JOURNAL OF CATALYSIS **118**, 175–191 (1989)

High-Activity Methanol Synthesis Catalysts Derived from Rare-Earth/Copper Precursors: Genesis and Deactivation of the Catalytic System

ROGER M. NIX,* ROBERT W. JUDD,*,[1] RICHARD M. LAMBERT,*,[2] J. ROBERT JENNINGS,† AND GEOFFREY OWEN‡

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, United Kingdom; †I.C.I. Chemicals & Polymers plc, Research Department, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, United Kingdom, and ‡I.C.I. Films, Research & Technology Department, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE, United Kingdom

Received September 23, 1988; revised February 13, 1989

The activation of $CeCu_2$ and NdCu intermetallic precursors to yield highly active methanol synthesis catalysts has been investigated using microreactor techniques under pressures of 10–15 bar. Activation procedures using synthesis gas alone and using hydrogen pretreatment with subsequent oxidation in either syngas or N_2O are evaluated and compared. Reactive frontal chromatography was employed to perform *in situ* measurements of the specific copper surface area: values for active catalysts are typically less than 0.5 m^2/g and do not correlate with the synthesis activity. The thermal stability and resistance to poisoning of these materials was also studied. They exhibit irreversible deactivation at temperatures greater than 523 K and the activity of oxidized catalysts cannot be fully regenerated on rereduction. Exposure of the active catalysts to CO_2 leads to complete loss of synthesis activity at 473 K and results in the formation of a strongly bound CO_2 complex. This CO_2 cannot be fully desorbed below the thermal sintering temperatures of the catalysts. These data and earlier results are rationalized on the basis of an active site for methanol synthesis which involves Cu entities intimately associated with the rare-earth-oxide phase that is generated during activation. © 1989 Academic Press, Inc.

INTRODUCTION

The reactive decomposition of intermetallic compounds of transition metals with the rate earths (*RE*) or actinides yields highly active heterogeneous catalysts for a wide range of important chemical reactions (*1–4* and Refs. therein). This novel preparative technique involves selective oxidation of one metal component to yield the oxide support and therefore differs fundamentally from more commonly utilized procedures for the production of supported metal catalysts in which a calcination stage is followed by selective reduction of the active metal. Our earlier *in situ* XRD studies of the activation and performance of a series of such catalysts (*5*) indicated that their extraordinarily high activity may be associated with a specially intimate interaction between the metal and oxide components. This in turn may reflect the essentially atomic dispersion of the two metals in the alloy precursor and the relatively mild conditions employed in its activation. The use of Cu–*RE* intermetallics as precursors for methanol synthesis catalysts was first reported by Wallace and co-workers (*6, 7*); this work was followed by more detailed investigations dealing primarily with Cu–Th precursors (*8, 9*), such catalysts having given the most promising results in the initial studies.

More recent investigations in our own laboratories have concentrated on the use

---

[1] Present address: British Gas plc, Research & Development Division, London Research Station, Michael Road, London SW6 2AD, UK.

[2] To whom correspondence should be addressed.

0021-9517/89 $3.00

of *RE* metals which are more readily available and easier to handle. A wide range of alloy compositions and stoichiometries were screened (*10, 11*) and activities comparable to those of Cu–Th catalysts were obtained by using *in situ* activation in CO/H_2 process gas under mild conditions. Furthermore, it was found that at high pressures significant conversions could be achieved at temperatures as low as 80°C (*12*). We have characterized the process of catalyst activation by *in situ* XRD studies (*5*), temperature-programmed oxidation (*13*) and inelastic neutron scattering (INS) (*14*); discharged catalysts have also been extensively examined by a wide variety of techniques (*10, 11, 15*). The single most important conclusion to emerge from these studies is that the mechanism by which low-temperature methanol synthesis occurs on these catalysts is very different from that which operates on commercial $Cu/ZnO/Al_2O_3$ catalysts (*16, 17*).

The present paper describes our most recent investigations in which frontal chromatographic, steady-state, and transient microreactor techniques were applied to the study of these novel materials to further elucidate both the activation process and the nature of the active surface.

EXPERIMENTAL

All experiments were carried out in a combined high-pressure/frontal chromatography system for catalyst characterization. The single pass, vertical fixed-bed reactor consisted of a $\frac{1}{4}$-in.-o.d. stainless-steel tube contained within an aluminium bronze "reactor block," the temperature of the catalyst itself was monitored by a sheathed thermocouple incorporated within the reactor tube and in contact with the catalyst charge.

Exit gas analysis was carried out using a quadrupole mass spectrometer (MS) sampling via a fixed capillary leak from an independently pumped line connected to two sampling points on the reactor system. A BBC microcomputer was used to control the MS unit in a manner allowing rapid multimass signal acquisition; this same computer controlled the operation of the automated flow-switching valves and recorded other system parameters (gas flow, pressure, temperature, time).

Ingots of the intermetallic compounds were prepared by high-vacuum electron-beam melting and consolidation of the constituent metals in the manner described previously (*10*). Alloy charges of 0.5–1.1 g were crushed in an argon atmosphere to a particle size of 100–500 μm and mixed with a quantity of borosilicate beads (300 μm; alloy/diluent wt ratio 1 : 1–1 : 3) to accommodate the bulk expansion and fragmentation of the alloy which occurs during the activation process; the diluted charge was then loaded into the reactor tube.

Reactant gases were obtained from BOC Ltd (Special Gases) and used without further purification: hydrogen (CP grade: ≥99.999% pure), premixed CO/H_2 (33 : 67; impurities: $O_2 \leq 5$ ppm, $H_2O \leq 2$ ppm, and $CO_2 \leq 20$ ppm), premixed $CO/CO_2/H_2$ (32 : 2 : 64; impurities: $O_2 \leq 3$ ppm and $H_2O \leq 10$ ppm), oxygen, and carbon monoxide (Research grade). Copper surface-area measurements were carried out using premixed N_2O (2.6%) in helium. Helium (CP grade: ≥99.999% pure) was further purified by passage through a molecular-sieve trap at ambient temperature. Activation and steady-state measurements were carried out under 15 bar total pressure; pulsing and temperature-programmed experiments were run under atmospheric pressure. For TPD experiments the catalyst was cooled from reaction temperature under the reactant gas mixture, the feed switched to pure helium carrier gas (flow rate 60 standard cubic centimeters (sccm)), and the temperature then ramped at 30 K/min to 633 (±10) K. In the case of oxygen-pulsing experiments the reactor was depressurized and flushed out with pure He at the reaction temperature for a period of about 5 min prior to initiation of data acquisition and switching of the gas flow to pure oxygen (35 sccm).

Determination of copper metal surface areas by catalytic decomposition of N_2O has been extensively investigated (*18–20*): the reactive frontal chromatography technique used in this work is similar to that described by Chinchen *et al.* (*20*). After exposure to methanol synthesis conditions the reactor was depressurized and flushed with He at the reaction temperature before cooling to 333 K; the gas flow was then switched under computer control to the N_2O/He mixture (flow rate ca. 42 sccm) and data acquisition started. Automation of the gas-feed switching ensured excellent reproducibility of the "dead volume delay time" for a given flow rate (ca. 10 s at 42 sccm).

RESULTS

On the basis of previous studies (*5, 10, 11, 13*) of binary *RE*–Cu systems two precursors were selected for more extensive, comparative study, namely, NdCu and Ce Cu_2; experiments were aimed at elucidating the following:

(a) the activation mechanisms of the alloys in synthesis gas atmospheres and the role of hydrogen incorporation in precursor activation;

(b) the nature of the active catalyst surface and the identity of catalytically relevant surface species;

(c) the mechanisms of deactivation (including the influence of H_2O, O_2, CO_2, and thermal treatments).

