

Probing Surface Properties and Reaction Intermediates During Heterogeneous Catalytic Oxidation of Acetaldehyde

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The influence of Cu on various metal oxide supports was investigated for the catalytic oxidation of acetaldehyde (ACA). The activity of the catalysts towards ACA conversion and the CO₂ yield decrease in the order: Cu/CeO₂ > Cu/TiO₂ ≈ Cu/ZrO₂ > Cu/Al₂O₃ > Cu/SiO₂. Spontaneous adsorptive conversion of ACA to surface carboxylates, such as bridging and bidentate acetates, was detected over the basic supports CeO₂, TiO₂, and ZrO₂. Detailed temperature-programmed studies found the

high activity of Cu/CeO₂ to stem mainly from the intrinsically high activity of the CeO₂ support. In contrast, similar studies on Cu/TiO₂ demonstrated the activity improvements imparted by Cu were predominantly additive. Despite the difference in origin of ACA oxidation activity over Cu/CeO₂ and Cu/TiO₂, the overall concerted effects of basicity-induced carboxylate formation and availability of surface oxygen were thought to be overriding factors crucial in the overall catalytic reactivity.

Introduction

Acetaldehyde (ACA) is a noxious volatile organic compound (VOC) that originates from a variety of domestic and industrial sources. The widespread use of aldehyde-based resins and construction materials in modern building interiors, coupled with lower levels of indoor ventilation, can result in elevated concentrations of ACA.^[1] ACA can also result from incomplete combustion of fuel oxygenates, such as ethanol and corresponding ethers (diethyl ether and ethyl *tert*-butyl ether),^[2,3] which is becoming increasingly important as more governments mandate the use of ethanol–petrol blends. ACA is a potent carcinogen and prolonged, low-level (0.5 ppm) exposure has been shown to induce a variety of detrimental health effects.^[4] ACA can also indirectly compromise domestic air quality by acting as a precursor in the photochemical formation of tropospheric ozone.^[5] In light of these concerns and amidst increasingly stringent indoor air-quality regulations, low-cost methods for ACA removal are being investigated.

Low temperature (< 573 K) catalytic conversion of ACA to CO₂ and H₂O is one potential means of removal, as it avoids the finite adsorption capacities and excessive energy inputs associated with conventional physisorption^[6] and noncatalytic combustion techniques, respectively. Complete ACA oxidation has been demonstrated over a range of materials,^[7,8] with Pt/TiO₂ catalysts shown to achieve 100% conversion of 10 000 ppm ACA at 498 K.^[9] Despite the potential of precious metal-based catalysts, limitations due to their expense and poisoning susceptibility underline the need to identify cheaper, more robust alternatives. Base-metal catalysts have been investigated, in which Cu-, Co-, and Mn-based catalysts were found to demonstrate competitive activity levels for ACA oxidation.^[10] Aside from lower material costs, these catalysts have shown resistance to deactivation by high moisture concentrations, which are likely to be present in domestic environments.

Herein, we report our investigations of Cu supported on different metal oxides (CeO₂, TiO₂, ZrO₂, Al₂O₃, and SiO₂) for complete catalytic ACA oxidation. These catalysts were synthesized by one-step flame spray pyrolysis and were thoroughly characterized by us^[11,12] as well as by others.^[13,14] Previous reports suggest that catalytic ACA oxidation is likely to occur via a succession of adsorption, dissociation and oxidation reactions,^[15] however, the energetics, kinetics and active sites for these processes are yet to be established. The potential for Mars–van Krevelen-type surface reactions between ACA and the oxide support, as proposed for other Cu-catalysts,^[16] may also contribute to the overall catalytic activity. Owing to a lack of information regarding ACA desorption and decomposition kinetics, we focused on identifying the fundamental oxidation mechanisms occurring on the catalyst surface. Key reaction intermediates were identified during the total mineralization pathway of ACA and used to assess how oxygen availability at the surface contributed to the overall catalytic performance.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cctc.200900099>.

