

# Thermal Stability and Reducibility of ZnO and Cu/ZnO Catalysts

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The decomposition of N<sub>2</sub>O has been widely employed by catalytic scientists to selectively measure Cu surface areas in supported Cu catalysts. The present studies on binary Cu/ZnO catalysts show, however, that under highly reducing conditions the decomposition of N<sub>2</sub>O on the reduced surface of the ZnO component of the catalyst can contribute significantly to the overall N<sub>2</sub>O decomposition, leading to high apparent Cu surface areas. Furthermore, it is clear that the susceptibility of the oxide to reduction in such catalysts is substantially enhanced by the presence of the metal and that CO is a much more powerful reducing agent in this respect than H<sub>2</sub>. The origin and catalytic implications of these observations are discussed.

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## 1. INTRODUCTION

The production of methanol from synthesis gas feeds has been a subject of extensive investigation over recent decades. Most of the commercial catalysts for this synthesis process are based on a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> formulation, and it is generally accepted that the main role of the alumina is as a structural stabilizer. In other respects there is surprisingly little agreement, however, with much dispute about both the role of the gas phase reagents and the nature of the active site in these catalysts (1). One of the more widely accepted theories proposes that the synthesis activity is purely related to the copper surface area in such catalysts (2): the measurement of this copper meal area is thus of key significance. The main technique employed for this measurement involves a reactive titration using N<sub>2</sub>O, in which the elemental copper surface area is derived from the amount of N<sub>2</sub>O decomposition which occurs in the formation of a saturated monolayer of atomic oxygen on the metallic copper surface (3–7). Even in this instance, however, there is wide variation in the optimal temperature reported (which is limited at the two extremes by the activated nature of the decomposition reaction and the necessity to avoid any bulk oxidation) and the proposed stoichiometry of uptake. The latter factor is an important source of error in the absolute surface area determination, but should not

significantly affect the relative values obtained for different catalysts.

It is implicit to the application of this technique to Cu/ZnO catalysts that the reactivity of the copper is similar to that observed for pure bulk samples and that there is no reaction on the ZnO component (or indeed any other component) of the catalyst. In the work reported here we specifically address the latter consideration and in accord with other recent work (8) suggest that such titration measurements may not necessarily purely reflect the copper surface area and can, furthermore, provide interesting new insights into the nature of such catalysts. These measurements were initially carried out on samples treated in pure He and H<sub>2</sub> atmospheres. In syngas catalyst feed mixtures, however, CO is widely regarded as being a more effective reducing agent than is H<sub>2</sub> (2, 9–11); in so far as the copper component is concerned this is in accord with measurements on single crystal copper substrates which show that CO oxidation by preadsorbed oxygen is very facile (12). A further set of experiments were therefore carried out in which fresh catalyst samples were exposed to a pure CO atmosphere at increasing temperatures prior to the N<sub>2</sub>O titration measurements.

## 2. EXPERIMENTAL METHODS

These experiments were carried out in a standard laboratory flow microreactor system, modified to permit *in situ* surface area measurements using a frontal chromatographic technique as described by Chinchin *et al.* (7). The system consists of a high pressure gas mixing manifold for reactive gases, and a separate manifold for pure helium and preprepared helium mixtures. The gas feed may be rapidly switched between the helium and mixtures of helium with other gases for the surface area measurements. A computer-interfaced quadrupole mass spectrometer was employed for post-reactor analysis for all the surface area measurements; this used a differentially pumped, multi-stage controlled gas input. A more detailed description of the apparatus can be found elsewhere (13).

In this study, measurements were made on two types of catalyst samples using charges of ca. 500 mg:

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(i) ZnO; formed from the thermal decomposition of commercial basic zinc carbonate. The carbonate was pretreated under He by heating to 250°C at 10°C min<sup>-1</sup>, held at this temperature for 240 min, and then heated to 400°C at 10°C min<sup>-1</sup> with the temperature maintained at this final value of 400°C for 4 min.