NdCu Precursors

(*1*) *Synthesis gas activation and thermal stability.* NdCu samples were pretreated under 15 bar H_2 at 348–358 K for 90 min and then heated slowly (2 K/min) to 423 K before switching to the synthesis gas mixture. Using this procedure, however, the alloy charges employed in these experiments (mean particle size ~300 μm) were not significantly converted to the intermetallic hydride and the marked benefits of extensive (10 h 348–423 K) hydrogen pretreatment reported in our earlier *in situ* XRD work (*5*) were not evident. Activation was therefore carried out at the higher temperature of 473 K and initial activities were relatively low (1.2–1.5 mol MeOH (STP) kg^{-1} h^{-1} after 1–2 h on line); this illustrates how the complex nature of this system (*5*) results in the optimum pretreatment conditions being very sensitive to the exact physical state of the alloy precursor.

Increasing the reactor temperature above 523 K under synthesis conditions for a few minutes led to an irreversible loss of activity. Figure 1 shows the variation of product yield with time for a NdCu-derived catalyst, initially activated at 473 K but then cooled to 333 K before being heated in a stepwise manner to 573 K. The methanol synthesis activity reaches a steady-state level (3.15 mol MeOH (STP) kg^{-1} h^{-1} at GHSV ≈22,000 h^{-1}) within ca. 10 min of the temperature stabilizing at 473 K. The subsequent increase in reactor temperature to 573 K, however, while initially giving rise to a small increase in the synthesis activity, ultimately leads to a significantly lower methanol yield.

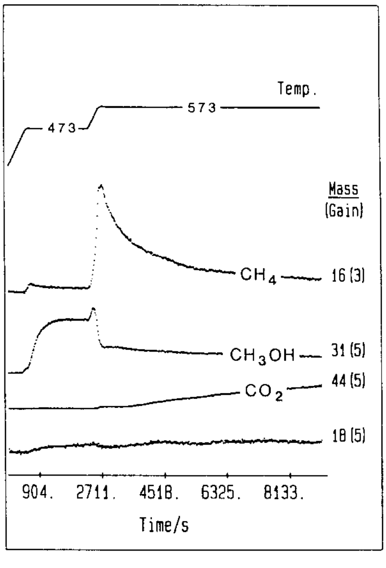

FIG. 1. High-temperature deactivation. Product evolution with time for a NdCu-derived catalyst under 15 bar CO/H_2 at 473–573 K.

(2) *Temperature-programmed desorption.* Desorption spectra for a catalyst activated at 473 K and then cooled under the reactant gas mixture are shown in Fig. 2A. A small amount of methanol desorbs in a broad peak between 350 and 430 K but the main feature is the extensive hydrogen desorption which begins at ca. 330 K and maximizes at ~545 K. There is also substantial evolution of methane and CO at high temperatures (~575 K). Interestingly, very similar behavior was observed in H_2 TPD/TPR experiments in which the reactor was cooled from 473 K under flowing He and the temperature then raised with the catalyst under a hydrogen feed of 1 bar. Methane and CO desorption were again predominant at high temperatures but some methanol was still produced at lower temperatures, which could imply the presence of a large reservoir of precursor species. In neither case was there any evidence for CO_2 or H_2O desorption.

One other feature of these experiments was the speed with which steady-state activity was reestablished after a desorption sweep. This occurred within ca. 4 min at 473 K after a He TPD run and the induction period appears to be even smaller after heating to high temperature in H_2.

(3) *Exposure to oxygen.* The effects of pulsing oxygen onto the catalyst were compared at various reaction temperatures; this was carried out on the same catalyst sample with exposure to syngas in between each experiment. At 473 K the main desorption product was methanol and the introduction of oxygen did not lead to a significant increase in the bed temperature ($\Delta T \leq 4$ K). (Note that the experiment does not permit distinction between displaced preformed methanol and any reactively formed methanol which would incorporate oxygen atoms from the pulse.) Synthesis activity was reduced essentially to zero by the oxygen treatment but was partially regenerated with continued exposure to reaction conditions, reaching a value equivalent to about half the original level after 2 h on line.

After increasing the reactor temperature to 513 K, the second pulse of oxygen gives rise to a substantial exotherm (~70 K), a

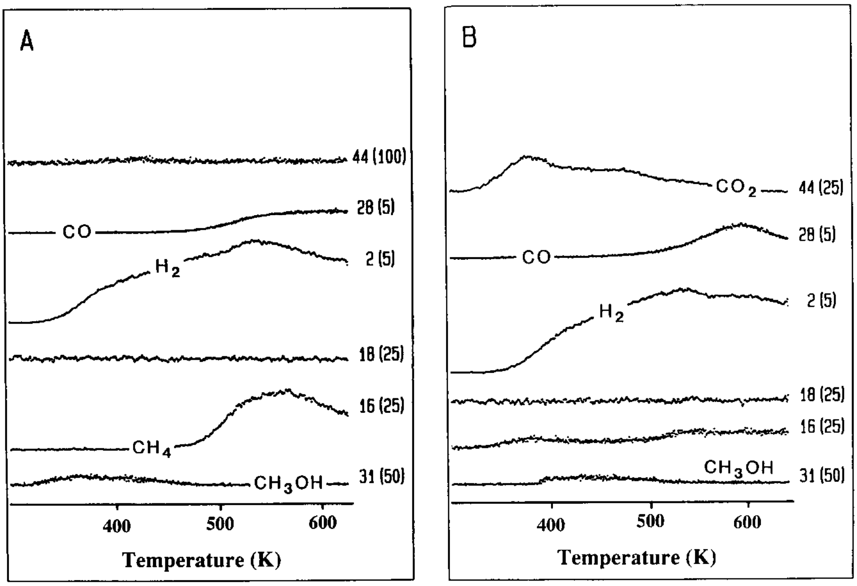

FIG. 2. TPD spectra for a NdCu-derived catalyst: (A) after activation at 473 K; (B) after exposure to a 2% CO_2 syngas mixture.

large H_2 desorption peak, and small amounts of CO_2 and CO (Fig. 3A). These are rapidly followed by a significant methanol peak and the establishment of a low but steady-state level of water production. Steady-state synthesis activity was further reduced (~30%) by this second oxygen treatment, and a transient peak of CO_2 generation was evident upon switching back to the syngas mixture.

Increasing the reactor temperature to 573 K under the process gas resulted in a substantial increase in the CH_4 and CO_2 yields, i.e., similar behavior to that shown in Fig. 1, but in this case it had little effect on the methanol synthesis rate; nevertheless, the final activities at 573 K were very similar in the two experiments. The main products of pulsing oxygen at this temperature were CO_2 and H_2O and the exotherm was much less marked. Furthermore, after H_2 reduction (Fig. 3B), the methanol synthesis activity was virtually unchanged. The onset of water production in Fig. 3B is probably associated with the reaction of the hydrogen with partially oxidized copper; reduction of bulk neodymium oxide will only contribute to this process at the highest temperatures. Some of the high-temperature features (e.g., the CO_2 peak) in this TPR experiment are also attributable purely to thermal desorption/decomposition rather than reaction.