Results and Discussion

Steady-State Acetaldehyde Oxidation

During initial saturation of the metal oxide surfaces with ACA, no simultaneous increase in CO₂ concentration was detected, indicating that ACA was being chemisorbed on the surface. Figure 1 portrays ACA conversion, and corresponding CO₂ pro-

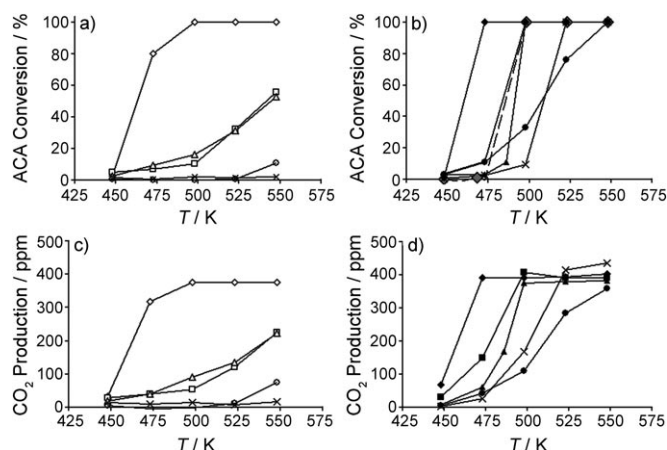


Figure 1. ACA conversion by a) neat CeO₂ (◇); TiO₂ (□); ZrO₂ (△); Al₂O₃ (○); SiO₂ (×) and b) 4 wt.% Cu-loaded metal oxides (filled symbols represent Cu-loaded metal oxides) and pure CuO (●). Corresponding CO₂ production by c) neat and d) 4 wt.% Cu-loaded metal oxides.

duction, by the neat and Cu-loaded metal oxides with increasing temperature.

CeO₂ was the only bare support metal oxide to attain 100% ACA conversion over the temperature range considered, which was achieved at 498 K (Figure 1 a). TiO₂ and ZrO₂ provided similar activity profiles with a distinct upturn in ACA conversion between 498 and 523 K. Al₂O₃ demonstrated a low ACA oxidation capability (~11%) at 548 K, whereas SiO₂ displayed negligible activity at all temperatures.

The loading of Cu onto CeO₂ had a marginal effect on ACA conversion (Figure 1 b) with 100% oxidation achieved at 25 K lower than for the neat material. The effect of Cu on the activity of the other metal oxides was much more pronounced, with all metal oxides exhibiting 100% ACA conversion by 548 K. TiO₂ and ZrO₂ both reached 100% conversion by 498 K, and Al₂O₃ attained complete conversion by 523 K. The presence of 4 wt.% Cu on SiO₂ introduced ACA oxidation activity with 100% ACA removal achieved at 548 K.

The activity profile for CuO (Figure 1 b) indicated complete ACA conversion, which was achieved by 498 K. Comparing this profile with the neat and Cu-loaded TiO₂ profiles, it appears that the improved activity with the addition of Cu is predominantly an additive rather than a synergistic effect. This additive effect is also present for ZrO₂ and Al₂O₃, although it occurs at increasingly higher temperatures. The Cu may be responsible for the marginal increase in performance of CeO₂. However, the similarity of the neat and Cu-loaded activity profiles implies

that ACA conversion is dominated by the CeO₂ support. Although Cu promotes activity on SiO₂, the slower rate of increase in conversion with temperature, compared with the other metal oxides, suggests that the activity imparted by the Cu is tempered by the support in this case.

The corresponding CO₂ production profiles for both the neat and Cu-loaded metal oxides (Figures 1 c and 1 d, respectively) indicate a stoichiometric relationship between ACA consumed and CO₂ produced, demonstrating complete oxidation of ACA and its intermediates, according to Equation (1).



The onset of catalytic activity for the Cu-loaded metal oxides, particularly TiO₂, ZrO₂, and Al₂O₃, resulted in temporarily greater-than-stoichiometric CO₂ production, which likely resulted from the oxidation of ACA previously chemisorbed on the catalyst surface at lower temperatures. This effect was not observed for the neat metal oxide catalysts.

