

Temporal and Oscillatory Behavior Observed during Methanol Synthesis on a Cu/ZnO/Al₂O₃ (60:30:10) Catalyst

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Abstract

The rate of Methanol synthesis over a Cu/ZnO/Al₂O₃ (60:30:10) catalyst has been measured using CO₂/H₂ (10:90) and CO/CO₂/H₂ (10:10:80) streams at 433, 443, 453, 463 and 473 K. Using the CO₂/H₂ stream, it requires 12×10^3 s to achieve steady-state performance; this time reduces to 5.4×10^3 s on increasing the temperature to 463 K. Using the CO/CO₂/H₂ stream, steady State performance is not achieved even after 14.4×10^3 s at 433 K but is achieved after 9×10^3 s at 463 K. Significant deviations from steady state behavior (~40% of steady state) are observed only at 453 K and only using the CO₂/H₂ feed when gas chromatography (GC) is the analysis system. When the reactor output is connected directly into a flame ionization detector (FID), oscillation is observed at all temperatures studied using a CO₂/H₂ stream. Injection of CO into the CO₂/H₂ stream, which is synthesizing methanol at 473 K, produces a sharply spiked increase in the rate of methanol synthesis followed by an oscillatory relaxation to steady state behavior. At 433 and 443 K, the injection of CO into the CO₂/H₂ stream again produces the sharply spiked increase in the rater of methanol synthesis, which returns to the baseline value without oscillations.

Keywords

Methanol Synthesis, Cu/ZnO/Al₂O₃ Catalyst, Oscillations

1. Introduction

The precise nature of the origin of activity in catalysis has been a subject of investigation since the discovery of the performance. From the observation that small amount of S adsorbed on a Pt catalyst selectively poisoned its capacity to

hydrogenate ketones but not nitrobenzene (the latter required larger amounts of S for its poisoning), H.S. Taylor concluded that the catalyst surface exposed certain sites, which has called active centers [1]. He also concluded that the amount of surface, which is catalytically active, is determined by the reaction catalyzed. Taylor's view of an active surface was a static one on which some of the atoms were active.

Somorjai expanded this view with his introduction of the concept of a "flexible" surface [2]. In this concept, adsorption of the reactant causes restricting of the surface, the collective rearrangement of which produces the active center. Somorjai's view of a dynamic surface has had its ultimate validation experimentally in scanning tunneling spectroscopy (STEM) where adsorbents have been shown to cause the atoms of the metal surface to migrate. The adsorption of oxygen on Cu (110) has been shown to induce the migration of Cu from step edges to form Cu-O-cu rows in a direction orthogonal to the (110) direction [3] [4]. More surprisingly, however, the adsorption of hydrogen on Cu (110), which, is weakly adsorbed on the surface but which, migrates under the surface of the Cu (110), causes reconstruction of the Cu (110) [4].

The most dramatic demonstration of reconstruction of surfaces and of its effect on catalytic reaction rates is to be found in the work of Ertl, who, using a photo-emission electron microscope, showed the Pt (110) surface to be in a state of continuous fluxional reconstruction during the oxidation of CO [5]. This fluxional reconstruction was mirrored by oscillation in the rate of production of CO₂ [5]. What was also surprising was that large areas of the surface ($\sim 10^5$ A²) are self-organized in that these areas have adsorbed on them either CO or O exclusively.

While the adsorbate induced self-organization of a well-order single crystal surface may be conceptually acceptable, it is surprising that oscillations have been observed in the oxidation of CO over supported Pt catalysts [6] and in the oxidation of CH₃OH over polycrystalline Cu foil [7].

Hadden and co-workers have demonstrated that hydrogen treatment of a Cu/ZnO/Al₂O₃ catalyst produces a given surface morphology [8]. They have also shown that if oxygen is adsorbed on this morphology and then removed by CO reduction, the original morphology is reconstructed [8]. This evidence demonstrates that the Cu/ZnO/Al₂O₃ catalyst has the potential to oscillate. Nevertheless, no oscillations have been detected in the rate of CH₃OH synthesis (which encompasses these reactions) over this catalyst.

This paper now reports, however, on marked deviations in the rate of CH₃OH synthesis from the CO₂/H₂ feed over a Cu/ZnO/Al₂O₃ (60:30:10) catalyst observed using gas chromatographic (GC) analysis of the product. It also reports on oscillations in the CO₂/H₂ reaction to form CH₃OH over the Cu/ZnO/Al₂O₃ catalyst observed using an on-line flame ionization detector (FID). Injection of CO into CO₂/H₂ stream, which is producing CH₃OH, causes a sharp spike in the rate of CH₃OH and oscillatory return to baseline activity.

2. Experimental

The Catalyst

The catalyst used in this study was an industrial Cu/ZnO/Al₂O₃ (60:30:10) methanol synthesis catalyst which was provided by ICI Syntex. Its method of precipitation by Na₂CO₃ precipitation of the mixed Cu/Zn/Al nitrate solution followed by filtration, washing, drying, and calcination has been described previously [9]. The crushed catalyst (0.5 g, 300 - 350 μm) was loaded into the microreactor and reduced *in situ* in an H₂/He stream (5% H₂, 101 kPa, 25 cm³·min⁻¹) by raising the temperature from ambient to 513 K at 5 K·min⁻¹. The catalyst was then held under the H₂/He stream for 16 h at 513 K to ensure complete reduction. The catalyst had a total surface area of 65 m²·g⁻¹ and a Cu metal area 30 m²·g⁻¹ by N₂O reactive frontal chromatograph [10].