(ii) Cu/ZnO; prepared by standard coprecipitation of carbonates from an aqueous solution of the nitrates using 1 M Na<sub>2</sub>CO<sub>3</sub> at 70–80°C. After very thorough washing and drying, the samples were calcined in air at 350°C for 6 h and stored in sealed vessels; the composition of the calcined catalyst by weight was 34% CuO. Once charged into the reactor, the individual catalyst charges were first heated at 10°C min<sup>-1</sup> under He to 350°C and then held for 60 min at this temperature. After cooling to 50°C the gas feed was switched to pure H<sub>2</sub> (99.999%) and the temperature was ramped at 5°C min<sup>-1</sup> to 175°C, held at 175°C for 30 min, ramped at 5°C min<sup>-1</sup> to 200°C, and maintained at this final temperature for 60 min. To ensure complete reduction of the Cu component, the sample was further treated by adding CO to the H<sub>2</sub> gas feed for a further 10 min at 200°C, before finally being flushed with pure H<sub>2</sub> for 10 min at 200°C and cooled under He.

The total surface area was measured using a mixture of ca. 18% N<sub>2</sub> in He containing 2% Ne as a marker species. The samples were first cooled rapidly under a flow of pure helium to -196°C using liquid nitrogen cooling. The gas was then switched to the N<sub>2</sub>/Ne/He mixture and the time delay between the Ne and N<sub>2</sub> breakthrough was determined from the recorded mass spectrometer traces. A description of the analysis procedures is given in Appendix I and the estimated nonsystematic errors in the averaged readings given are ±1 m<sup>2</sup> g<sup>-1</sup>.

The reactive N<sub>2</sub>O titration procedure employed a 2% N<sub>2</sub>O in He mixture to measure the extent of N<sub>2</sub>O decomposition on the sample, hereafter referred to as the N<sub>2</sub>O-titratable (NT) surface area. This was carried out with the sample held at 60°C and the oxygen uptake determined from the time delay between the N<sub>2</sub> and N<sub>2</sub>O fronts. The values determined are given in terms of an apparent Cu surface area per gram of catalyst, assuming that all the uptake was due to decomposition of N<sub>2</sub>O on reduced copper surface to a fixed surface stoichiometry (based on a saturation coverage of  $\theta = 0.5$  and a uniform distribution of the low index (111), (100), and (110) surface planes of copper). Estimated nonsystematic errors in the readings given are ±0.3 m<sup>2</sup> g<sup>-1</sup>, although as mentioned previously the uncertainty of uptake may give rise to a substantial, systematic error in the absolute values.

All measurements and pretreatments were carried out at a total absolute reactor pressure of 1 atmosphere. In order to study the stability of the ZnO and Cu/ZnO samples in various atmospheres, the pretreated charges were heated

in each gas at progressively higher temperatures. This was accomplished by raising the reactor temperature to the desired value with the catalyst under He and then exposing the sample to a feed of the required gas (pure He, H<sub>2</sub>, or CO) for a period of 90 min. After each of these heating stages the samples were cooled under He to 60°C where the N<sub>2</sub>O-titratable surface area could be measured. The reactor temperature was then lowered to -196°C and two total surface area measurements were undertaken (with heating to around -100°C in pure He in between the measurements). Control experiments showed the original N<sub>2</sub>O titration to have only a very slight and systematic effect on the measured total surface area. On completion of these adsorption measurements, and before proceeding to the next stage of treatment, the samples were raised under He to 200°C and subjected to a standard rereduction procedure involving exposure to a pure CO feed for 15 min.

### 3. RESULTS

#### 3.1. Treatment of ZnO in He and H<sub>2</sub>

The total surface area of ZnO samples treated under pure He showed little variation following heating in He at temperatures up to 350°C. This latter temperature is still below the maximum temperature attained during sample pretreatment and the ZnO samples had thus effectively been already stabilized up to this temperature. At higher treatment temperatures there was a progressive decrease in the total surface area, indicating the onset of further thermally induced sintering of the samples. Typical results for pure ZnO are given in Table 1.