(4) Exposure to carbon dioxide. The effectiveness of CO_2 as a poisoning agent is demonstrated in Fig. 4 where the gas supply to a NdCu-derived catalyst (already partially deactivated by heating to 630 K in a TPD (He) experiment) was switched from CO_2-free syngas to the mixture containing 2% CO_2 at a temperature of 473 K. There is no detectable increase (≤ 1 K) in the catalyst-bed temperature so the transient increase in methanol yield (ca. $1.2–2.0 \times 10^{19}$/g catalyst) is definitely not associated with an exotherm.

TPD spectra for the CO_2-poisoned catalyst are shown in Fig. 2B. Comparison with data from the active catalyst (Fig. 2A) shows that while the spectra have certain features in common the high-temperature methane peak is now very much less appar-

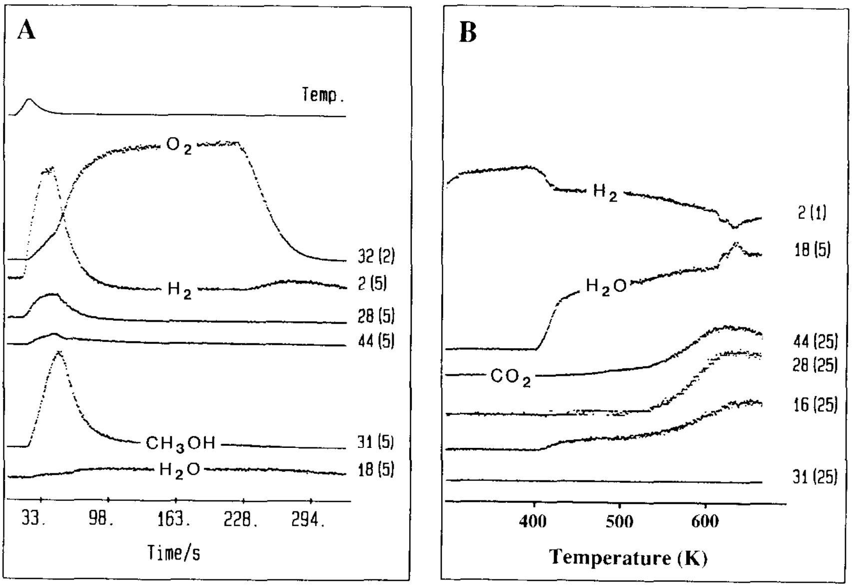

FIG. 3. (A) Effect of pulsing O_2 onto a NdCu-derived catalyst at 573 K; (B) temperature-programmed reduction after oxygen treatment at 573 K.

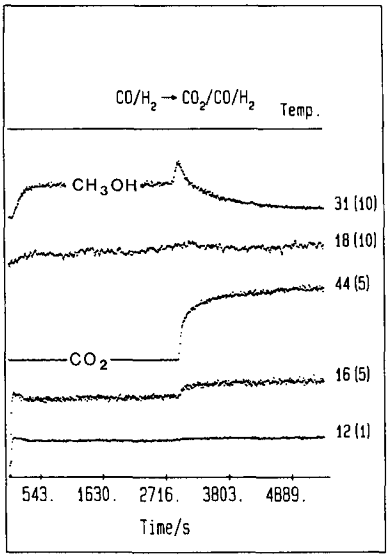

FIG. 4. Variation of product yield upon switching the gas feed to a NdCu-derived catalyst from a CO_2-free syngas mixture to one containing 2% CO_2.

ent and CO_2 desorption occurs in a broad asymmetric peak which maximizes at ca. 365 K and extends to over 480 K.

CeCu₂ Precursors

(*1*) *Synthesis gas activation.* Activation of $CeCu_2$ precursors under 15 bar syngas was studied at 423, 473, 513, and 573 K. Figure 5A shows the activity profile for such a precursor heated in a stepwise manner from 373 to 473 K. Under these conditions, methanol activity begins only upon heating to 473 K and is preceded by a small transient peak in the production of methane. Activation at 423 K occurred at a much slower rate, with a gradual rise in the methanol yield over a period of several hours and a far less marked peak in methane yield. By contrast, rapid (30 K/min) heating directly to 573 K gives rise to a very high initial methane yield, together with small amounts of C_2 and C_3 hydrocarbons, but a *lower* steady-state level of synthesis activity (Fig. 5B). Furthermore, after ca. 45 min on line a rapid increase in the CO_2 yield is evident. There was no detectable exotherm during the activation process in any of these experiments.

The activation behavior described above may be compared with that observed when the $CeCu_2$ precursor is first treated with pure hydrogen. Figure 5C shows the variation in product yields during activation in syngas at 473 K following pretreatment under 15 bar H_2 at 373 K for 90 min. The initial methane transient is now very much more pronounced and the initial methanol activity substantially higher. The origin of the irregularities in the methanol yield after ca. 1.5 h on line is not clear, but flow instability arises from massive expansion of the solid which occurs upon activation with a concomitant decrease in conductance of the reactor. After correction for variations in the flow, the methanol yield is found to be virtually constant over the period 2000–8600 s. Methanol productivity (ca. 8.1 mol MeOH (STP) kg^{-1} h^{-1} at GHSV ~20,000 h^{-1}) and selectivity compare very favorably with values reported at higher temperatures and pressures (*10*).

The effects of pretreating the alloy under 10–15 bar D_2 at 373 K were also investigated. In one such experiment, after 150 min pretreatment the reactor was cooled to 333 K, flushed out with CO/H_2, pressurized, and the temperature then ramped (10 K/min) to 473 K. All $CH_{4-x}D_x$ isotopic combinations were evident, albeit only briefly and in low concentration for higher x values. Similarly, isotopic variants of methanol, incorporating up to at least three D atoms, were also produced. Although their concentration in the exit gas decreased with time, very low levels of D-containing molecules could still be observed even after 2.5 h on line. If, on the other hand, the reactor temperature was ramped to only 423 K after switching to the CO/H_2 feed, then most of the deuterium exchanged out of the intermetallic hydride before there was any significant production of methanol. Nevertheless, the efficiency of activation was still noticeably higher than for charges which had not been pretreated.