The reactor system

The reactor was a tubular fixed bed Pyrex microreactor, the catalyst being housed in a central bulb shaped section (2 cm dia) with a thermocouple lodged in the middle of the bed. The reactor was placed in a metal block with was heated by an electric heating element controlled by a Newtronic controller.

In one set of experiments, analysis of the products was effected by injecting a known volume of the product gas on to Porapak-Q column (80 - 100 mesh size, 0.25 cm dia, 05 m long) by sweeping out a calibrated sample loop (2 cm³) of a six-port injection valve. A flame ionization detector (FID) detected the effluent from the gas chromatographic column. In a second set of experiments, the reaction products were passed directly into FID through a capillary 2 cm long. This detected changes in the concentration of the methanol product in real time as a function of changing the feed composition.

The Gases

The N₂, He, H₂/He (5% He), CO₂/H₂ (10:90) all were supplied by Electrochem Ltd. (ECM). They were 99.999% pure and were used direct from the cylinder. The CO was supplied by Matheson and was 99.997% pure.

3. Result and Discussion

The Rate of Methanol Synthesis over the Cu/ZnO/Al₂O₃ Catalyst from a CO₂/H₂ (10:90) Stream

Figure 1 is the dependence of the rate of methanol synthesis from a CO₂/H₂ mixture (10% CO₂, 101 kPa, 25 cm³·min⁻¹) on time at 433, 443, 453, 463 and 473 K per Cu atom (the turnover number (TON)) of Cu/ZnO/Al₂O₃ catalyst (05g). The concentration of methanol in the gas stream was determined by injecting samples of the product stream (2 cm³ from a 6-port sample valve) at 3 min intervals on to a gas chromatography column (Porapak Q, 80 - 100 mesh size, 105 m long, 6 mm dia) the eluent of which was detected by a flame ionization detector.

Prior to taking these rate measurements, Cu/ZnO/Al₂O₃ catalyst was pre-reduced as described in the experimental section. Having reduced the catalyst at 513 K,

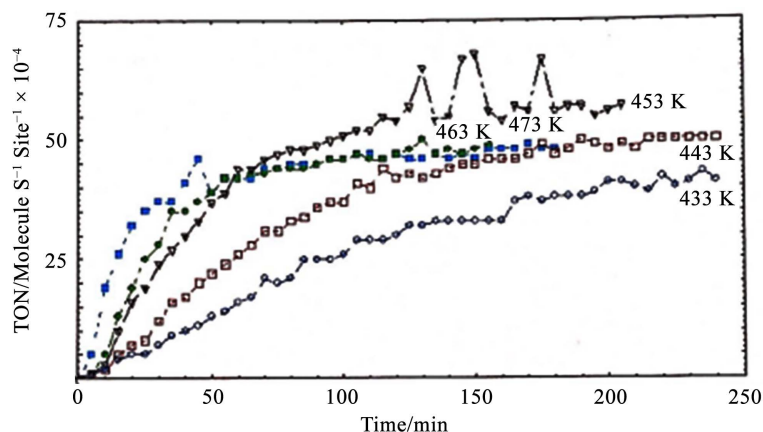


Figure 1. The time dependence of the TON per Cu atom of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst for methanol synthesis at 433, 443, 453, 463 and 473 K from a CO₂/H₂ (10:90, 101 kPa) stream at 3 min intervals using gas chromatography.

the flow was switched to He and the temperature held at 513 K for 30 minutes. The temperature was then lowered to the reaction temperature under the Heat which point the flow was switched to CO₂/H₂ mixture. After having measured the rate of methanol synthesis from CO₂/H₂ stream for 4h at any one temperature, the catalyst was exposed to the H₂/He mixture (5% He, 101 kPa, 25 cm³·min⁻¹) for 1h at 513 K before lowering the temperature under the H₂/He stream to the new reaction temperature, switching the flow to the CO₂/H₂ stream and measuring the rate at the new temperature. The rate of methanol synthesis from the CO₂/H₂ stream was measured in an ascending and descending order of the temperature, the results being entirely reproducible and any given temperature regardless of the order of making the measurement.

There are two important points, which can be made about these rate measurements. These are: 1) the steady state rate of methanol synthesis is not achieved instantaneously upon switching flows from H₂/He to CO₂/H₂ requiring roughly 4 h for this to occur at 433 K; steady state performance is achieved after 1½ h at 473 K, and 2) significant deviations from steady state performance are observed at 453 K after the catalyst has been on-line for 2h-these deviations are real and beyond the experimental error of the system.

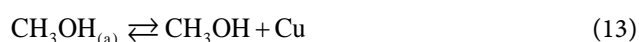
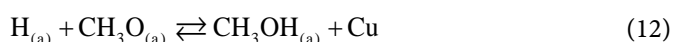
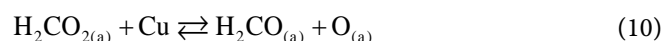
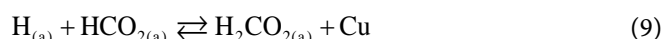
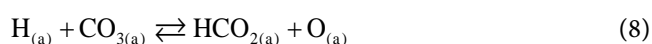
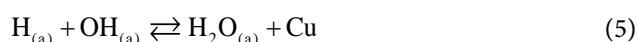
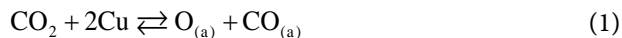
The Time Dependence of the Establishment of steady state Behavior

In a series of papers we have shown that Cu is the active component for methanol synthesis of Cu/ZnO/Al₂O₃ catalysts [10]-[15]. We have established that it is the CO₂ component of the industrial used CO/CO₂/H₂ feed, which is the direct precursor to methanol [12]. (The role of the CO is to maintain the Cu in a more highly reduced, more active state, H₂ being a less efficient reductant than CO [11].)