Corresponding data for the treatment of a ZnO sample in pure hydrogen are also given in Table 1, from which it

TABLE 1

Thermal Treatment of ZnO in Helium and Hydrogen

Temperature (°C)	Gas	NT area (m <sup>2</sup> g <sup>-1</sup> )	Total SA (m <sup>2</sup> g <sup>-1</sup> )
Pre		0.0	56.9
250	He	0.0	57.7
300	He	0.0	56.4
350	He	0.0	54.6
400	He	0.1	51.7
450	He	0.0	44.7
500	He	0.0	38.4
Pre		0.0	60.8
200	H <sub>2</sub>	0.0	51.6
250	H <sub>2</sub>	0.0	48.3
300	H <sub>2</sub>	0.3	50.6
350	H <sub>2</sub>	0.0	39.4
400	H <sub>2</sub>	0.2	25.7
450	H <sub>2</sub>	0.0	19.6
500	H <sub>2</sub>	0.0	12.4

can be seen that the total surface area shows both a more rapid decrease with treatment temperature and a significantly greater overall decrease, leading us to conclude that the gas phase atmosphere can be important in determining the extent of sintering upon thermal treatment. This in itself is an interesting observation but, for the subsequent comparison with the Cu/ZnO catalyst samples, it is more important to note that treatment of pure ZnO at temperatures up to 500°C, even in a 100% H<sub>2</sub> feed, does not lead to a measurable N<sub>2</sub>O-titratable surface area. This indicates that the extent of surface and/or bulk reduction of the pure ZnO samples is very small, since we would expect any surface O vacancies created in the reduction process to be readily titrated by N<sub>2</sub>O (see Section 3.3).

In a further set of experiments, ZnO samples were again subjected to treatment in He or H<sub>2</sub> at progressively increasing temperatures and the N<sub>2</sub>O-titratable and total surface areas redetermined as previously. However, in this instance the N<sub>2</sub>O-titratable surface area was also determined for a second time immediately after the standard rereduction treatment in CO that followed the first titration. The total surface area data was in good agreement with previous runs, with the area remaining virtually constant below 400°C in He and falling steadily following treatment in H<sub>2</sub>. All the N<sub>2</sub>O titration measurements again gave null results within experimental error. These data were obtained as a double control for the later measurements on the Cu/ZnO samples, but again confirmed the conclusions reached from the previous N<sub>2</sub>O-titration data in that there was no evidence for any appreciable reduction of the ZnO sample in H<sub>2</sub>.

### 3.2. Treatment of Cu/ZnO in He and H<sub>2</sub>

The initial measurements on these binary samples were carried out exactly as described in the Experimental section. Typical data for treatment in He are shown in the top section of Table 2. The total surface area, which in this case consists of contributions from both the ZnO and the Cu crystallites, showed a progressive decrease beginning at temperatures above 250°C. The onset of major structural changes is thus at lower temperatures than observed for the pure ZnO samples. The N<sub>2</sub>O-titratable surface area similarly showed a progressive decrease, apparently accelerating at temperatures above 400°C. In line with previous workers who have employed the N<sub>2</sub>O titration technique under these conditions, we will attribute the N<sub>2</sub>O decomposition observed in these experiments purely to the reaction on the metallic surface of copper crystallites giving an initial Cu surface area in the freshly prepared catalyst of slightly over 15 m<sup>2</sup> g<sup>-1</sup>, falling to around 11 m<sup>2</sup> g<sup>-1</sup> after 90 min at 300°C and to under 6 m<sup>2</sup> g<sup>-1</sup> at 500°C. A comparison of the Cu surface areas and total surface areas in Table 2 then shows that the initial decrease in total area is due principally to sintering of the copper crystallites. Significant loss of ZnO surface area in the binary catalyst is not evident below 350°C, i.e.,

TABLE 2

Thermal Treatment of Cu/ZnO in Helium and Hydrogen

Temperature (°C)	Gas	NT area (m <sup>2</sup> g <sup>-1</sup> )	Total SA (m <sup>2</sup> g <sup>-1</sup> )
Pre		15.1	65.4
200	He	14.9	68.6
250	He	13.1	69.7
300	He	11.0	61.8
350	He	9.8	58.1
400	He	8.8	48.1
450	He	7.7	35.2
500	He	5.9	28.5
Pre		13.6	61.5
200	H <sub>2</sub>	12.9	62.3
250	H <sub>2</sub>	13.5	61.5
300	H <sub>2</sub>	13.9	55.2
350	H <sub>2</sub>	15.3	45.6
400	H <sub>2</sub>	14.8	35.8
450	H <sub>2</sub>	11.4	25.5
500	H <sub>2</sub>	8.3	16.2

comparable to the maximum temperature achieved during calcination of the binary precursor.