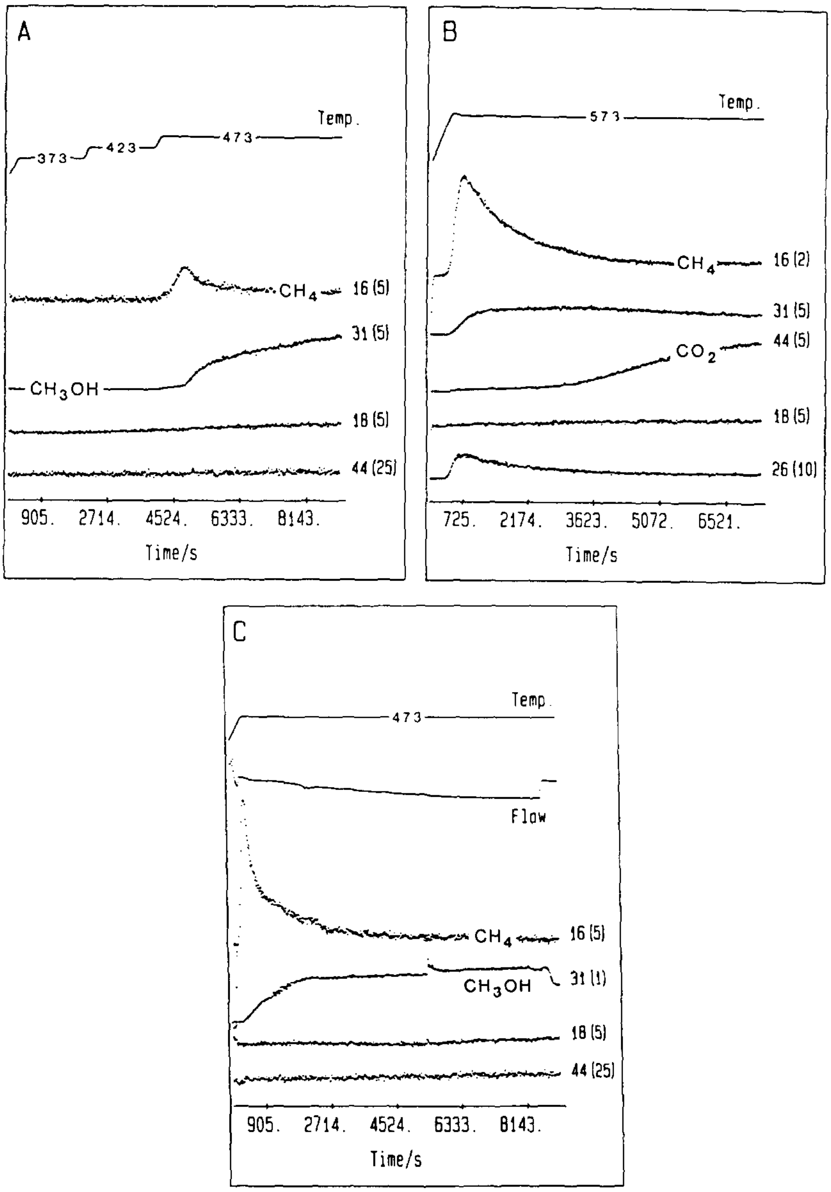

FIG. 5. (A–C) Initial activation of $CeCu_2$ alloys in syngas under various conditions; (C) H_2 pretreated.

The effect of interrupting synthesis by switching from the process gas to a pure H_2 feed was also studied for freshly activated catalysts running at 473 K. Methanol activity decayed very rapidly after the removal of CO but was completely restored within 20 s of switching back to the process gas.

(2) *Alternative activation procedures.* In order to determine whether interaction with hydrogen is the critical factor in alloy activation, an alternative procedure was studied in which N_2O was used as the oxidant. After exposure of the alloy to 15 bar H_2 at 373 K for ca. 1 h, the gas feed was switched to a 2.6% N_2O/He mixture (5 bar) and the temperature ramped rapidly to 473 K. At this temperature a significant amount of the initially absorbed hydrogen rapidly de-

sorbed, and at a flow rate of 70 sccm decomposition of the nitrous oxide (Eq. 3) was complete:

$$N_2O_{(g)} \rightarrow O_{(s)} + N_{2(g)}. \qquad (1)$$

Results of a control experiment (Fig. 6A) show that at this flow rate the extent of decomposition is negligible at 333 K and ca. 10% at 373 K, while at temperatures of 413 K and above conversion is complete. It can also be clearly seen that the oxidation process is accompanied by evolution of molecular hydrogen into the gas phase but with no detectable water generation. The completion of oxidation (Fig. 6B) is accompanied by the termination of this hydrogen desorption and by a small peak of H_2O. (The residual 28-amu signal arises from fragmentation of N_2O^+ in the MS ion source.) Water appears in the very final

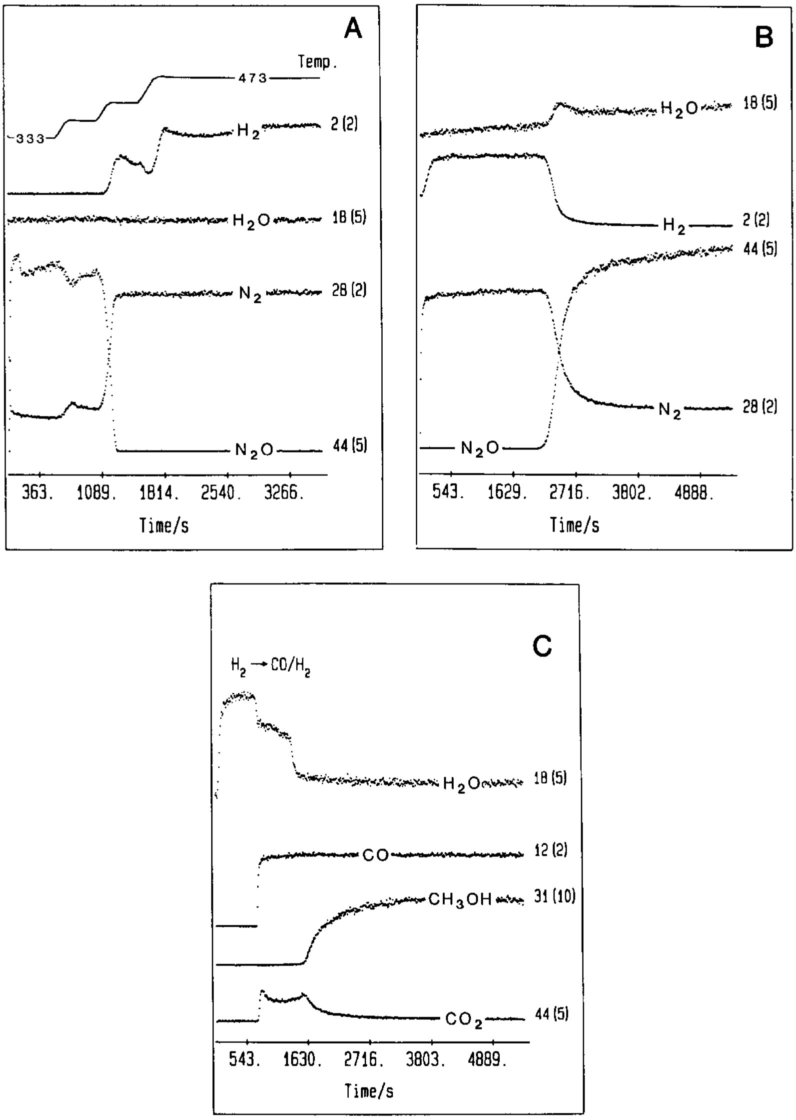

FIG. 6. (A) Reaction of H_2-pretreated $CeCu_2$ with a 2.6% N_2O/He mixture (5 bar) at 333–473 K; (B) completion of oxidation at 473 K; (C) evolution of the exit gas composition during subsequent reduction with pure H_2 followed by exposure to CO/H_2.

stages of oxidation because it is only at this stage that there is briefly an excess of N_2O for oxidation of the released H atoms, and H_2O reduction (by remaining hydrides) is sufficiently slow to permit net production of water. Total oxygen uptake by the catalyst can be simply determined from the N_2O concentration, the gas flow rate, and the time to N_2O breakthrough; it corresponds to an overall stoichiometry of $CeCu_2O_{2.5}$.

Upon completion of N_2O oxidation the gas feed was switched first to He, then to 15 bar pure H_2 for 15 min, and finally to 15 bar syngas, all at 473 K. Figure 6C shows the evolution of the exit gas composition as a function of time. The catalyst is reduced by the treatment in hydrogen generating water in the gas phase. Most of this water production can undoubtedly be attributed to reduction of copper previously oxidized by the N_2O. This process is incomplete at the time of switching to the syngas mixture and reduction by both H_2 and CO is observed. The subsequent rise in methanol synthesis activity correlates with completion of reduction by CO; the production of water appears to terminate slightly earlier, a point that is discussed below. The initial methanol activity (per unit mass of catalyst) is about a factor of 4 lower than that observed for the most active syngas-treated alloys.