The mechanism by which the CO₂ is converted to methanol is by hydrogenation of an adsorbed formate species [13], the formate being formed by hydrogenation of an adsorbed carbonate [14].

The oxygen on the surface of the Cu, required for the formation of an ad-

sorbed carbonate, is provided by the dissociative adsorption of the CO₂ [15], the surface hydrogen, required for all hydrogenation reactions, being provided by the dissociative adsorption of H₂. The following set of elementary reactions (reactions (1) to (13)) describes in detail the mechanism of methanol synthesis from a CO₂/H₂ over Cu component of a Cu/ZnO/Al₂O₃ catalyst.



(The subscript (a) refers to adsorbed species).

Depending on the conditions (composition of the gas phase, temperature, flow rate, weight of catalyst), at steady state, the surface of the copper will be populated to varying extents by the following adsorbed species, O_(a), CO_(a), CO_{3(a)}, H_(a), HCO_{2(a)}, H₂CO_{2(a)}, H₂CO_(a), H₂CO_(a), CH₃OH_(a), OH_(a) and H₂O_(a).

The adsorption of CO₂ on Cu (110) and on the Cu component of a Cu/ZnO/Al₂O₃ catalyst has been shown to be activated [16] [17]. The activation energies measured were 67 [16] and 86 kJ·mol⁻¹ respectively [17]. At 400 K, for the 86 kJ·mole⁻¹ activation energy the dissociative sticking probability of CO₂ on the clean surface of the Cu component of Cu/ZnO/Al₂O₃ catalyst is 6 × 10⁻¹². (On a Cu surface pre-covered with H_(a) as is the case here it would be lower than this). Assuming a value of 6 × 10⁻¹² for the CO₂ sticking probability, for a CO₂/H₂ (10:90, 101 kPa) stream, it would require 2240 s to produce a monolayer coverage of O_(a) by the dissociative adsorption of CO.

Recognizing that steady state reaction would occur at somewhat less than monolayer coverage by O_(a) and acknowledging: 1) that the dissociative sticking probability of CO₂ will be lower than the value 6 × 10⁻¹² calculated for a clean surface due to the inhibiting effect of the pre-adsorbed hydrogen and 2) that the O_(a) produced by the dissociative adsorption of CO₂ will be removed by adsorption of H₂ (whose sticking probability is 10⁶ times greater than that of CO₂) and reaction to the form water, it is entirely reasonable that steady state reaction

would be established at 463 K only after 90 min.

The length of time for the establishment of steady state reaction, the prerequisites for which is the establishment of steady state oxygen coverage, is the time constant for reactions (1) to (5) above. (It should be noted from **Figure 1** that the time to establish steady state performance decreases as the temperature of reaction is increases.) Therefore, a plot of the natural logarithm of the reciprocal of the time taken to establish steady state performance against the reciprocal of the temperature is the overall reaction energy for the reactions 1 - 5. The value obtained is 43 $\text{kJ}\cdot\text{mol}^{-1}$ (**Table 1** lists the time for the establishment of steady state performance, the reciprocal of these times, the temperatures, the natural logarithm of the reciprocal of these times and the reciprocal for the temperatures).

The overall activation energy for the formation of methanol from CO_2/H_2 mixture can be obtained from the data in **Figure 1**. A plot of the natural logarithm of the steady state rate of methanol synthesis, from CO_2/H_2 stream. Against the reciprocal of temperature at temperature below those at which equilibrium had occurred (equilibrium occurred at 453 K and above), gives an activation energy for methanol synthesis from CO_2/H_2 of 42 $\text{kJ}\cdot\text{mol}^{-1}$. This value is remarkably similar to that required for the establishment of the steady state oxygen coverage of the copper. The similarity may be a coincidence. Alternatively, it could be taken to imply that having established the steady state oxygen coverage, the adsorption of CO_2 on it forms a carbonate and its sequential hydrogenation steps are negligibly activated.

The turnover number per Cu atom of the $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst for methanol synthesis from CO_2/H_2 reported here (0.41×10^{-4} to 0.57×10^{-4} molecule $\text{site}^{-1} \text{s}^{-1}$) are similar to those reported by Chorkendorff and co-workers [18] and by Campbell and co-workers [19], Chorkendorff and co-workers reported a value of the turnover number for methanol synthesis from CO_2/H_2 (1:1404 kPa) at 543 K of 2.7×10^{-4} molecule $\text{site}^{-1} \text{s}^{-1}$ over Cu (100) [18], while Campbell and co-workers reported a value of 1.2×10^{-4} molecule $\text{site}^{-1} \text{s}^{-1}$ for methanol synthesis from CO_2/H_2 at 510 K and 505 kPa over a polycrystalline Cu foil [19].

Reaction from steady state behavior

It is clear from **Figure 1** that significant deviation from steady state behavior are observed these are most pronounced at 453 K but are also observed at 473 K. The gas chromatographic method used for the measurement of the concentration of methanol has an accuracy of $\pm 5\%$. The deviations noted at 433 K ($\sim 5\%$)

Table 1. Temperature dependence of the time achieve steady state performance.