For the Cu/ZnO samples treated in H<sub>2</sub>, the total surface area was again found to decrease slightly more rapidly than was found to be case in He, consistent with the previous observations on pure ZnO. The corresponding results for the initial N<sub>2</sub>O titration data for Cu/ZnO heated in a H<sub>2</sub> atmosphere, however, show a clear anomaly. The apparent Cu surface area initially increased as the treatment temperature was raised above 300°C, before dropping away at temperature above 400°C (Table 2); similar results have been seen previously by, for example, Burch and Chappell (14). In other experimental runs of this type which were carried out to ensure the reproducibility of those measurements, the apparent Cu surface area after treatment at 500°C occasionally approached the total surface area.

To investigate this phenomenon further, the experiments were repeated but an additional N<sub>2</sub>O titration measurement was made after the standard rereduction treatment at 200°C that followed the first titration measurement. For samples that had been heated only in He there were no significant differences between the two N<sub>2</sub>O-titratable area determinations. This is not unexpected if all the N<sub>2</sub>O decomposition is occurring on the Cu surfaces present in the sample, but does at least confirm that the Cu was maintained in the fully reduced state during the treatment in He and was not subject to surface oxidation by adventitious impurities. By comparison, for processing in H<sub>2</sub> at temperatures above 250°C there was a clear difference between the initial N<sub>2</sub>O measurements and those carried out after the rereduction (Fig. 1). The latter values of the N<sub>2</sub>O-titratable surface area showed only a very slight, but monotonic, decrease with increasing temperature whereas the initial values again

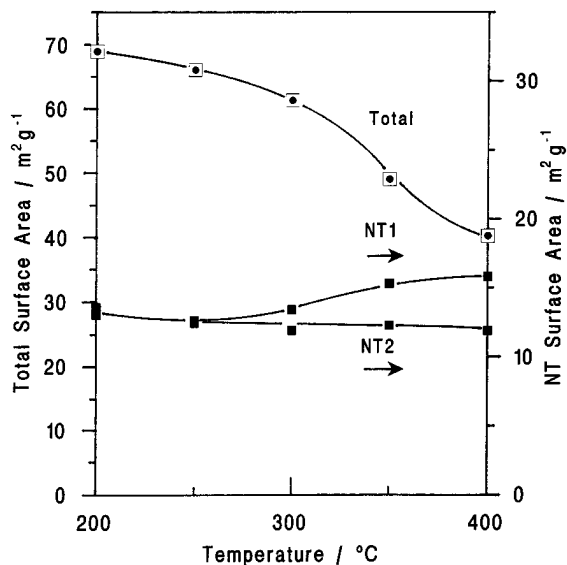


FIG. 1. Variation of the initial N<sub>2</sub>O-titratable (NT1) surface area, total surface area, and N<sub>2</sub>O-titratable area after rereduction (NT2) for a Cu/ZnO sample treated in a H<sub>2</sub> gas feed.

pointed to a maximum after treatment at around 400°C, as previously observed. In line with the data obtained in He atmospheres, we will attribute the results from the second set of N<sub>2</sub>O measurements purely to decomposition on the metallic copper surface present in these samples. We note, however, that the Cu surface area is not showing quite such a marked fall with temperature that was evident in the earlier work with He (Table 2) and attributed to thermal sintering. The area of actual Cu surface titrated in the initial measurement should be the same as the value obtained from the second measurement, yet the amount of N<sub>2</sub>O decomposition is clearly greater following the treatment of the catalyst in H<sub>2</sub> at elevated temperatures; in fact, the discrepancy shows a steady increase with temperature. The origin of this additional N<sub>2</sub>O decomposition is discussed more thoroughly below, but we note at this point that the results strongly suggest that it is not just the Cu surface area that is contributing to the titration measurement and that some of the N<sub>2</sub>O is decomposing on defective (reduced) ZnO or other Zn phases produced by the H<sub>2</sub> treatment. Since this effect is *not* observed for pure ZnO there appears to be an interaction when the ZnO and Cu phases are in close proximity which facilitates ZnO reduction.