(*3*) *Temperature-programmed desorption.* TPD spectra from the active catalyst (Fig. 7A) show desorption of CH_4, CO, and H_2 in the same temperature interval (580–595 K), together with very small quantities of other hydrocarbons, and methanol desorption at around 390 K. After partial poisoning by CO_2 (Fig. 7B), methanol desorption is still observed but at a rather higher temperature (~440 K). The high-temperature methane desorption peak is far less pronounced, but substantial CO_2 desorption in this temperature regime is now evident. In regard to the high-temperature desorption features, it is worth noting that treatment of deactivated catalysts with H_2 at 573 K resulted in bulk reduction to give H_2O in the gas phase, and also evolution of methane.

(*4*) *Exposure to oxygen.* Oxygen exposure was carried out in both isothermal pulsing and temperature-programmed modes. Figure 8A shows the yields of CO, CO_2, and H_2O throughout a temperature-programmed oxidation run. It should be

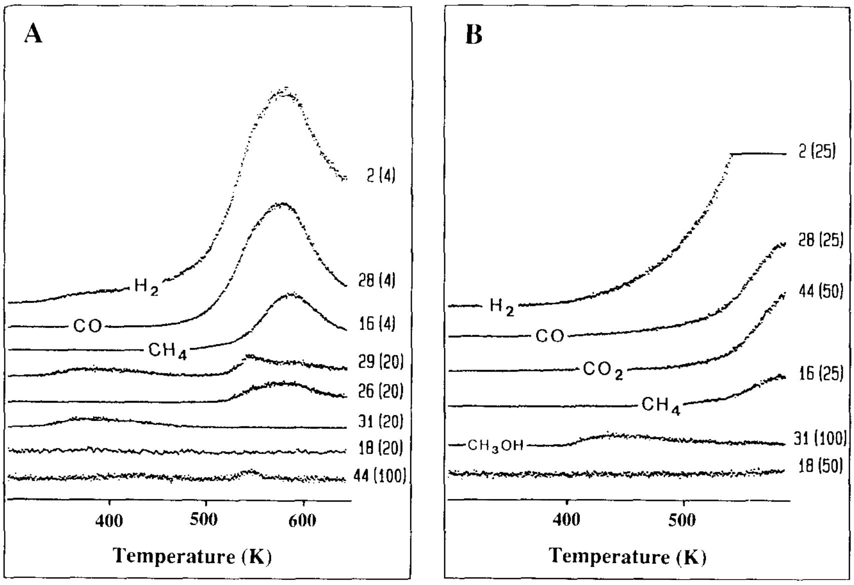

FIG. 7. TPD spectra from (A) an active $CeCu_2$-derived catalyst and (B) a CO_2-poisoned catalyst.

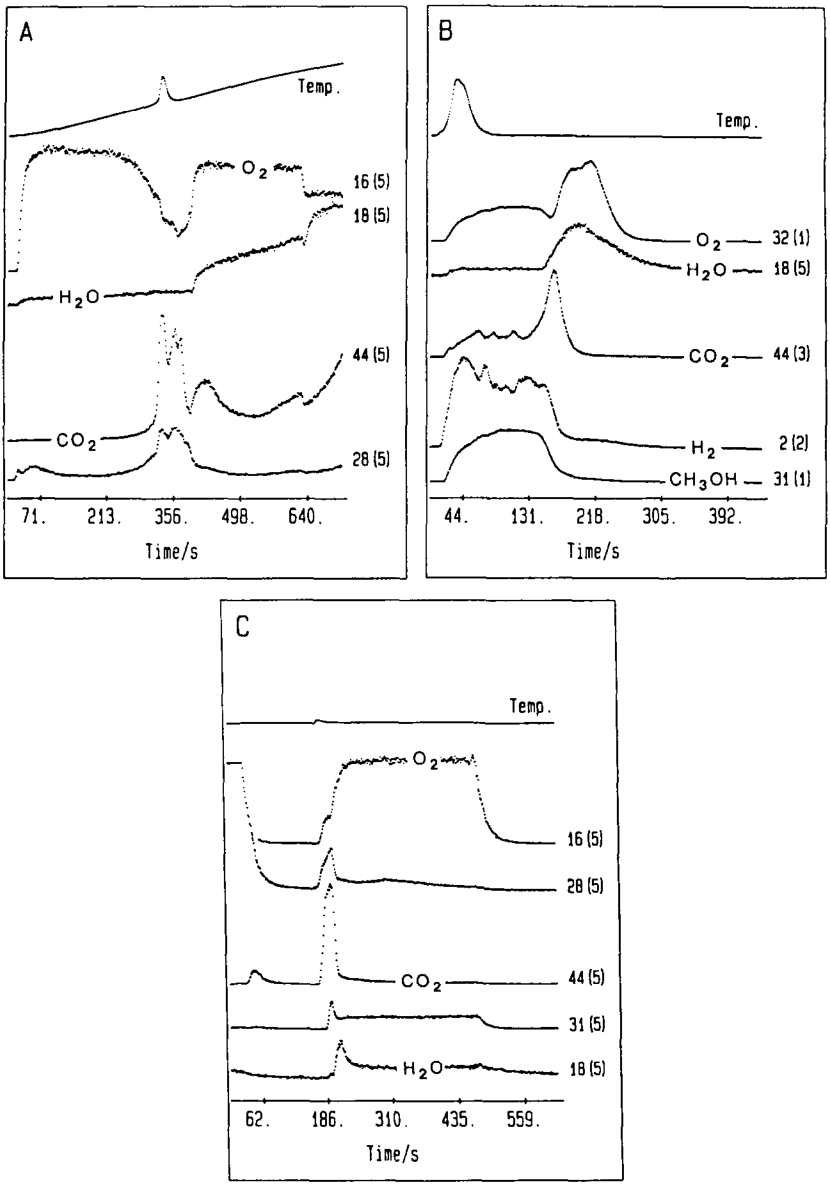

FIG. 8. (A) Temperature-programmed oxidation (267–625 K); (B,C) O_2-pulsing experiments on $CeCu_2$-derived catalysts; (C) deactivated catalyst.

noted that decreases in the 16 amu (O^+) signal do not necessarly correspond to consumption of oxygen, since desorption or displacement of other species into the gas phase also inevitably reduces the concentration of oxygen at the sampling point. One of the most striking features of the experiment is the very large exotherm (~150 K) that occurs in the middle of the temperature ramp. This is accompanied by substantial evolution of CO_2 although it is not immediately apparent whether the carbon gasification is the cause or an effect of the exotherm. There is, however, some indication from the 16 amu signal that CO, CO_2, and H_2O are not the only products. This is confirmed by pulsing experiments at 473 K which show that the main species evolved are methanol and H_2 (Fig. 8B); these are followed by a sharp CO_2 peak and the generation of water in a similar way to that observed in the temperature-programmed experiment. By contrast, pulsing of O_2 onto deactivated catalysts (Fig. 8C) gives rise primarily to CO_2 followed by H_2O with very little methanol and only a small (≤ 15 K) exotherm.