T/K	(1/T)/K ⁻¹	t/s	(1/t)/s ⁻¹	ln(1/t)/s ⁻¹
463	2.16×10^{-3}	5400	1.85×10^{-4}	-8.59
453	2.21×10^{-3}	7200	1.39×10^{-4}	-8.88
443	2.26×10^{-3}	10500	9.52×10^{-5}	-9.26
433	2.31×10^{-3}	12000	8.33×10^{-5}	-9.39

are within experimental error, however, those observed at 453 K (40%) and at 473 (20%) are outside experimental error and are real.

Inspection of the time dependence of the establishment of steady state performance at 453 K shows a continuous rise in the rate of methanol synthesis until, after approximately 130 min on steam and just before steady state performance is achieved, the significant excursions from steady state performance are observed.

At the point of the onset of these deviations/oscillations the coverage of Cu by adsorbed oxygen atoms, $O_{(a)}$, will be at its maximum as will the CO concentration deriving from CO_2 decomposition. Adsorbed oxygen has been shown to reconstruct the surface of Cu (110) [3]. The Cu (110) surface is shown in **Figure 2**; the (2×1) O-Cu surface is shown in **Figure 3**. We have shown that CO reduction of surface oxidized polycrystalline Cu (reactions (2) and (1)) results in a reconstruction of the surface which involves a less in the fraction of surface subtending the (110) face and again in a (211) face (**Figure 4**) [20]. Treatment of this reconstructed surface with hydrogen results in the partial restoration of the (110) face [20]. The rates of these reactions, which occur simultaneously during methanol synthesis, will be maximized at or near the onset of steady state performance and are probably responsible for the deviations/oscillations. Indeed, we had predicted previously that methanol synthesis had the potential to exhibit oscillating behavior because of these reconstructions included by adsorption and reaction [20].

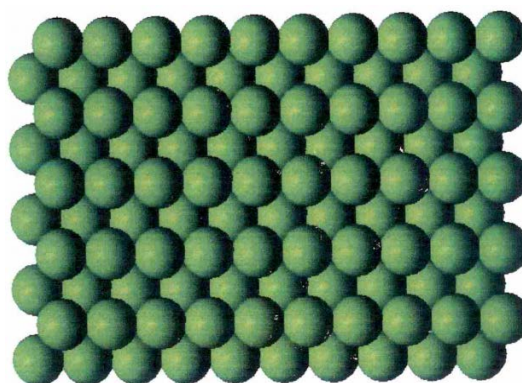


Figure 2. Structural model of the Cu (110) surface.

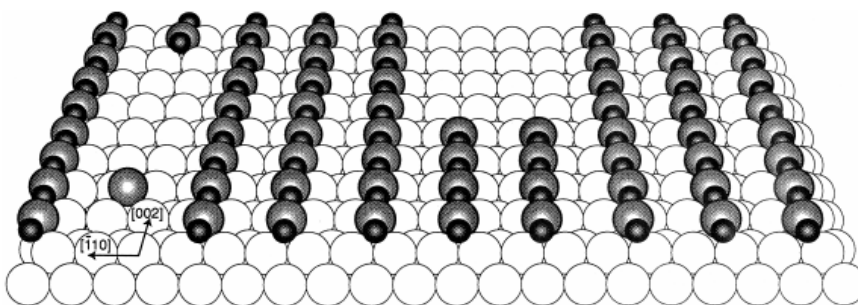


Figure 3. Structural model of the (2×1) O-Cu surface [3].

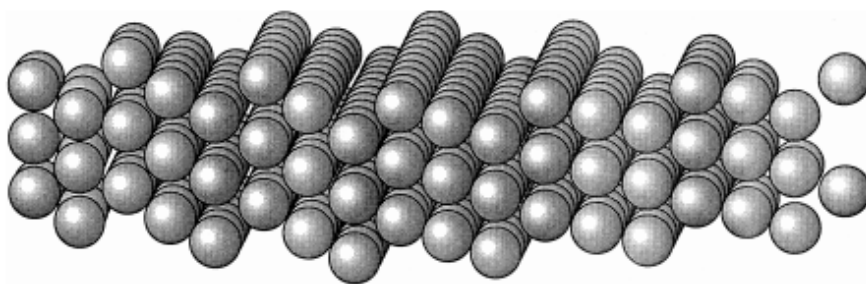


Figure 4. Structural model of the Cu (211) surface.

The model being proposed here is that at given times in the reaction, large areas of the surface have the (2×1) O-Cu structure, this is reduced and switches of the Cu (211) structure which we have shown to be less active for the decomposition of CO_2 than Cu (110) [21]. The rate of reaction, therefore, decreases. The adsorption of hydrogen on Cu (211) at a given coverage causes its reconstruction to the more active Cu (110) [20] and the cycle recommence.