### 3.3. Effect of Heating in CO Atmospheres

From the N<sub>2</sub>O titration data of Table 3 it is evident that a pure ZnO sample showed a small, but statistically significant, reduction upon heating in CO to temperatures greater than 300°C. Since such an effect was not evident upon treatment in H<sub>2</sub>, this confirms our earlier comments regarding the relative reducing power of the two agents and is in line

TABLE 3  
Thermal Treatment of ZnO in Carbon Monoxide, with Rereduction Measurements

Temperature (°C)	Gas	NT area #1 (m <sup>2</sup> g <sup>-1</sup> )	Total SA (m <sup>2</sup> g <sup>-1</sup> )	NT area #2 (m <sup>2</sup> g <sup>-1</sup> )
200	CO	0.0	43.6	0.0
250	CO	0.0	44.3	0.0
300	CO	0.9	46.3	0.0
350	CO	0.7	47.8	0.0
400	CO	1.5	44.9	0.0

with the thermodynamics of oxidation of these two gases. In summary, CO can be seen to be a more effective reducing agent than H<sub>2</sub> and apparently capable of introducing significant numbers of oxygen vacancies into the ZnO surfaces at temperatures above 300°C. N<sub>2</sub>O decomposition was not evident after the standard rereduction treatment, consistent with the initial null result for treatment in CO at 200°C. These latter measurements also confirm that the initial exposure to N<sub>2</sub>O at 60°C is effective in fully reoxidizing the defective ZnO, i.e., that N<sub>2</sub>O is indeed an appropriate agent for titrating any surface O vacancies of ZnO.

Results for treatment of Cu/ZnO in a CO atmosphere are given in Fig. 2. The stronger reducing power of CO is once again evident, as witnessed by the much larger discrepancy between the two N<sub>2</sub>O titration measurements when compared with previous data and the earlier onset of ZnO reduction. Thus, while the total surface area and second N<sub>2</sub>O measurement performed after mild rereduction provide evidence for slow sintering, the initial N<sub>2</sub>O measurements

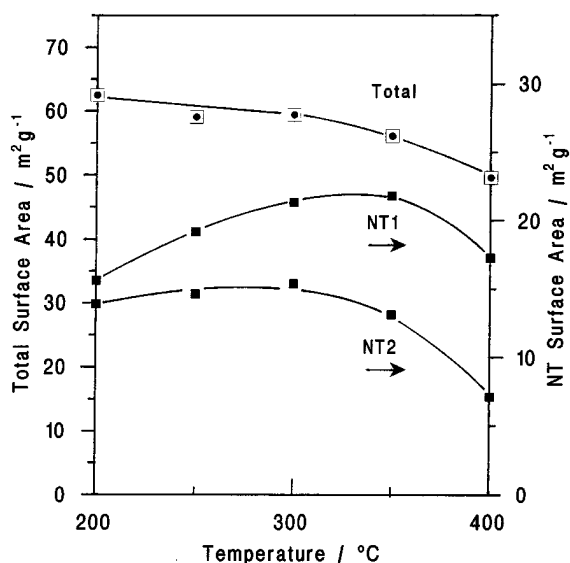


FIG. 2. Variation of the initial N<sub>2</sub>O-titratable (NT1) surface area, total surface area, and N<sub>2</sub>O-titratable area after rereduction (NT2) for a Cu/ZnO sample treated in a CO gas feed.

show a clear maximum at around 350°C, arising from the combination of a decrease in the real Cu surface area and an increase in the amount of N<sub>2</sub>O required to reoxidize the ZnO. A comparison of the excess N<sub>2</sub>O decomposition observed in the first titration with the ZnO surface area (obtained from the difference of the total surface area and second N<sub>2</sub>O titration measurements) indicates that a significant fraction of the ZnO surface is reduced if the vacancies are truly surface localized or, alternatively, that there is a buildup of the concentration of defects in the near-surface layers. While bulk reduction of the ZnO cannot be completely excluded, we note that the consequent limitations on the kinetics of reoxidation would be expected to show up in the N<sub>2</sub>O titration measurements and such effects were not evident.

