystalline $CeO_2$. The average Au crystallite size was estimated at ~190 Å using the FWHM of the Au(111) diffraction peak and the Scherrer equation; the average ceria crystallite size was ~110 Å. (Note that this observation also indicates that the level of activity associated with the $CeO_2$ is undetectably low.)

Clearly, the $CeAu_2$ alloy is not as reactive towards $CO/H_2$ or $H_2$ + $CO/H_2$ as $CeCu_2$, which transforms rapidly under mild conditions (*6*, *9*), for example 15 bar $CO/H_2$ and 100°C. In the present case, the high transformation temperature of the alloy means that $Au/CeO_2$ systems are not generated at temperatures below those at which $CeCu_2$-derived catalysts are already thermally deactivated (*6*). Therefore, an alternative, lower temperature activation procedure was sought.

Our earlier work (*2*) demonstrated that the transformation of the CeAg alloy into $Ag/CeO_2$ was effected at significantly lower temperature in $N_2O$/He than in $CO/H_2$ or in $H_2$ + $CO/H_2$. The Ag particles thus generated were also much smaller (~40 Å), so the extent of interaction between metal and oxide phases was greater.

An *in situ* XRD experiment performed using equipment described elsewhere (*5*) and 1-bar $N_2O$/He at a flow rate of 20 sccm and temperatures between 100 and 180°C revealed that no transformation occurred at 100°C, but that the alloy was completely converted into poorly crystalline $CeO_2$ and elemental Au at temperatures >150°C. The average $CeO_2$ particle size was estimated at 75 Å and that of gold at 65 Å.

Following activation in $N_2O$/He at 1 bar and 180°C of a new charge in the microreactor, the gas feed was switched to pure He to flush the reactor and the sample was cooled to room temperature. The gas feed was then switched to $CO/H_2$ and the pressure increased to 20 bar. The temperature was then slowly ramped to 200°C and *a very low level of methanol synthesis activity resulted*; the catalyst productivity was approximately two orders of magnitude lower than that of catalysts derived from $CeCu_2$ under similar conditions: ~0.1–0.2 and 16.4 mol methanol (STP)/kg/h, respectively. This low level of

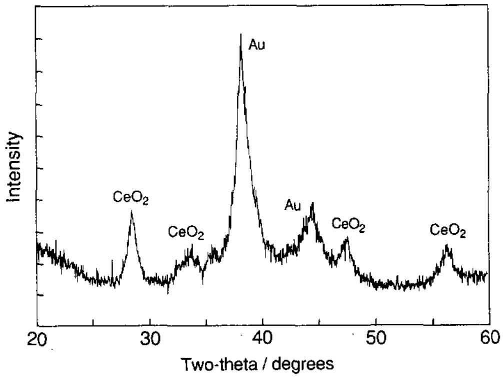

FIG. 1. XRD pattern of Au/$CeO_2$ methanol synthesis catalyst derived from $CeAu_2$ by activation in 1-bar $N_2O$/He at 180°C.

activity was certainly due to the sample: recall that there was *no* detectable activity after $CO/H_2$ "activation," even at considerably higher reaction temperatures (see above).

Figure 1 shows the *ex situ* XRD pattern of this low activity Au/$CeO_2$ catalyst. The pattern, in combination with the Scherrer equation, reveals that the average Au particle size was ~69 Å and the average $CeO_2$ particle size was ~98 Å. In addition, the broad nature of the base of the main Au diffraction feature reveals that there were a substantial concentration of more highly dispersed Au particles within the catalyst.

The implications of this result, i.e., the observation of a very low level of methanol synthesis activity from the $N_2O$-activated Au/$CeO_2$ catalyst are not clear. Such low levels of methanol production relative to $CeCu_2$-derived catalysts would have been below the detection limit of the gas chromatograph used for activity measurements in our work on Ag/$CeO_2$ catalysts. It is, therefore, conceivable that the Ag/$CeO_2$ and Au/$CeO_2$ catalysts have similar activities, in which case the observed activity might correspond to the unpromoted activity of the cerium oxide phase. Under the same conditions used for testing the $CeAu_2$-derived system, methanol production from 0.45 g of highly crystalline, low surface area ceria is detectable at 280°C. The intrinsic activity of the disordered and defective cerium oxide phase derived from $CeAu_2$ (and CeAg) could well be much higher than that of commercially available crystalline ceria.

Calculations of oxygen vacancy concentrations using the junction effect theory, indeed even theoretical determination of whether a Schottky barrier is formed, are precluded by the absence of accurate values for the relevant solid state parameters, in particular the band gap and work function of cerium oxide. The work functions of Ag, Cu, and Au are ~4.26, 4.65, and 5.10 eV, respectively (*8*); so, as pointed out above, if Schottky barrier formation occurs in the Cu/$CeO_2$ system it *must* occur in Au/$CeO_2$. Thus the activity observed from Au/$CeO_2$ could indicate a role for the junction effect mechanism. However, if Schottky barrier formation (and the resulting increase in oxygen vacancy concentration) is also solely responsible for the extremely high activity of the $CeCu_2$-derived catalyst, why is the activity of the $CeAu_2$-derived system so poor? It may be that the oxide surface area of the $CeAu_2$-derived system is far lower. Alternatively, the oxide/metal contact area may be substantially lower in the case of Au/$CeO_2$ than in the case of Cu/$CeO_2$. The metal particle size data do *not* support this view strongly, since in both cases highly dispersed transition metal particles are present on a highly defective ceria support phase. The most natural explanation, however, for the high activity of the Cu/$CeO_2$ catalyst, is that active sites involving copper species are responsible. This is consistent with the widely accepted view that Cu plays a key role in methanol synthesis.

Nevertheless, it would be interesting and certainly worthwhile to examine systems derived from a much more cerium-rich Ce/Au alloy; with such a precursor, intrinsically more reactive, it may be possible to hinder the sintering of gold, thereby increasing the Au/$CeO_2$ contact area by incorporation/encapsulation of the Au in the oxide during the activation process.

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