Following exposure of an active catalyst to a pulse of oxygen, switching the gas feed directly back to the syngas mixture (after flushing with He) leads to a very high transient level of CO_2. This effect can be avoided by first switching to a pure hydrogen feed and only reverting to the synthesis mixture after water production has ceased. The results in Fig. 9, however, show that reduction cannot proceed to completion with H_2 alone and that further reduction by CO is required before any methanol synthesis is observed. The amount of CO_2 generated in this second stage of reduction corresponds to ca. 9×10^{19} molecules/g catalyst; this is more than could be expected for a purely surface phenomenon and also substantially exceeds the amount observed when unsupported Cu_2O is first reduced in hydrogen and then exposed to CO (*21*).

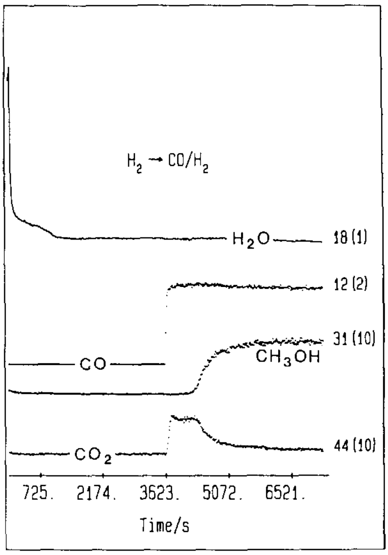

FIG. 9. Reduction of a $CeCu_2$ catalyst in pure H_2 and syngas under 15 bar/473 K after exposure to a O_2 pulse.

(*5*) *Exposure to H_2O.* Experiments were carried out to test the effect of low levels of water in the process gas. The feed gas (total pressure 10 bar) was switched between the dry syngas mixture and an identical mixture that had been passed through a high-pressure "bubbler" containing distilled water at 298 K: assuming complete equilibration, this should have introduced into the gas an H_2O content of ca. 3000 ppm. The methanol yield at 473 K initially appeared to increase slightly and then to fall away rather more rapidly than observed with dry process gas; no CO_2 evolution was detected.

N_2O Titrations

A summary of the results of titrating various catalysts with the N_2O/He mixture at 333 K is presented in Table 1. The amount of N_2O decomposition, quoted as a "copper-surface-area equivalence" (CSAE, measured in m^2/g precursor), is determined using the method described by Chinchen *et al.* (*20*). This assumes that all the decomposition is due to titration of elemental copper surface area, a point discussed in more detail below. The main features of these experiments are:

(i) The measured areas are *very low* by comparison with conventional methanol synthesis catalysts (*22–24*).

(ii) There is no obvious correlation between the activity of a given catalyst at various stages of evolution and the amount of N_2O decomposition, nor does any such correlation exist with the relative activities of different catalysts.

(iii) Treatment in H_2 at 513–573 K leads to significantly greater decomposition but this is partially reversed by reexposure to synthesis conditions.

DISCUSSION

(*1*) *Catalyst activation.* The outstanding feature of the activation studies is the dem-

TABLE 1

N_2O Titrations of Alloy-Derived Catalysts and *RE* Oxides

Precursor	Treatment		CSAE (m^2/g)
$CeCu_2$ (#1)	SG 473 K	2 h	0.4
		4 h	0.1
$CeCu_2$ (#2)	SG 473 K	5 h	0.0
		8 h	0.0
	+SG 513 K	2 h + SG(CO_2) 1h	0.1
	+H_2 573 K	2 h	2.4
	+SG 513 K	1 h	0.2
$CeCu_2$(#3)	SG 513 K	2 h	0.3
	+H_2 513 K	30 min	8.2
	+SG 513 K	1.5 h	1.9
$CeCu_2$ (#4)	SG 473 K	3 h + SG 573 K 2 h	2.0
	+H_2 573 K	10 min	3.3
$CeCu_5$	SG 513 K	3 h	1.1
		4 h	2.0
NdCu	H_2 348 K	1.5 h + SG 423 K 2 h	0.0
	+SG 473 K	30 min + TPD (H_2)	2.1
NdH_x	H_2 373 K	1 h	0.0
	+SG 513 K	3 h	0.0
	+H_2 573 K	1 h	0.2
CeO_2	H_2 623 K	20 min	0.0

Note. SG, synthesis gas; SG(CO_2), synthesis gas containing 2% CO_2; CSAE, copper surface-area equivalence (see text).

onstration that hydrogen pretreatment has beneficial effects on the activation of alloy precursors over a wide range of conditions; thus, the efficiency of $CeCu_2$ activation is enhanced for both synthesis gas (Figs. 5A, 5C) and N_2O oxidation. In the latter case the stoichiometry achieved after H_2-pretreatment ($CeCu_2O_{2.5}$) suggests that the alloy is *fully* decomposed at 473 K with complete oxidation of the Ce component to CeO_2 and only partial bulk oxidation of copper (although it is possible that a little unreacted alloy or cerium hydride is protected by oxide encapsulation). This can be compared with the results of a temperature-programmed oxidation study of the same system (*13*) in which the unhydrided intermetallic was treated with a 5% N_2O/N_2 mixture (1 bar). The total weight gain on heating to 848 K was only 6.5%, equivalent to a stoichiometry of $CeCu_2O_{1.1}$.

The initial activity of syngas-activated $CeCu_2$ was still significantly higher than the N_2O-activated alloy after comparable hydrogen pretreatment. The intrinsic activity, furthermore, could be much higher since the extent of activation in the former case is probably significantly lower (*10, 13*). Nevertheless, it may be possible to further optimize the performance of N_2O-oxidised catalysts by using an N_2O/H_2 activation mixture, by working at higher pressures, and by ensuring that H_2 reduction is complete before switching to the CO/H_2 synthesis mixture (thereby minimizing exposure to CO_2).

(*2*) *Catalyst stability*. The first mechanism by which catalyst deactivation can occur is thermally controlled. The behavior exemplified in Fig. 1 is irreversible and cannot therefore be attributed purely to thermodynamic restrictions or to a drastic reduction in selectivity at high temperatures. The logical conclusion, therefore, is that active centers are irreversibly destroyed under such conditions. The large transient methane peak that accompanies deactivation might be indicative of further oxidation of unreacted alloy or rare-earth hydride,

$$2NdCu\text{-}H_x + 3CO + (6 - x)H_2 \rightarrow 3CH_4 + 2Cu + Nd_2O_3 \quad (2)$$

$$2NdH_y + 3CO + (6 - y)H_2 \rightarrow 3CH_4 + Nd_2O_3, \quad (3)$$

or could represent the removal of a "surface" carbon species that is built up during activation or synthesis.

The important role of CO_2 in catalyst deactivation is now well documented for a wide range of alloy precursors (Refs. (*5*, *10*, *11*) and Fig. 4). While the interpretation of the H_2O exposure results presented here is necessarily provisional, the data do support the assertion that the poisoning observed with CO_2 truly represents an effect attributable to this molecule alone and is not a consequence of H_2O generated by the reverse water gas shift reaction. The mechanism of poisoning is believed to involve the formation of a strongly bound "carbonate-like" surface species (*11*). The TPD results (Figs. 2B and 7B) are consistent with this interpretation and the substantially higher desorption temperature of CO_2 from $CeCu_2$-derived catalysts as compared with those from NdCu also correlates with the irreversible deactivation and partially reversible poisoning, respectively, exhibited by these two materials upon exposure to synthesis gas containing CO_2 at 513 K (*11*). It is also clear that the CO_2 complex cannot possibly be fully desorbed below the thermal sintering temperature of the catalysts.

Oxygen exposure (at levels ~7 mmol/g catalyst) was also found to be very detrimental to the low-temperature synthesis activity of the catalysts; residual high-temperature activity was much less susceptible to O_2 exposure. Similarly, the residual activity of O_2-exposed catalysts was substantially less prone to high-temperature deactivation.