### 3.4. Extended Duration Tests

All the previous experiments involved heating samples in the requisite gas for a period of 90 min. From these results it is not immediately clear as to whether the reduction effects observed are representative of the equilibrated steady state of the catalyst or whether the exposure time is a factor in the extent of reduction. Kinetic limitations are most likely to be apparent at the lower temperatures and additional tests were therefore carried out in which the charges were exposed to a H<sub>2</sub> feed for progressively longer times at a constant temperature of 275°C. Although the time periods concerned are still short compared to those of industrial usage, these investigations can provide an insight into gradual degradation of samples through extended exposure to reductive gases at elevated temperatures.

Treatment of pure ZnO at this temperature for periods up to 11.5 h, however, did not cause a significant decrease in the total surface area, while N<sub>2</sub>O titration measurements consistently showed that no significant reduction of the ZnO occurred.

By contrast, the data of Table 4 for a Cu/ZnO sample show that while the initial Cu surface area measurements apparently show a relatively constant copper surface area, this actually masks an underlying decrease in the real Cu surface area (which tends to a value of around 11 m<sup>2</sup> g<sup>-1</sup>) and a progressive increase in the N<sub>2</sub>O decomposition due to the reoxidation of ZnO. It is not clear whether any further reduction beyond that observed after 690 min cumulative exposure time would occur at this temperature, but the implications of these observations are that the extent of ZnO reduction in the Cu/ZnO samples over long periods of exposure to reducing atmosphere is likely to be more significant than is indicated by the initial measurements reported in this work in which exposure was limited to 90 min.

### 3.5. Reoxidation by Exposure to Other Gases

As seen from the above results, pure ZnO seems to be very hard to reduce to any considerable extent. When in

TABLE 4  
Effect of Extended Thermal Treatment of Cu/ZnO  
in Hydrogen at 275°C

Cumulative time (min)	Incremental time (min)	NT area #1 (m <sup>2</sup> g <sup>-1</sup> )	Total SA (m <sup>2</sup> g <sup>-1</sup> )	NT area #2 (m <sup>2</sup> g <sup>-1</sup> )
0	0	13.7	60.8	13.7
120	120	13.7	56.7	11.9
300	180	13.9	55.9	11.3
690	390	14.6	50.6	11.3

close proximity to Cu (as in the Cu/ZnO sample), however, there appears to be a much enhanced susceptibility to partial reduction. This has been shown to be the case when Cu/ZnO is subjected to either H<sub>2</sub> or CO at elevated temperatures, the extent of reduction depending upon both the temperature and the time of exposure to the reducing conditions. At 60°C N<sub>2</sub>O is capable of oxidizing both the reduced Cu and ZnO surfaces. Experiments were therefore carried out to see if the partially reduced ZnO component of the catalyst could be reoxidized without the Cu component being substantially affected.

Some success was achieved by using CO<sub>2</sub> at relatively low temperatures. More specifically, whenever partially reduced ZnO (and inevitably fully reduced Cu) was exposed to pure CO<sub>2</sub> at 25°C for a period of 15 min, the ZnO component of the Cu/ZnO was reoxidized (or, at least, passivated by formation of a strongly bound CO<sub>2</sub> adsorption complex which cannot be displaced by N<sub>2</sub>O at 60°C) while the Cu surface remained fully reduced.

These findings are illustrated by an experiment in which a sample of Cu/ZnO was baked for 90 min in H<sub>2</sub> at 350°C, a sufficiently severe regime to ensure partial reduction of the ZnO (see Fig. 1). After flowing CO<sub>2</sub> over the sample at 25°C the N<sub>2</sub>O titration gave an apparent Cu surface area of 11.1 m<sup>2</sup> g<sup>-1</sup>. A second measurement after the sample had been raised in He to 200°C and then subjected to the standard CO reduction procedure gave a value of 11.2 m<sup>2</sup> g<sup>-1</sup>, in excellent agreement with the initial value, indicating that the treatment in CO<sub>2</sub> was effective in removing the N<sub>2</sub>O decomposition observed over and above that attributable to the metallic copper surface area.

## 4. DISCUSSION

Since we have already presented the results of these studies in the context of the proposed interpretation, we concentrate in this section on discussing the justification of some of the basic assumptions that have been made and consider these results in relation to those of other workers.