The Rate of Methanol Synthesis over the Cu/ZnO/Al₂O₃ Catalyst from a CO/CO₂/H₂ (10:10:80) Stream

Figure 5 shows the dependence of the TON per Cu atom of methanol synthesis from CO/CO₂/H₂ mixture (10% CO, 10% CO₂ and 80% H₂, 101 kPa, and 25 cm³·min⁻¹) on time at 433, 443, 453, and 463 K over the reduced Cu/ZnO/Al₂O₃ Catalysts (0.5 g). By comparing this figure with **Figure 1**, four main points can be made. These are: 1) the time to the establishment to steady state performance is greater at any temperature for a CO/CO₂/H₂ stream than for a CO₂/H₂ stream, 2) the steady state rate of methanol synthesis at 453 K from a CO/CO₂/H₂ stream is the same as that from a CO₂/H₂ stream at that temperature, 3) the steady state rate of methanol synthesis at 463 and 473 K is higher from a CO/CO₂/H₂ stream than from a CO₂/H₂ stream and 4) no significant deviation from steady state behavior are observed at 453 or 463 K from a CO/CO₂/H₂ stream whereas they had been observed from CO₂/H₂ stream at these temperatures.

While it may appear to be self-evident, nevertheless it is worth stating that all of these differences result from the addition of CO to the gas stream. The longer time to the establishment of steady state behavior is due to the added CO removing the surface oxygen $\text{O}_{(a)}$ more rapidly than the H₂ [11] so that it requires a longer time to establish the steady state $\text{O}_{(a)}$ surface population. The absence of oscillation suggests that not only does the CO slow the establishment of the steady state $\text{O}_{(a)}$ coverage, it stops the formation of large coherent areas of the (2×1) O-Cu structure.

The steady state of methanol synthesis at 453 K from CO/CO₂/H₂ stream is exactly the same as that from a CO₂/H₂ stream at the same temperature whereas at 433 and 443 K, it appears to be lower from a CO/CO₂/H₂ stream and at 463 and 473 K, it is higher. The lower rate of methanol synthesis from CO/CO₂/H₂ stream at 433 and 443 K after 1.44×10^4 s relative to that from a CO₂/H₂ stream at the same temperatures is due to steady state conditions not having been established at these temperatures due to the reduction of $\text{O}_{(a)}$ by CO. The higher rate

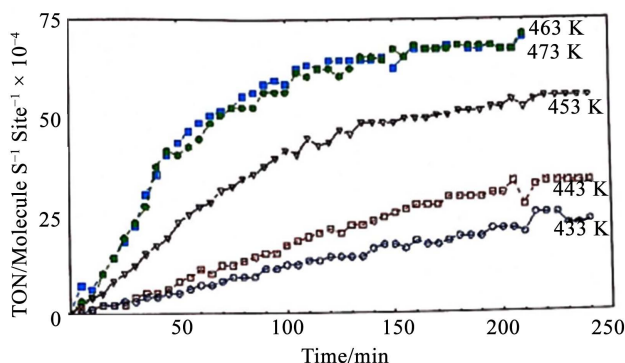
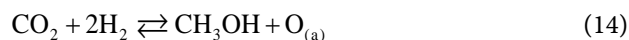


Figure 5. The time dependence of the TON per Cu atom of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst for methanol synthesis at 433, 443, 453, 463 and 473 K from a CO/CO₂/H₂ (10:10:80, 101 kPa) stream at 3 min intervals using gas chromatography.

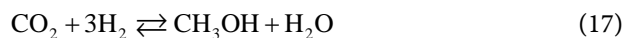
of methanol synthesis at 463 and 473 K from CO/CO₂/H₂ relative to that from CO₂/H₂ at the same temperatures is due to the CO having changed the position of equilibrium. The overall reactions involved in the presence of CO are:



This gives a net reaction of



In the absence of CO the overall reaction is



The changes in enthalpy and free energy for reaction 16 are: $\Delta H_{298} = -90.64 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta G_{298} = -25.34 \text{ kJ}\cdot\text{mol}^{-1}$, whereas those for reaction 17 are: $\Delta H_{298} = +3.3 \text{ kJ}\cdot\text{mol}^{-1}$. This accounts for the different equilibrium conditions for a CO/CO₂/H₂ mixture compared to a CO₂/H₂ mixture. Under the conditions used here for the CO₂/H₂ reaction, equilibrium is achieved at ~453 K whereas for the CO/CO₂/H₂ reaction it occurs at ~463 K. The fact that the steady state rate at 453 K for the CO₂/H₂ and the CO/CO₂/H₂ reactions are the same is due to reaction 15 occurring to a negligible extent at 453 K.

The Effect of Pulsing CO (4.98×10^{19} molecules) into a CO₂/H₂ Stream (10:90, 101 kPa, 25 cm³·min⁻¹) is Producing Methanol at Steady State.

To measure the response of pulsing CO (2 cm³ from a calibrated sample valve) into a CO₂/H₂ stream which was producing methanol at steady state, the Porapak Q column was removed from the end of the catalyst bed and the product gases from the reactor were based directly to the flame ionization detector (FID) via a capillary (2 cm long). The CO₂/H₂ reaction is 99.99% selective in the production of methanol. Since methanol and H₂ are the only species of the effluent gases from the reactor (CO, CO₂, H₂, H₂O and CH₃OH) which are detectable by the FID and since the H₂ concentration is essentially constants, the changes in the FID response are solely the result of changes in the concentration of CH₃OH in the product gases.

