(Non)formation of Methanol by Direct Hydrogenation of Formate on Copper Catalysts†

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We have attempted to hydrogenate adsorbed formate species on copper catalysts to probe the importance of this postulated mechanistic step in methanol synthesis. Surface formate coverages up to 0.25 were produced at temperatures between 413 and 453 K on supported (Cu/SiO2) copper and unsupported copper catalysts. The adlayers were produced by various methods including (1) steady-state catalytic conditions in CO2–H2 (3:1, 6 bar) atmospheres and (2) exposure of the catalysts to formic acid. As reported in previous work, the catalytic surface at steady state contains bidentate formate species with coverages up to saturation levels of ∼0.25 at the low temperatures of this study. The reactivity of these formate adlayers was investigated at relevant reaction temperatures in atmospheres containing up to 6 bar H2 partial pressure by simultaneous mass spectrometry (MS) and infrared (IR) spectroscopy measurements. The yield of methanol during the attempted hydrogenation (“titration”) of these adlayers was insignificant (<0.2 mol % of the formate adlayer), even in dry hydrogen partial pressures up to 6 bar. Hydrogen titration of formate species produced from formic acid also failed to produce significant quantities of methanol, and attempted titration in gases consisting of CO–hydrogen mixtures or dry CO2 was also unproductive. The formate decomposition kinetics, measured by IR, was also unaffected by these changes in the gas composition. Similar experiments on unsupported copper also failed to show any methanol. From these results, we conclude that methanol synthesis on copper cannot result from the direct hydrogenation of (bidentate) formate species in simple steps involving adsorbed H species alone. Furthermore, experiments performed on both supported (Cu/SiO2) and unsupported copper catalysts gave similar results, implying that the methanol synthesis reaction mechanism involves only metal surface chemistry. Pre-exposure of the bidentate formate adlayer to oxidation by O2 or N2O produces a change during this titration as the copper surface is rereduced. These results indicate that coadsorbates related to surface oxygen or water-derived species may be critical to methanol production on copper, perhaps assisting in the hydrogenation of adsorbed formate to adsorbed methoxyl.

1. Introduction

Methanol is thought by many to be the ideal fuel because it is easily transportable, can be readily synthesized from synthesis gas derived from extensive coal reserves, and can be steam-reformed to generate hydrogen for fuel cells. As such, there has been considerable research activity on catalytic methanol synthesis,1–17 including a number of mechanistic studies employing model materials, such as Cu/SiO2.3–5 Prior investigators have proposed that stepwise hydrogenation of adsorbed formate species is the dominant reaction pathway for methanol production on copper catalysts.3–5,14–17 Current microkinetic models include such a pathway with a sequence of reactions involving adsorbed H. Anticipating the results herein, “direct” hydrogenation is taken here to mean such a straightforward mechanism in which adsorbed H species alone are sufficient to accomplish the reaction. Monolayer amounts of copper bound formate species are visible by IR spectroscopy under a wide range (100–300 °C) of reaction conditions; however, direct evidence of methanol production via the reaction of such adsorbed formate species under high-pressure hydrogen conditions has not been presented to date. Support for this assertion could come from attempted titration experiments in hydrogen-containing atmospheres that simultaneously probe the formate adlayers, for example, with IR, and the methanol production rate using mass spectrometry. Such experiments have not been previously performed and serve as motivation for the studies described here.

2. Experimental Section

Attempted titration experiments of surface-bound formate species on pure Cu and supported Cu/SiO2 catalysts employed the following strategies:

(1) Steady-state methanol synthesis was carried out at moderate temperatures with a 3:1 D2/CO2 reactant gas mixture. During reaction, methanol-D production rates were quantified by mass spectrometry (MS), whereas potential adsorbed reaction intermediates were identified with IR spectroscopy. The input feed was then switched to either pure Ar or D2 gas streams...
with continued probing of the catalyst surface adlayers with transient IR and reaction products with MS. In this way, we can infer the relevance of adsorbed formate in methanol production and directly distinguish this process from the competitive decomposition of formate back into the reactants (i.e., D₂ and CO₂).