It has been proposed in this work that the additional N<sub>2</sub>O decomposition observed for the Cu/ZnO catalysts subjected to highly reducing conditions arises from the partial

reduction of the ZnO phase in these materials. Conceivably, it might alternatively be associated with a second copper-containing phase, which is more resistant to reduction than the metallic copper crystallites that form the majority copper-containing phase in the reduced catalyst. We discount this possibility, however, on the following grounds:

(i) The progressive increase in the additional N<sub>2</sub>O decomposition with increasing temperature is more compatible with the gradual increase in reduction of a bulk oxide phase (as is indeed observed for the pure oxide at higher temperatures (15)) than reduction of a minority copper-containing phase.

(ii) There is no evidence from electron microscopy/X-ray microanalysis for incorporation of significant amounts of copper in an additional phase in these catalysts (16).

(iii) The response of the reduced system to CO<sub>2</sub> exposure is similar to that observed for defective ZnO (17) and other oxide surfaces.

The possibility of the excess N<sub>2</sub>O decomposition being associated with reaction with hydrogen occluded into the subsurface regions of the zinc oxide is also excluded on the basis of the work of Berndt *et al.* (18) and by the fact that the additional N<sub>2</sub>O decomposition may be induced by treatment with CO.

There are a number of precedents for the suggestion that the presence of a metal in intimate contact with an oxide can enhance the reducibility of the oxide. This is, indeed, a feature of some of the theories for explaining SMSI-type phenomena in metal/oxide systems (19) and also the basis of the junction effect theory for methanol synthesis proposed by Frost (20). Various spectroscopic investigations of metal oxide overlayers on metallic substrates have also revealed a higher propensity for oxide reduction in the presence of such interfaces (e.g., 21).

We note at this point that the baseline for all the N<sub>2</sub>O measurements on the Cu/ZnO catalysts was the state attained after exposure to 1 atmosphere of CO at 200°C. It is an inherent assumption, as mentioned previously, that after this treatment the N<sub>2</sub>O decomposition is purely associated with titration of the exposed metallic copper surface. Some reduction of the oxide is possible, however, even at this low temperature, as witnessed by the results of Fig. 2. The difference observed in these two measurements represents the difference between CO exposures of 15 min and 90 min. A linear extrapolation to zero exposure time in this particular case would still indicate a real copper surface area in excess of 13.5 m<sup>2</sup> g<sup>-1</sup> and, hence, tend to support the statement that the measurements performed after mild rereduction are indeed principally representative of the pure copper surface. It should be recognized, however, that we cannot completely exclude the possibility of a contribution to all of these values from a very much more facile reduction process involving ZnO.

The mechanism by which the oxide reduction is enhanced has not been directly addressed in this work, but there are at least three clear possibilities which could lead to the promotion of reduction in such highly dispersed materials.

(i) Alloy formation. The thermodynamics of reduction of ZnO in regions adjacent to the Cu/ZnO interface or of ZnO decorating the copper particles may be modified by Cu–Zn alloying (i.e., brass formation) (22, 23). Similar effects have been observed in other metal/ZnO systems (24, 25).

(ii) Adsorbate spillover. The surface activity of reducing agents (e.g., atomic hydrogen, CO) on the oxide can be enhanced by spillover from adjacent metallic surfaces (21, 26). Alternatively, irreversible spillover of oxygen from the oxide to the metal, followed by scavenging by H<sub>(ads)</sub> and CO<sub>(ads)</sub> can enhance oxide reduction (27).

(iii) Electronic promotion. The energetics of oxygen vacancy creation in the oxide may be modified (and hence the vacancy concentration increased) by the presence of the metal (20).

A distinction can be made between the first proposal which is necessarily a feature unique to the particular binary metal/oxide system and the latter two mechanisms which simply promote the intrinsic chemistry of the oxide. Unfortunately, we are unable to distinguish between the various possibilities purely on the basis of the results presented here and, indeed, these mechanism are not necessarily exclusive (for example, adsorbate spillover and alloy formation could both contribute to the observed enhancement in reducibility). We would note, however, that (ii) and (iii) clearly lead to the promotion of oxygen vacancies at the oxide's surface and since any such defective surface generated is likely to be more catalytically active than the stoichiometric oxide (28), this may have important implications regarding the role of the oxide in the catalytic applications of these materials.