Figures 6-8 show the effect of pulsing CO (4.98×10^{19} molecules) into a CO₂/H₂ Stream (10:90, 101 kPa, 25 cm³·min⁻¹) which was producing CH₃OH at 433, 443 and 473 K respectively. At 433 K, the CO was injected after the CO₂/H₂ Stream had been reacting with the catalyst for 209, 211 and 217 min. Immediate upon the CO reaching the catalyst there is a sharp increase in the rate of methanol synthesis; the turnover number increases from a steady state value of 4.2×10^{-4} molecule site⁻¹ s⁻¹ to peak value of 9.5×10^{-4} molecule site⁻¹ s⁻¹, the transient peak in the rate is 2.3 times the steady state rate. The peak value 9.5×10^{-4} molecule site⁻¹ s⁻¹ obtained by pulsing CO into CO₂/H₂ Stream should be compared with a value of 3.3×10^{-4} molecule site⁻¹ s⁻¹ obtained from a CO/CO₂/H₂ stream (10:10:80) which had been on-line at 443 K for 230 min, **Figure 6**. The total amount of CH₃OH in the spike produced by injection of CO (4.98×10^{19} molecule) is 1.48×10^{18} molecules.

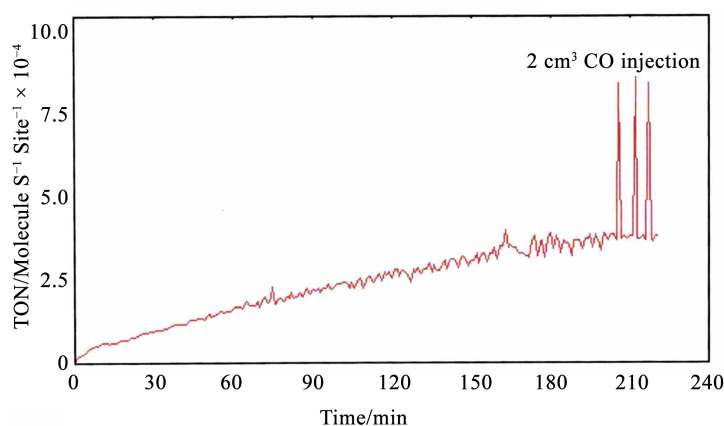


Figure 6. The time dependence of the TON per Cu atom of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst for methanol synthesis at 433 K from a CO₂/H₂ (10:90, 101 kPa) stream measured continuously using an on-line Flame Ionization Detector (FID), CO (4.98×10^{19} molecules) is injected into the CO₂/H₂ stream at 206, 211 and 217 min.

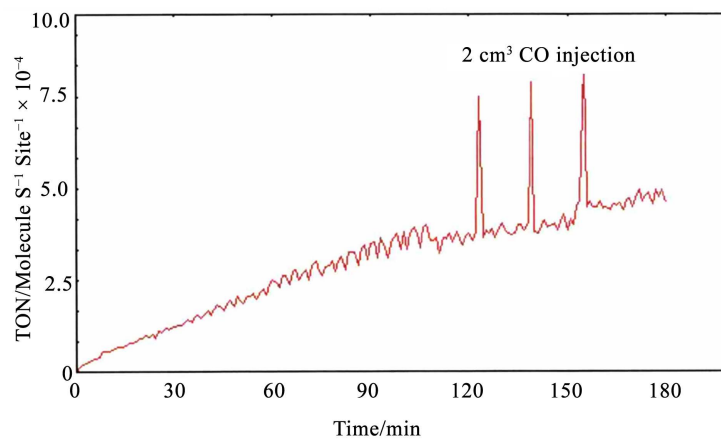


Figure 7. The time dependence of the TON per Cu atom of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst for methanol synthesis at 443 K from a CO₂/H₂ (10:90, 101 kPa) stream measured continuously using an on-line Flame Ionization Detector (FID), CO (4.98×10^{19} molecules) is injected into the CO₂/H₂ stream at 122, 137 and 154 min.

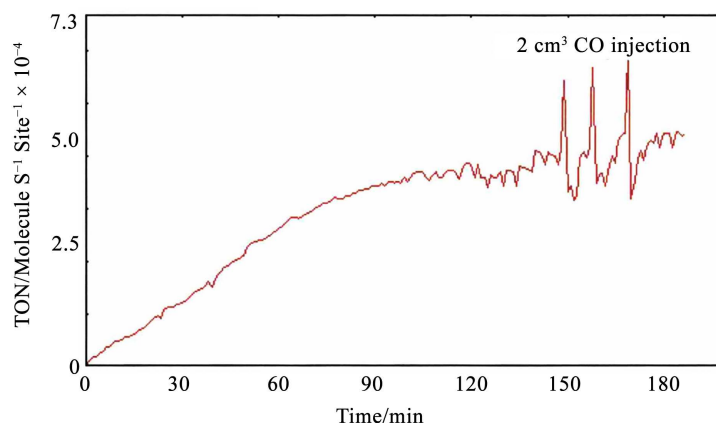


Figure 8. The time dependence of the TON per Cu atom of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst for methanol synthesis at 473 K from a CO₂/H₂ (10:90, 101 kPa) stream measured continuously using an on-line Flame Ionization Detector (FID), CO (4.98×10^{19} molecules) is injected into the CO₂/H₂ stream at 148, 158 and 168 min.

Three points should be noted from **Figure 6**. These are: 1) directly after the sharp pulse in the increase in the rate of CH₃OH synthesis occasioned by the injection of CO, the rate returns to its original value, 2) each injection of CO produces exactly the same increases in rate even though there is only 5 to 6 min interval between the injections and 3) there are clear indications that the rate of reaction is oscillating, these oscillations occur initially after the CO₂/H₂ stream has been on line for ~60 min when the rate oscillates by 25% of its steady state value and again after 170 min on line when the rate again oscillates by 25% of its steady state value. Between these two extremes, the rate oscillates by about 14% of its steady state value. Remembering that the reaction rate is being monitored by an on line FID which, responds solely to changes in the concentration of CH₃OH in the gas phase, these oscillations are not a function of inaccuracies of the analyses system and are real.