(2) A complementary approach of generating pure formate adlayers involved exposure of the Cu catalysts to deuterated formic acid. This surface adlayer was also subsequently exposed to either pure Ar or D₂, with simultaneous IR and MS probing as before. These experiments are believed to provide a more direct probe of the role of surface formate hydrogenation in methanol synthesis, without complications (e.g., chemistry) arising from the presence of nonformate adlayer species that might be present but undetected (by IR spectroscopy) during steady-state reaction in D₂/CO₂ mixtures.

(3) Finally, similar experiments were performed following exposure of copper-bound formate adlayers to O₂ or N₂O. It has been reported that the bonding configuration of formate species converts from bidentate to monodentate upon surface oxidation of Cu/SiO₂ catalysts. Therefore, these experiments partially address the possibility that certain coadsorbates may affect the reactivity of adsorbed formate species upon exposure to hydrogen alone.

**Apparatus.** A custom-made transient kinetic analysis (TKA) apparatus was used for these studies. This instrument combines traditional TKA capabilities of rapid gas switching and mass spectrometric analysis of the reactor effluent with operando rapid-scan transmission infrared spectroscopy of adsorbed species on the catalyst surfaces. The apparatus has been previously described in detail, so only a brief description is included here. The reactor temperatures are PID-controlled (Watlow) from 150 to 770 K, with a reactor volume of 0.5 cm³ and high pressure limit of 10 bar. The reactor is loaded with 35 mg catalyst, of which 4 mg are pressed onto a tungsten mesh centered in the optical path of a transmission FTIR spectrometer. The spectrometer is a Bruker IFS/66S FTIR instrument equipped with a broadband MCT detector and fast (320 kHz) data acquisition electronics. Gas flows were controlled by a series of mass flow controllers ( Alicat Scientific) and switching valves (VICI Valco), which allow flow rates from 1 to 200 sccm with arbitrary reagent gas mixtures. Both the gas refresh rate in the reactor and FTIR scan rates are optimized to achieve fast response times as low as ∼1 s for the combined spectroscopic/gas analysis TKA experiments. Integration of FTIR peaks versus time is used to represent coverages of surface species, whereas real-time MS signals are recorded for gas-phase product identification and quantification. Multiple FTIR and mass spectral data acquisitions are made relative to a common time axis. An unsupported copper catalyst was also used in this study. In the experiments with unsupported catalysts, the operando reactor in the TKA system was replaced with a larger-volume (3 cm³) tubular reactor. This reactor was not equipped with FTIR windows and utilized only the MS capabilities.

**Catalyst Samples.** The 10 wt % Cu/SiO₂ catalyst employed in this study was prepared by incipient wetness impregnation using Cu(NO₃)₂ hydrate (Aldrich, 98-100% with low metal and salt impurities) and a mesoporous silica support material (stated BET surface area of 150 m²/g). Prior to use, the catalyst was first calcined in zero air overnight at 623 K and reduced within the reactor with pure H₂ (6.0 bar) at 553 K for at least 2 h. XPS analysis of the catalyst before and after use revealed primarily Si, O, and Cu features (>98%). The estimation of exposed copper surface sites was obtained by a standard N₂O titration method for polycrystalline copper (e.g., CuO + N₂O → Cu₂O + N₂). Typically, ∼3.5 µmol (0.10 µmol/mg × 35.0 mg) of catalyst sites exists in any given Cu/SiO₂ sample. The methanol synthesis turnover frequency (TOF) measured under the standard condition of 413 K and D₂/CO₂ 3:1 at 6 bar was stable at 3.6 ± 0.2 × 10⁻⁶ s⁻¹.

An unsupported copper catalyst was prepared from ultrapure copper powder (Alfa Aesar spherical powder, 2 µm average diameter). Catalyst (4 g) was gently loaded into the tubular reactor without pressing. Overnight reduction in H₂ at low temperatures (453 K) produced a catalyst with sufficient methanol synthesis activity for our experiments while minimizing the sintering of the unsupported copper. The N₂O titration method showed 1.3 µmol sites/g of this material by comparison with the 100 µmol sites/g on the supported catalyst. The methanol TOFs under the standard condition for 5 g of this catalyst assuming this measured site count were in the range of (2 to 3) × 10⁻⁶ s⁻¹, similar to those observed on the Cu/SiO₂ catalyst. Slow site loss, probably by sintering, was noted on this unsupported catalyst over time.