As far as the implications of these results to the use of N<sub>2</sub>O decomposition as a technique for the *in situ* determination of copper surface areas is concerned, we make the following comments. The measurements reported here were observed under highly reducing conditions; i.e., the effects are most likely to be evident after treatment in pure H<sub>2</sub> or CO, or H<sub>2</sub>/CO feed mixtures. The addition of CO<sub>2</sub> (or, indeed H<sub>2</sub>O) to the gas feed, as found in most commercial implementations of these catalysts, is likely to have a significant effect on the extent of such behavior, as evidenced by the limited CO<sub>2</sub> studies reported above. In conducting such measurements, the extent and nature of any treatment in between catalytic operation and the surface area determination (specifically exposure to a more reducing atmosphere), and the composition of the gas phase during cooling, is likely to be crucial to the observed titration results. Clearly, the presence of any strongly adsorbed species on the surface of the oxide (e.g., carbonate, formate, methoxy)

will also tend to block N<sub>2</sub>O decomposition even if the surface is highly reduced.

The second main point to come from these studies is the observation that treatment in hydrogen consistently causes a greater loss in catalyst surface area than is observed in He atmospheres. This effect appears to be principally (if not exclusively) related to the oxide and would therefore be consistent with previous reports that facile migration of ZnO may occur in such systems during high temperature treatment in a reducing atmosphere (23, and refs. therein). We would emphasize, however, that in our work this effect is only observed with H<sub>2</sub> and not with CO and is seen for both ZnO and Cu/ZnO samples; the mechanism of transport must therefore be a specific feature associated with the presence of H<sub>2</sub> and not purely related to the extent of reduction of the oxide. Although zinc itself is relatively volatile, surface science studies of model Cu/ZnO systems have shown that there is no significant sublimation of Zn from supported oxide layers under high vacuum conditions until temperature well in excess of 400°C are achieved (29–32), and we therefore propose that this hydrogen-assisted ZnO migration is more likely to proceed by a surface migration mechanism than by gas phase transport.

## 5. CONCLUSIONS

In this paper we have reported on the results of an in-depth investigation of the application of the N<sub>2</sub>O titration technique to the study of ZnO and Cu/ZnO catalysts. The results show clearly that great caution has to be exercised in the interpretation of the results of such measurements. Most significantly, we have also demonstrated that the technique can be employed to investigate the reducibility of such catalysts. In particular, the reducibility of ZnO is substantially enhanced in the presence of metallic copper. This effect is clearly evident following treatment in H<sub>2</sub> at temperatures exceeding 250°C and for treatment in CO at temperatures as low as 200°C. The stability of highly dispersed ZnO has also been shown to be dependent upon the gas phase atmosphere, with strong evidence for a facile H-assisted sintering mechanism.

## APPENDIX I: DETERMINATION OF THE TOTAL SURFACE AREA BY N<sub>2</sub> ADSORPTION

A single point measurement was used to estimate the total surface area of both the ZnO and Cu/ZnO samples. More specifically, the surface area,  $A$ , of the sample was estimated from

$$A_{\text{Total}} = \left( \frac{PF\Delta t}{kT} \right) \times \left( \frac{17.8}{100} \right) \times 16.4 \times 10^{-20} \text{ m}^2,$$

where  $P$  is the total gas pressure ( $= 101325 \text{ N m}^{-2}$ ),  $F$  the corrected gas flow rate ( $\text{m}^3 \text{ s}^{-1}$ , measured at NTP),  $\Delta t$  the

time delay (s) between the Ne and N<sub>2</sub> fronts,  $k$  the Boltzmann constant, and  $T$  the temperature of flow rate measurement ( $= 25^\circ\text{C}$ ). The cross-sectional area of the physisorbed N<sub>2</sub> was taken as  $16.4 \times 10^{-20} \text{ m}^2$  (33). While the absolute values of the surface area given by this method are likely to be systematically in error due to the ill-defined coverage obtained during this simple single point measurement, the relative values obtained for a particular type of sample should accurately reflect any changes in the total surface area.

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