(*3*) *State of active catalyst.* The major crystalline phases in all the active alloy-derived catalysts are the respective rare-earth oxide and elemental copper (*5*, *8*, *10*). The present work also suggests, however, that a large reservoir of hydrogen (in the form of intermetallic or rare-earth hydride) is still present in the syngas-activated catalysts; thus in addition to copious H_2 desorption during TPD (Figs. 2 and 7) the evolution of CH_4 at high temperatures occurs not only in flowing hydrogen but also in He. This probably results from the reaction of desorbing bulk hydrogen and "surface carbon." The presence of significant quantities of rare-earth hydride even after substantial exposure to synthesis conditions has since been confirmed by inelastic neutron scattering (*14*).

Many of the experiments also point to the presence of carbonaceous species on the surface of the active catalysts. As discussed above, these yield CH_4 at high temperatures during treatment with H_2 or He, and also yield CO_2 upon exposure to oxygen. This "carbon" could be deposited during the course of the reaction or might be only a product of the activation process. The activation is conventionally represented by the generalized reaction

$$RCu_x + yCO + (2y)H_2 \rightarrow RO_y + yCH_4 + xCu \quad (4)$$

which assumes that all carbon is removed as methane and that the rare earth is fully oxidized. The integrated yield of methane is, however, frequently very much less than expected (*10*). This has been attributed to the small extent of alloy activation at low temperatures, but it is possible that there is more alloy decomposition than this would suggest, with a significant amount of carbon being initially retained on the catalyst. *In situ* XRD studies show peaks characteristic of the fluorite-based structure of the rare-earth oxides, but substantial incorporation of atomic carbon into this phase cannot be discounted; this may have implications with regard to the electronic structure of the oxidized system (*26*). The greater methane yield at higher activation temperatures might therefore arise not only from a greater extent of alloy decomposition but also from the more facile gasification of deposited carbon at elevated temperatures.

Some build-up of carbonaceous species during synthesis was evident from the results on N_2O-activated $CeCu_2$ catalysts, this being the one case where it is possible to separate activation and synthesis definitively. It is also clear from Figs. 1 and 5B that there is indeed extensive C–O-bond cleavage on these catalysts at high temperatures (573 K); this is reflected in the significant CH_4 and CO_2 yields, and may result from either direct dissociation of CO or from C–O cleavage in partially hydrogenated surface species. The reaction to yield CH_4 and CO_2 could be stoichiometric under these conditions (*11*):

$$2CO + 2H_2 = CH_4 + CO_2. \quad (5)$$

However, net deposition of carbon is also a possibility, especially at lower temperatures, although no large-scale build up of elemental carbon is evident either by XRD (*5*) or by electron microscopy (*15*).

The above discussion concerning hydride and carbonaceous species does not detract from the fact that the major phases present are the rare-earth oxide and elemental copper. In this context, the exposed Cu surface area and the oxidation state of the surfaces of these two phases are crucial parameters. As mentioned previously, the dissociation of N_2O on elemental copper surfaces is well documented; with these systems, however, the possibilities of reaction with unoxidized intermetallic rare-earth hydride and substoichiometric rare-earth oxide need to be considered also. The first of these does not appear to be important under titration conditions (333 K/1 bar) as shown by the experiment (Fig. 6A) with prehydrided Ce Cu_2; similarly, control experiments with NdH_x indicate negligible reaction with the binary hydride at this temperature. The decomposition of N_2O on Nd_2O_3 and other rare-earth oxides has been studied by Read (*25*) but the rate is only significant at much higher temperatures. It is possible, however, that the rare-earth oxides generated by alloy activation display very different reactivity to N_2O; the enhanced decomposition observed after treatment in H_2 would tend to support this view. Such treatment leads to the generation of methane which could arise from the removal of carbon from the rare-earth-oxide surface, thereby exposing highly defective and substoichiometric oxide which is reactive to N_2O *under titration conditions*. It may be, therefore, that the only cases in Table 1 where N_2O decomposition can be almost exclusively attributed to titration of elemental copper surface area are the higher Cu-content alloys (e.g., $CeCu_5$) and high-temperature syngas-treated samples (e.g., $CeCu_4$) (*4*). Nevertheless, it is still clear that **the exposed elemental copper surface area is not a significant variable in determining the activity of these catalysts.**

The response of these systems to oxidizing atmospheres raises a question concerning the optimum oxidation level of the active catalyst. The virtually instantaneous rise in methanol activity observed after interrupting synthesis at 473 K by switching to a pure H_2 feed strongly suggests that the active sites cannot be significantly over-reduced by hydrogen at this temperature. (There is, however, evidence for bulk reduction of the *RE*-oxide phases at higher temperatures.) Furthermore, the effects observed during the induction period following oxygen pulsing (Fig. 9) and upon first exposing the N_2O-activated catalyst to a syngas feed (Fig. 6C) show that the catalysts, once taken to too high an oxidation level, cannot be *sufficiently* reduced by hydrogen alone. On the other hand, it may be that in a 33 : 67 CO/H_2 mixture the active site is indeed reduced below the optimum oxidation level. The evidence for this assertion comes from the CO_2 experiments where prior to the decay in activity there is a significant increase in the methanol yield which may be attributable to the effects of the CO_2/CO redox couple, before poisoning begins to dominate the behavior.

(4) The nature of the active site. Some care needs to be exercised in the interpretation of all the results on the basis of a single active-site model; much of the work suggests that there may be more than one active site, or even a distribution of such sites. In particular, the residual activity observed at high temperatures ($\geq$513 K), after transient heating to high temperatures, and after exposure to oxygen, appears to be very much less susceptible to decay and poisoning than the higher activity levels observed with freshly activated catalysts at lower temperatures. It would seem therefore that the most active sites are also those that are the least stable, from both thermal and chemical viewpoints. This would imply that activation is best carried out at higher pressures and lower temperatures. The extraordinary low temperature activities observed at high pressures (*12*) are consistent with this view.

The very low copper surface areas measured by N_2O titration are rather surprising in view of the mean crystallite size determined from XRD patterns (~200 Å, Ref. (*5*)). This could indicate a very small extent of alloy activation. As mentioned earlier, the essentially complete activation of the alloy observed with N_2O exposure after H_2 pretreatment is not thought to be representative of syngas-activated samples (especially in the absence of prehydrogenation). However, since the *in situ* XRD measurements do show complete conversion of the precursor alloy within the sampling depth, and bearing in mind the degradation of the alloy that occurs during activation, a lower limit can be put upon the extent of activation. This ranges from ~50% (10 μm aggregates) to ~10% (50 μm aggregates). These values are still too large to account for the very low surface areas measured since, in the absence of CO_2 or H_2O in the feed gas, the exposed surface of copper crystallites should be fully reduced (*22–24*) and titratable.

The logical conclusion following from this is that either

(i) the surfaces of the Cu crystallites visible by XRD are in some way passivated to N_2O titration, or

(ii) the XRD-visible copper represents only a small fraction of the total amount present and that the remainder is in a very highly dispersed form that is also inert to N_2O titration.

In the first instance, it is possible that the copper is predominantly encapsulated by a thin layer of *RE* oxide under reaction conditions, and thus inaccessible to gas-phase molecules, in other words, that something akin to the SMSI "decoration" effect occurs with these materials. There is, however, no electron microscopic or other spectroscopic evidence to support this view. By contrast, the presence of additional copper directly associated with the rare-earth-oxide component has been shown using EDAX/STEM (*10, 15*).