**Gas Handling.** In all experiments reported here, 10 sccm gas flows were used with total pressures of 6.0 bar. Temperatures were varied in these experiments and are explicitly given when results are described. The reactor gas flushing time constant in these experiments is less than 15 s in all cases. The gas flows used in these experiments are: (1) D₂/CO₂ mixture: 7.5 sccm D₂ and 2.5 sccm CO₂; (2) D₂ reactant only gas: 7.5 sccm D₂ and 2.5 sccm Ar; (3) Ar inert gas: 10 sccm Ar; (4) deuterated formic acid flow: 3 nmol/sec (0.5 µL/h) deuterated formic acid carried by 10 sccm Ar flow; (5) O₂/Ar mixture: 9.0 sccm Ar and 1.0 sccm O₂; and (6) N₂O mixture: 1% in Ar: 10 sccm.

**Data Collection and Analysis.** For the transient experiments, the samples were first exposed to gas mixture #1 at reaction temperatures until steady-state production of methanol was achieved. The gas mixture was then switched to expose the sample to either gas mixture #2 or #3 while maintaining the same flow rates and total gas pressures. Time-resolved FTIR spectra (TR-FTIR) are plotted to show the real-time evolution of surface species upon switching. Signal intensity is integrated from the formate O=-(DC)=O symmetric stretching band at 1330 cm⁻¹. The surface IR spectra are dominated by bidentate formate features. No other bands attributed to active species were observed, and the framework symmetric mode is the most useful for these studies. Other features, such as the high-frequency modes, are compromised by interference from IR bands due to inactive support bound species. Such experiments were performed for ∼60 min after the gas switches, and the TR-FTIR collection rates were set at ∼1 min⁻¹ to optimize signal-to-noise levels while still being able to measure the transient behavior. Methanol production rates are normalized to CO₂ input rates, which are kept constant at 2.5 sccm (1.86 µmol/sec). The TOFs are extracted from data of methanol production rate and measured number of surface-active copper sites.

We followed a similar procedure to examine the reactivity of formate produced from formic acid. In this case, gas stream #4 was used in place of the D₂/CO₂ stream (#1). We investigated the effect of oxidized copper by inserting a pulse of O₂ (stream #5) or N₂O (stream #6) between the adlayer preparation and its attempted titration.

The kinetics experiments were all performed with the fully deuterated gas species (D₂, DCOOD) for two reasons: (1) the decay kinetics are substantially slower than that in the H system, allowing better resolution in the time-dependent IR
data and, more importantly, (2) the mass spectrum of the perdeutero methanol product (CD₃OD) was free from background interferences, allowing much higher sensitivity in the MS results. The IR spectra in this Article are from the H system rather than the D system, allowing more direct comparison with previous published reports. The systematic isotope effects on the IR spectrum were discussed in our previous paper.

Red shifts of 25–35 cm⁻¹ of the main O–C–O stretch features are associated with D substitution for H in formate.

3. Results and Discussion

Figure 1 shows the transient buildup of both surface formate coverage by IR (Figure 1a) and d-methanol production by MS (Figure 1b), obtained following exposure of a 10 wt % Cu/SiO₂ catalyst to a D₂/CO₂ (3:1) gas mixture at various temperatures. In these experiments, a switch from D₂/Ar to D₂/CO₂ (both at 6 bar) was made at time = 0, and the six IR transients in Figure 1a correspond to the six temperatures, 353, 373, 393, 413, 423, and 433 K (Figure 1a (a–f)). Applying first-order exponential fitting to Figure 1a (a–d), we obtained formate formation time constants of 784, 551, 212, and 169 s for reaction at 353, 373, 393, and 413 K, respectively. From these data, an Arrhenius analysis yielded an activation energy of 33 kJ/mol for deuterated formate formation at 6 bar for a D₂/CO₂ 3:1 mixture. (The other two formate coverage curves at higher temperatures change too rapidly and are thus affected by the time resolution (73 s) of the FTIR sampling rate.) For methanol-D mass spectrometric detection (fragmentation of atomic mass unit 34 for CD₃O⁺), only the three highest temperature (413, 423, and 433 K) product formation curves are shown in Figure 1b (a–c) because insufficient product methanol-D formation was observed at the lowest temperatures. Comparing the sets of curves in Figure 1a,b, the time constants for the methanol gas product transients are significantly slower: 490, 389, and 329 s for 413, 423, and 433 K, respectively. This mismatch of the time constants in the two simultaneous measurements demonstrates that the methanol production rate is not linearly dependent on formate surface coverage during this transient.