The activation energy for CO reduction of surface oxidized Cu on the Cu/ZnO/Al₂O₃ has been measured to be 28 kJ·mol⁻¹ [22]. Habraken and co-workers found values of 28.32 and 25 kJ·mol⁻¹ for the Co reduction of surface oxidized Cu (100), Cu (111) and Cu (110) [23] [24] [25] respectively, while Ertl and co-workers measured a value of 20 kJ·mol⁻¹ for the CO reduction of Cu (100) [26].

Taking values of 28 kJ·mol⁻¹ for the CO reduction of surface oxidized Cu on the Cu/ZnO/Al₂O₃ catalyst and of 20 kJ·mol⁻¹ for CO reduction of surface oxidized Cu (100) as the two extremes, the reaction probabilities for a CO/O_(a) reaction at 433 K are 4.2×10^{-4} (28 kJ·mol⁻¹) and 3.9×10^{-3} (20 kJ·mol⁻¹). On the basis of these reaction probabilities the predicted amounts of O_(a) removed from the surface of the Cu at 433 K by the injection of CO (4.98×10^{19} molecules) are 2.1×10^{16} O_(a) atoms (28 kJ·mol⁻¹) or 1.9×10^{17} O_(a) atoms (20 kJ·mol⁻¹). Therefore at 433 K, for each atom of O_(a) removed from the surface there are either 64 (28 kJ·mol⁻¹) or 7 (20 kJ·mol⁻¹) molecules of CH₃OH produced.

The important point to not is that many more molecules of methanol pro-

duced per surface oxygen atom $O_{(a)}$ removed. It is unlikely; therefore, that this increase in rate occurs because of the removal $O_{(a)}$ atoms which cause site blocking. The improbability of the site blocking argument is that the sticking probability of CO_2 on clean Cu is so low ($\sim 10^{-11}$) that releasing free sites would not produce an immediate spiked increase in rate.

What appears to be happening is that the removal of the $O_{(a)}$ from the (2×1) O-Cu causes a reconstruction of that surface which results in the release of sub-surface hydrogen. This hydrogen then hydrogenates the formate species, which Bowker and co-workers have shown to be adsorbed in islands [27] to methanol.

The results of injecting CO into a CO_2/H_2 stream (10:90, 101 kPa, $25 \text{ cm}^3 \cdot \text{min}^{-1}$) which was producing CH_3OH at 443 K, are shown in **Figure 7**. The effect is similar to that observed at 433 K. Immediate upon the pulse reaching the catalyst there is a sharp increase in the rate of CH_3OH synthesis, the turnover number rising from $4 \times 10^{-4} \text{ molecule site}^{-1} \text{ s}^{-1}$ to a peak of $8.4 \times 10^{-4} \text{ molecule site}^{-1} \text{ s}^{-1}$ an increase in rate by a factor of 2.1. The rate of CH_3OH synthesis returns to baseline after the CO has passed through the reactor. The total amount of CH_3OH produced in the spike by the injection of CO (2 cm^3 or 4.98×10^{19} molecules) is 1.23×10^{18} molecule. The reaction probability for the $CO/O_{(a)}$ reaction at 443 K for a $20 \text{ kJ} \cdot \text{mol}^{-1}$ activation energy is 4.4×10^{-3} and for a $2.8 \text{ kJ} \cdot \text{mol}^{-1}$ activation energy is 5.0×10^{-4} so that for CO pulse of 4.98×10^{19} molecules the lower energy barrier would remove $2.2 \times 10^{17} O_{(a)}$ atoms and the higher energy barrier would remove $2.5 \times 10^{16} O_{(a)}$ atoms. Therefore using the lower activation energy, the calculation suggests that for each atom of adsorbed oxygen removed 3 molecules of CH_3OH are produced, whereas the higher energy barrier would predict that each $O_{(a)}$ atom removed from the surface produces 49 CH_3OH molecules. The lower amount of methanol formed per $O_{(a)}$ removed at this higher temperature simply reflects the lower steady state formate population at the higher temperature [28]. A complete listing of the reaction probability for the two energy barriers at 433, 443, and 473 K, the predicted amounts of $O_{(a)}$ atoms removed and the amount of CH_3OH produced in the pulsed increase in rate is given in **Table 2**.

Figure 8 shows the effect of pulsing CO (4.98×10^{19} molecules) into a CO_2/H_2 Stream (10:90, 101 kPa, $25 \text{ cm}^3 \cdot \text{min}^{-1}$) which was producing CH_3OH at 473 K. The effect is qualitatively deferent from that observed at 433 and 443 K. At 473 K, there is a sharp pulse in the rate of CH_3OH synthesis occasioned from a

Table 2. The dependence of the amount of CH_3OH produced on the amount of $O_{(a)}$ atoms removed from the surface.