Highly dispersed clusters of zero-valent copper supported on and entrained in the oxide would still tend to imply a high Cu surface area, in contradiction to the *in situ* N_2O measurements which reveal very low metal areas, probably attributable to the large Cu crystallites alone. On the other hand, a very intimate contact with the *RE* oxide (e.g., very small clusters of Cu embedded within and coordinated to the oxide matrix) might give a form of copper that is active for methanol synthesis but unreactive with respect to N_2O decomposition under the conditions employed.

The rare-earth oxides produced by low-temperature synthesis gas activation of intermetallic precursors clearly do differ at least structurally and probably also electronically from the materials which are formed by standard calcination techniques. Since it is well established that rare-earth oxides do exhibit some activity for methanol synthesis (*28, 29*), it is conceivable that this unusual form of oxide in itself could be the source of activity. Deactivation at higher temperatures could then arise from the removal of carbon by reaction with hydrogen leading to further oxygen incorporation and increasing crystallinity of the rare-earth oxide. There are, however, several major difficulties with this hypothesis, specifically the observations that

(i) the N_2O-activated $CeCu_2$ catalysts exhibit a relatively high level of synthesis activity despite the generation of *more crystalline, carbon-free oxide,* and

(ii) $CeAg_2$, which has the same crystallographic structure (*30*) as $CeCu_2$, yields a catalyst which shows no measurable activity (*10*).

Taken together these points indicate that copper, in one form or another, must participate in the predominant synthesis mechanism over these alloy-derived catalysts. It is therefore suggested that the most active sites involve copper dispersed in the highly disordered *RE* oxide initially produced by low-temperature syngas activation. The thermal deactivation mechanism discussed above in connection with the oxide would then lead to loss of these sites and migration of some of the copper to give further growth of the large copper crystallites; this would be accompanied by the formation of more stable active sites involving copper which remains intimately associated with the relatively well-ordered oxide generated by this process. It is these latter sites that are likely to be responsible for the high-temperature (>473 K) activity. In each case, the extent to which methanol synthesis occurs on the highly dispersed copper as opposed to the surface of the associated oxide matrix is a question which awaits further investigation.

CONCLUSIONS

1. Optimum activation of the intermetallic precursors generally requires that the alloy be pretreated in pure hydrogen at low temperature prior to exposure to the process gas; the increase in efficiency is very sensitive to the extent and conditions of pretreatment and the physical state of the precursor. The hydrogen absorbed in the pretreatment stage is intimately involved in the oxidative decomposition of the alloy and early synthesis of methanol.
2. There is no correlation between catalyst activity and N_2O-titratable surface area; furthermore, the metallic Cu surface areas measured by this technique are typically more than two orders of magnitude smaller than those found for commercial Cu-based methanol synthesis catalysts.
3. The experimental evidence suggests that there may be more than one type of active site and that the activation conditions determine not only the concentration of sites but also the level of activity of such sites. For the less active sites, at least, the optimum level of oxidation appears to be delicately balanced.
4. The most active sites are the least stable with regard to both thermal sintering and poisoning; this special activity may well be related to copper intimately associated with the highly defective oxide which is generated by the novel, low-temperature activation procedure.

ACKNOWLEDGMENT

This work was supported under a Joint Research Scheme funded by I.C.I. plc.

REFERENCES

1. Wallace, W. E., Elattor, A., Imamura, H., Craig, R. S., and Moldovan, A. G., *in* "The Science and Technology of Rare Earth Materials" (W. E. Wallace and E. C. Subbarao, Eds.), p. 329. Academic Press, New York, 1980.

2. Wallace, W. E., CHEMTECH, 752 (1982).

3. Barrault, J., Duprez, D., Percheron-Guegan, A., and Achard, J. C., *Appl. Catal.* **5,** 99 (1983); *J. Less-Common Met.* **89,** 537 (1983).

4. Barrault, J., Guilleminot, A., Achard, J. C., Paul-Boncour, V., Percheron-Guegan, A., Hilaire, L., and Coulon, M., *Appl. Catal.* **22,** 273 (1986).

5. Nix, R. M., Rayment, T., Lambert, R. M., Jennings, J. R., and Owen, G., *J. Catal.* **106,** 216 (1987).

6. France, J., and Wallace, W. E., Paper to the 12th Regional ACS Meeting, Pittsburgh, 1980.

7. Wallace, W. E., France, J., and Shamsi, A., *in* "Rare Earths in Modern Science and Technology," Vol. 3. Plenum Press, New York, 1982.
8. Baglin, E. G., Atkinson, G. B., and Nicks, L. J., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 87 (1981).
9. Daly, F. P., *J. Catal.* **89,** 131 (1984).
10. Owen, G., Hawkes, C. M., Lloyd, D., Jennings, J. R., Lambert, R. M., and Nix, R. M., *Appl. Catal.* **33,** 405 (1987).
11. Jennings, J. R., Lambert, R. M., Nix, R. M., Owen, G., and Parker, D. G., *Appl. Catal.*, in press.
12. Short, G. D., and Jennings, J. R., Eur. Pat. Publ. 117,944 to ICI plc.
13. Hay, C. M., Jennings, J. R., Lambert, R. M., Nix, R. M., and Owen, G., *Appl. Catal.* **37,** 291 (1988).
14. Nix, R. M., Lambert, R. M., Vorderwisch, P., Jennings, J. R., and Owen, G., in preparation.
15. Jennings, J. R., Lambert, R. M., Nix, R. M., Owen, G., and Shannon, M. D., in preparation.
16. Chinchen, G. C., Denny, P. J., Parker, P. J., Spencer, P. J., and Whan, D. A., *Appl. Catal.* **30,** 333 (1987).
17. Bowker, M., Hadden, R. A., Houghton, H., Hyland, J. N. K., and Waugh, K. C., *J. Catal.* **109,** 263 (1988).
18. Dell, R. M., Stone, F. S., and Tiley, P. F., *Trans. Faraday Soc.* **49,** 195 (1953).
19. Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young D. J., *Appl. Catal.* **7,** 75 (1983).
20. Chinchen, G. C., Hay, C. M., Vandervell, H. D., and Waugh, K. C., *J. Catal.* **103,** 79 (1987), and references therein.
21. Hadden, R. A., Ph.D. thesis, University of Glasgow, 1987.
22. Chinchen, G. C., and Waugh, K. C., *J. Catal.* **97,** 280 (1986).
23. Chinchen, G. C., Waugh, K. C., and Whan, D. A., *Appl. Catal.* **25,** 101 (1986).
24. Denise, B., Sneedon, R. P. A., Beguin, B., and Cherifi, O., *Appl. Catal.* **30,** 353 (1987).
25. Read, J. F., *J. Catal.* **28,** 428 (1973).
26. Nix, R. M., and Lambert, R. M., *J. Phys. Chem.*, in press.
27. Filippova, A. A., Davydov, A. A., and Shchekochikhin, Y. M., *Kinet. Katal.* **14,** 1333 (1973).
28. Maj, J., Colmenares, C. A., and Somorjai, G. A., *Appl. Catal.* **10,** 313 (1984); *J. Catal.* **95,** 385 (1985).
29. Japan-Kokai Tokkyo Koho JP 58,114,730 to Tokayama Soda Co., Ltd.
30. Iandelli, A., and Polenzona, A., *in* "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneidner, Jr., and L. Eyring, Eds.), Vol. 2. North-Holland, Amsterdam, 1979.