To investigate further the role of formate hydrogenation in methanol synthesis, we then exposed the formate adlayers produced under D₂/CO₂ to either a D₂ or an Ar atmosphere. Figure 2 presents these data, collected at 413 K, where the IR formate adlayers are shown by symbols for D₂ (a and b) and Ar (c and d) exposure (labels a,b). The corresponding MS signals are shown as continuous traces for the methanol-D product upon switching to D₂/Ar (c) or Ar (d). By plotting these two sets of data in one Figure, a direct comparison can be made between the transient responses of the methanol formation rate and formate surface coverage. The formate decay curves in both cases essentially overlap each other, indicating that the formate decay rate is not sensitive to the presence of hydrogen gas addition to inert Ar upon switching from the steady-state methanol synthesis gas mixture. The mass spectrometric signals also show that at most small amounts of methanol-D are produced after switching from the D₂/CO₂ reactant gas mixture to either gas.
Our previous work considered IR data alone and suggested that the adsorbed formate decay during attempted titration in deuterium (i.e., upon D₂/CO₂ → D₂ switching) occurs predominantly by thermal decomposition to the D₂ and CO₂ reactants rather than deuteration to methanol-D. Figure 2, to our knowledge, is the first time simultaneous transients have been recorded of IR formate coverages and mass spectrometric methanol production, allowing for a quantitative comparison of these processes. As noted above, the total number of surface copper sites available in these experiments was ~3.5 µmol. Previous studies employing STM and XPS techniques both concluded that formate coverages on Cu (111) surfaces, which should account for 90% or more of the total Cu surface in our catalysts, are 25% of a monolayer. On the basis of these values, a conservative estimation of surface formate species at steady state is between 0.5 and 1.0 µmol. In Figure 2a,b, the total surface formate coverage is reduced by ~2/3 of the steady-state coverage during the experiments, an amount estimated to be ~0.3 to 0.7 µmol. Integration of the methanol-D mass spectrometric signal (after D₂ switching and normalized to the constant CO₂ input signal at 2.5 sccm and 1.86 µmol/sec) yields a total quantity of methanol-D product in the transient of ~2.2 × 10⁻³ µmol, an amount only 0.3 to 0.8% of the total formate loss during the “titration” portion of the experiments. Therefore, as previously concluded, the formate decay in Ar and in D₂ at 413 K is dominated by thermal decomposition of formate to the reactants, D₂ and CO₂. Furthermore, in later stages in the experiment, no evidence of methanol-D production is seen, despite the presence of the significant amount of formate remaining on the catalyst.

Even the small amount of methanol formed in the early stages of the attempted titration in D₂ in Figure 2 cannot be directly associated with the hydrogenation of formate because of the possible role of other coadsorbates present during steady-state catalysis.

To make a more sensitive check on the possible role of D₂ in formate hydrogenation to methanol, we performed an additional transient experiment where the introduction of D₂ is delayed until after other possible steady-state adsorbates could decay but while a substantial amount of formate remained on the surface. The surface was prepared in the same way as in Figure 2, that is, via steady-state methanol synthesis reaction. The gas flow was then switched to Ar flow for 10 min, followed by a switch to a D₂ reactant only flow. The MS results (curve b in Figure 3) show only a baseline shift (due to the loss of a very small amount of Ar(36) intensity at m/e = 34 by both concentration and gas viscosity changes on switching) and show no hint of a pulse of D-methanol upon introduction of D₂. The data (IR and MS) from Figure 2 are re-plotted in Figure 3 for comparison. These data show that substantial amounts of formate (>85% of the saturated monolayer) were still present when D₂ was introduced. Therefore, this Figure clearly shows that reintroducing D₂ to a Cu catalyst containing a high formate surface coverage does not show any hint of methanol-D synthesis. An upper limit to the fraction of the formate adlayer that may have been hydrogenated to D-methanol as a result of introduction of D₂ is 2 × 10⁻³. Although the data are not shown here, similar attempted titration experiments with other gas compositions, particularly D₂/CO₂ 50:1 at 6 bar and pure H₂/CO₂ 3:1 at 6 bar also failed to show any hint of methanol production.