T/K	CO/O ₂ Reaction Probability		O atoms Removed		CH ₃ OH per O atom Removed	
	E = 20 kJ·mol ⁻¹	E = 28 kJ·mol ⁻¹	E = 20 kJ·mol ⁻¹	E = 28 kJ·mol ⁻¹	E = 20 kJ·mol ⁻¹	E = 28 kJ·mol ⁻¹
433	3.9×10^{-3}	4.2×10^{-4}	1.9×10^{17}	2.1×10^{16}	7	64
443	4.4×10^{-3}	5.0×10^{-4}	2.2×10^{17}	2.5×10^{16}	3	49
473	6.2×10^{-3}	8.1×10^{-4}	3.1×10^{17}	4.0×10^{16}	1.1	8.8

steady state value of 4.3×10^{-4} molecule site⁻¹ s⁻¹ to a maximum of 5.7×10^{-4} molecule site⁻¹ s⁻¹ by the injection of the CO molecule, an increase in rate by a factor 1.3. After the maximum, the rate no longer returns to the steady state value but falls below that point to a value only 0.8 of the original steady state value before oscillating back to the original steady state value. The second injection of CO produces a slightly higher peak value of methanol synthesis of 5.9×10^{-4} molecule site⁻¹ s⁻¹, a factor of 1.4 higher than the steady state value. After the maximum the rate falls below the steady state value to one (0.9 of steady state) slightly higher than the first minimum. The rate then oscillates back to a new higher steady state value 4.7×10^{-4} molecule site⁻¹ s⁻¹, and the third injection of CO produces a new higher maximum value of 6.6×10^{-4} molecule site⁻¹ s⁻¹, which is again 1.4 times the steady state value. This value of the transient maximum in the rate is the same as the steady state value produced by a CO/CO₂/H₂ stream (10:10:80, 101 kPa, and 25 cm³.min⁻¹) shown in **Figure 2**.

After the maximum, the rate falls to the original minimum value of 3.6×10^{-4} molecule site⁻¹ s⁻¹ after which point after four oscillations it reaches the higher steady state value of 4.7×10^{-4} molecule site⁻¹ s⁻¹. The total number of CH₃OH molecules in the pulse is 3.5×10^{17} which is only 1.1 times the number of O_(a) atoms removed by the CO (20 kJ.mol⁻¹ activation energy) or 8.8 times the number of O_(a) atoms removed (28 kJ.mol⁻¹ activation energy).

The fact that the rate of methanol synthesis falls below the steady state value indicates that the larger of O_(a) atoms removed by the CO pulse at the higher temperature causes a more extensive restructuring the copper surface to the less active Cu (211) surface. The reconstruction of this surface back to its steady state structure appears to involve several partial reconstructions.

The model of the nature of the mode of action of supported polycrystalline Cu in a Cu/ZnO/Al₂O₃ catalyst in methanol synthesis, which best describes the data produced in this paper is the following. It is one in which the surface is flexible and reconstructs as a result of adsorption of oxygen, produced by the decomposition of CO₂, and of hydrogen. To an extent, it incorporates some Somorjai's ideas [2]. However, this reconstruction does not form on active center, but forms large coherent areas of oxide and formate over layers as in Ertl model for Pt (110) [5]. Reduction of the oxide over layer by CO does not restore the Cu (110) from which it was formed but produces the Cu (211) surface, which is less active for CO₂ decomposition. Reduction of the (2 × 1) O-Cu over layer probably occurs at the interface between the (2 × 1) O-Cu over layer and the clean Cu surface, these reactions at the interface constituting the closest approximation to Taylor's active center [1].

After reduction of approximately 40% of the (2 × 1) O-Cu surface, the surface appears to reconstruct compulsively with the release of the subsurface hydrogen atoms [13] and the formation of the Cu (211) surface. Adsorption and incorporation of hydrogen in the Cu (211) restores the Cu (110) surface. The reconstruction appears to act coherently over large areas and so gives rise to the observed oscillations.

4. Conclusion

Hydrogen reduction of the polycrystalline copper oxide component of a Cu/ZnO/Al₂O₃ (60:30:10) catalyst produces a surface morphology of Cu, which is active in the decomposition of CO₂. This surface has been shown to comprise the Cu (110) face and the minority Cu (211) face. Reduction of the oxide over layer by CO does not restore the Cu (110) from which it is formed but produces the Cu (211) surface, which is less active for CO₂ decomposition. Reduction of the (2 × 1) O-Cu over layer probably occurs at the inter face between the (2 × 1) O-Cu over layer and the clean Cu surface. Treatment of this reconstructed surface with hydrogen results in the partial restoration of the (110) face. Injection of CO into the CO₂/H₂ stream, which is synthesizing methanol at 473 K, produces a sharply spiked increase in the rate of methanol synthesis followed by an oscillatory relaxation to steady state behavior. At 433 and 443 K the injection of CO into the CO₂/H₂ stream again produces the sharply spiked increase in the rate of methanol synthesis, which returns to the baseline value without oscillations. CO reduction of the polycrystalline copper oxide component of a Cu/ZnO/Al₂O₃ (60:30:10) catalyst produces a surface morphology of Cu, which is inactive in the decomposition of CO₂. This is in complete contrast to the surface morphology of the Cu produced by H₂ reduction of the polycrystalline copper oxide component of the Cu/ZnO/Al₂O₃ (60:30:10) catalyst. The fact that the rate of methanol synthesis falls below the steady state value indicates that the larger of O_(a) atoms removed by the CO pulse at the higher temperature causes a more extensive, restructuring the copper surface to the less active Cu (211) surface. This expects that removing O_(a) leads to a rebuilding of this surface resulting in the release of hydrogen below the surface, which in turn leads to the hydrogenation of formate, producing methanol.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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