Similar MS results to the experimental protocols above were observed on the unsupported copper catalyst; that is, there was no evidence of a contribution to methanol formation by direct hydrogenation of adsorbed formate. This behavior also provides strong evidence that the methanol synthesis reaction mechanism only involves chemistry on the metal surface.

Formic acid adsorption provides a contrasting method of producing formate. In these experiments, formic acid was exposed at the rate of 3 nmol/sec carried by pure Ar gas at 6 bar at 10 sccm (partial pressure of formic acid ~3 mbar) until a saturation surface formate coverage was achieved. As before, the attempted titration experiments were performed with the per-deuterated isotopomer formed from DCOOD, and the adlayers were exposed to D₂ or Ar. Before describing the attempted titration experiments, however, we first compare the IR formate bands on Cu/SiO₂ obtained by exposure to formic acid with the spectra observed during steady-state methanol synthesis in H₂/CO₂ mixtures in Figure 4 (all curves obtained at 453 K). Figure 4a shows the IR bands obtained during H-formic acid exposure. This spectrum is in good agreement with previous results for H-formic-acid-dosed Cu/SiO₂ surfaces, even though there are some differences in the experimental conditions used. After weakly bound molecular species are removed by extended purging in pure Ar, the formic-acid-exposed Cu/SiO₂ formate IR spectrum (Figure 4b) was almost identical to the steady-state H₂/CO₂-exposed surface (Figure 4c). The small differences are likely due to formic acid adsorption on the silica support (Figure 4d). Therefore, formate species produced by formic acid adsorption and during steady-state methanol synthesis are essentially identical in structure and coverage. Note that we have shown that adsorbed formate is bound in a bidentate configuration under steady-state reaction conditions, implying that this same geometry is adopted upon formic acid adsorption, a conclusion in agreement with prior reports.

The attempted titration in D₂ of deuterated formate produced by D-formic acid adsorption is shown in Figure 5. After 30 min...
of Ar purge, the DCOO\(^{-}\) adlayer was then switched to D\(_2/\)Ar reactant gas mixture. The Figure 5a curve shows the decay of the formate O–(CD)–O symmetric stretching band at \(\sim 1330\) cm\(^{-1}\) during this process. Overall, these results are similar to those seen for the D\(_2/\)CO\(_2\) formate adlayer in Figure 2b. The IR intensity obtained at saturation coverage of formate after formic acid exposure is somewhat higher (\(x \approx 1.2\)) than the D\(_2/\)CO\(_2\) exposed surface. In addition, the initial specific decay rate for formate from DCOOD dosing after switching to Ar was somewhat faster than that for the D\(_2/\)CO\(_2\) exposed surfaces. These modest differences could be partially due to the presence of formate species on the silica surfaces in the formic acid experiment. Other reaction intermediates, present (but not detected) during steady-state methanol synthesis, may also limit the saturation formate coverage under steady-state conditions. In any case, after 10 min of purging with Ar, both curves reach similar intensities, and subsequent decay rates are essentially identical, in agreement with the previous conclusion that formate decay rates do not depend on the presence of hydrogen. Notably, Figure 5, similar to Figure 3, shows that as Ar is switched to D\(_2/Ar\), the formic-acid-exposed surface with “pure” formate species yields no methanol-D signal above 1% of the maximum level observed during steady-state methanol synthesis (Figure 3). We attribute the small (\(\leq 1\%\)) signal excursions to baseline drift in the mass spectrometer. This result again demonstrates that hydrogen does not directly convert surface formate to methanol.

The results presented in Figures 3–5 strongly suggest that the small amount of methanol produced in the transient of Figure 2c does not have a contribution from direct formate hydrogenation. Instead, we suggest that the small methanol tail observed in Figure 2c is more likely related to surface species of much lower coverage, shorter lifetime, or otherwise undetectable by IR spectroscopy during reaction. For example, the methanol may arise from the continued presence of a steady-state reaction intermediate requiring both gas-phase D\(_2\) and CO\(_2\) for its formation.

As one possible alternative reaction intermediate, we note that a number of previous studies have demonstrated that formate can adopt both bidendate and monodentate binding geometries on copper surfaces (Scheme 1) under certain conditions.\(^{18,28–32}\) In particular, Rochester and coworkers\(^{18}\) demonstrated that exposure of formic acid to a mildly oxidized (N\(_2/\)O pretreated) Cu/SiO\(_2\) surface gives rise to IR peaks that they assigned to formate in a monodentate bonding configuration. To determine a possible role for such a monodentate formate species in the methanol synthesis mechanism, we first intentionally formed a significant concentration of monodentate formate on a Cu/SiO\(_2\) surface and probed its reactivity with D\(_2\) for methanol production. The catalyst was first exposed to steady-state reaction in (H\(_2,\)D\(_2)/\)CO\(_2\) mixtures at 413 K to form a saturated bidentate formate adlayer. The gas mixture was then switched to an O\(_2/\)Ar (stream #5) flow to promote mild surface oxidation. We monitored this process by continuously obtaining FTIR spectra (each scan taking \(\sim 70\) s) to verify the formation of monodentate formate. The spectra in Figure 6 document this process for the H-isotopic system. Spectra in set a were obtained under steady-state methanol synthesis conditions in H\(_2/\)CO\(_2\). As

![Figure 4. IR spectra in the formate stretch region for: (a) formic-acid-exposed Cu/SiO\(_2\) and (b) then purged with He for 8 h; (c) during steady-state methanol synthesis reaction in a 6 bar H\(_2/\)CO\(_2\) mixture; and (d) formic acid exposed pure silica, all at 353 K. The band at 1350 cm\(^{-1}\) is the O–C(H)–O symmetric stretch, and the band at 1550 cm\(^{-1}\) is the O–C(H)–O asymmetric stretch.](image)

![Figure 5. IR intensity of copper-bound adsorbed bidentate formate (DCOO\(_{ad}\), curve a) and the methanol gaseous product (CD\(_3\)OD, curve b) during attempted titration of formate derived from formic acid. The gas dosing sequence is noted at the top of the Figure with composition changes indicated by the arrows. Formic acid exposure (3 nmol/sec diluted in Ar) was followed by a switch to pure Ar at time \(t = 0\), then followed by a subsequent switch to D\(_2/\)Ar after a further 30 min. The conditions are 413 K and 6 bar total pressure.](image)

![Scheme 1](image)
before (Figure 4c), all IR peaks observed under these conditions can be assigned to bidentate formate species. A single IR spectrum labeled “b” is taken during the gas mixture switching to oxygen and shows the beginning of a transition between two steady-state conditions represented by the “a” set of spectra (before O₂) and the “c” set (after O₂). All spectra given by curves “c” span ~300 s of O₂ exposure. All show a uniform yet obviously different set of IR peaks compared with Figure 6a. Figure 6a shows a main peak at 1350 cm⁻¹ with a shoulder at 1364 cm⁻¹ and a somewhat broader feature at 1550 cm⁻¹. With the use of isotopic substitution, we have assigned these three features to the O–C–O symmetric stretching, C–H rocking, and O–C–O asymmetric stretching modes, respectively, of adsorbed formate in a bidentate bonding configuration. The spectra in Figure 6c show two primary peaks at ~1574 and 1364 cm⁻¹, essentially identical to those assigned to monodentate formate in ref 18.

In addition to temperature and pressure differences, the most important difference between the just described experiments and those of Rochester and coworkers is the gas exposure sequence in the oxidation process. Instead of exposing formic acid to an N₂O preoxidized Cu/SiO₂ catalyst to form monodentate formate directly, our experiments demonstrate the conversion of a bidentate formate adlayer upon oxidation with oxygen. Despite these differences, the observed formate feature changes are identical. Figure 6 is, to our knowledge, the first time that the transition from bidentate to monodentate formate species has been directly observed. Clearly, the bonding geometries of surface formate species on copper surfaces are very sensitive to the presence of coadsorbed oxygen.

A strong contrast was seen in the behavior of these postoxidized formate adlayers during their attempted titration in hydrogen-containing atmospheres when compared with the nonoxidized results in Figures 3 and 5. First, appreciable production of methanol is now associated with the introduction of D₂. Second, a simultaneous production of water is seen in the MS data. This water signal is from recombination of the copper surface sites according to the stoichiometry O(ad) + H₂ → H₂O, where the amount of O(ad) is, at most, that measured in the N₂O-based site determinations. Such behavior is seen both on the supported and unsupported catalyst, but the most direct example is shown in Figure 7 on the unsupported catalyst. In this experiment, the Cu surface monodentate formate was prepared in a slightly different manner from the previous experiment shown in Figure 6. First, as before, a bidentate formate adlayer was formed during the steady-state D₂/CO₂ reaction and subsequently purged with Ar for 10 min. The monodentate formate was formed, however, by exposure to 2% N₂O (rather than O₂) diluted in He gas mixture for 40 s. As already noted, prior work has shown that the combination of formic acid and this oxidant yields the monodentate formate on copper surfaces. The advantage of using N₂O exposure is to limit any “oxidation” of Cu to the first monolayer. The use of the unsupported catalyst also avoids complications of water readsoption on the support, which might alter the water transient. Otherwise, the behavior is similar to that observed on the supported catalyst with O₂. Following this oxidation by N₂O, a 10 min Ar flow was again used to purge the gas ambient. Then, similarly to the previous experiments, gas flow was switched to a D₂/Ar mixture. A substantial methanol pulse was observed, as shown by curve “a” in Figure 7. The maximum methanol production rate during this transient was ~50% of the steady-state methanol synthesis rate under a D₂/CO₂ flow. Following a similar quantitative estimation, as described above, the total yield of methanol product in this transient is ~1 to 2% of the total number of initial surface formate species. Therefore, decomposition to D₂ and CO₂ still dominates the formate reactivity under these conditions. This experiment is the first one to observe methanol production from formate upon exposure to hydrogen. The monodentate nature of the adlayer implies that monodentate formate might be the reactive species. IR data could not be obtained during this experiment on unsupported Cu. In any case, however, there is no evidence of the involvement of monodentate formate under steady-state catalytic conditions. Indeed, IR spectra obtained during steady-state methanol synthesis and during the attempted titration experiments (e.g., Figure 3c) show essentially no spectral features associated with monodentate formate. Even considering the overlapping of these IR features, its coverage must be one to two orders of magnitude lower than the bidentate formate. Considering that a largely monodentate adlayer still produces less methanol than the steady-state (largely bidentate) adlayer, direct hydrogenation of monodentate formate alone still cannot...
rationalize steady-state methanol synthesis rates. The role of other species or coadsorbates during reaction is therefore strongly implied.

A possible clue to the aspects of the methanol synthesis mechanism was, however, obtained in the just-described experiments. In particular, this experiment produced not only small amounts of methanol upon exposure of the monodentate formate adlayer to hydrogen but also significant amounts of water via reaction with the coadsorbed oxygen, which is required to form monodentate formate (curve b). In fact, the amount of water that is produced coincident with methanol, as shown in the upper curve in Figure 7, was at least 50 times more than the total amount of methanol produced. This result suggests the possibility that reaction intermediates related to water, surface hydroxyl groups being just one simple example, may play a crucial role in the mechanism of methanol synthesis. We note that water is a product of the methanol synthesis under catalytic conditions in CO2/H2 atmospheres and is also coproduced along with carbon monoxide by the reverse water gas shift reaction. We will more completely explore this possibility in a subsequent publication.33

Finally, we note that the experiments performed here were at temperatures lower than commercial methanol synthesis conditions (≥500 K), and, as such, it is possible that other processes may contribute under those conditions. Nevertheless, both the steady-state formate coverage and temperature dependence of the reaction rate behave smoothly throughout this range, and it is likely that hydrogenation of formate is not “direct” on copper catalysts under commercial conditions.

4. Conclusions

In model experiments where both bidentate formate and adsorbed H are present on copper catalysts, the direct hydrogenation of formate species does not occur at a rate consistent with methanol synthesis. The methanol synthesis pathway on copper must therefore include heretofore unrecognized coadsorbates, cooperative behavior between coadsorbates, or both. The results here further suggest that some water-derived adsorbate may assist in the hydrogenation of adsorbed formate to adsorbed methoxyl. That is, the dominant pathway to methanol synthesis may involve the hydrogenation of formate to methoxyl, but this does not occur with H2 alone, as suggested by previous literature. Instead, the reaction of adsorbed H and adsorbed formate to make adsorbed methoxyl may be catalyzed by the presence of some water-derived coadsorbate. These effects are not incorporated in current microkinetic models. The quantitative similarity of data obtained in the experiments on both supported (Cu/5SiO2) and unsupported copper catalysts verify that the methanol synthesis reaction mechanism involves processes only on the metal surface.

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