Acetaldehyde Adsorption

Figure 2 depicts the FTIR spectra of the neat and Cu-loaded metal oxides. The spectra of CeO₂, TiO₂, ZrO₂ and Al₂O₃ (Figure 2 a) are dominated by the endemic vibrations of each sup-

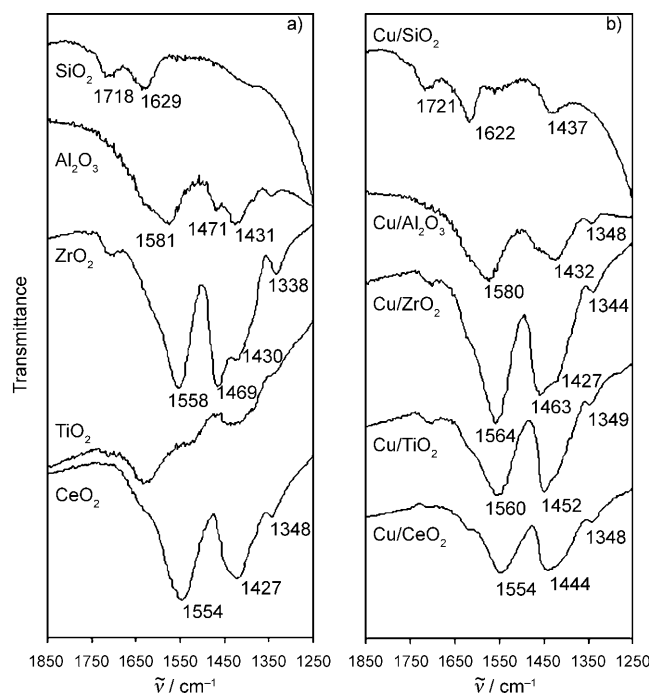


Figure 2. FTIR spectra of a) MO_x and b) 4 wt.% Cu/MO_x following exposure to 200 ppm ACA at 298 K.

port (see the Supporting Information, Figure S1). Signals most likely due to carbonate-like species are also observed. Exposure to acetaldehyde vapor at 298 K resulted in several additional signals that can be variously ascribed to adsorbed ACA and compounds resulting from its reaction on the surface. SiO₂ and

its corresponding 4 wt.% Cu-based catalyst displayed unique ACA adsorption behavior and will be discussed separately.

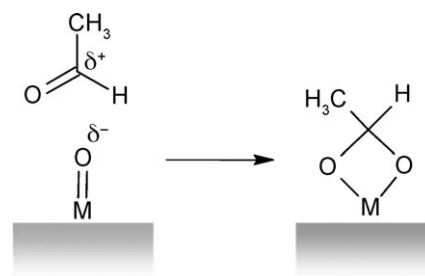
Over CeO_2 , TiO_2 , ZrO_2 , and Al_2O_3 , weak features in the range of $1725\text{--}1700\text{ cm}^{-1}$ correspond to the $\tilde{\nu}(\text{C=O})$ mode of adsorbed aldehyde.^[17] The new bands at $1600\text{--}1550\text{ cm}^{-1}$ ($\tilde{\nu}_{\text{as}}(\text{OCO})$)^[18] and $1460\text{--}1400\text{ cm}^{-1}$ ($\tilde{\nu}_{\text{s}}(\text{OCO})$)^[19] suggest that the acetaldehyde is spontaneously oxidized to an acetate group,^[20] a reaction that has been previously reported on several oxides and catalyst formulations.^[21,22] Weaker acetate signals were observed over Al_2O_3 , which may indicate a lower level of surface reactivity. Closer inspection of the spectra of CeO_2 , TiO_2 and ZrO_2 reveals the major signals of acetate species are flanked by an additional feature at about 1380 cm^{-1} . This signal suggests that a fraction of the adsorbed ACA may have also undergone a support-catalyzed aldol condensation to crotonaldehyde.^[17] As this product could have also been spontaneously oxidized to crotonic acid by interaction with the metal oxide, the signals associated with the stretching frequencies of O--C--O groups may contain more general information on the presence of adsorbed C_2+ -carboxylate species. Distinguishing between acetate groups and other carboxylate species is difficult.

Assuming that acetates represent the majority of the carboxylate species present on CeO_2 , TiO_2 , ZrO_2 , and Al_2O_3 (Figure 2a), the series of overlapping peaks in the symmetric stretch region ($1470\text{--}1400\text{ cm}^{-1}$) indicate a mixture of acetate binding configurations. By comparing the frequency difference between $\tilde{\nu}_{\text{as}}(\text{OCO})$ and $\tilde{\nu}_{\text{s}}(\text{OCO})$ maxima in this range to that of NaOAc ($\Delta\tilde{\nu}=164\text{ cm}^{-1}$), it can be inferred that acetates exist predominantly in a bidentate-type configuration^[23,24].

Although the adsorption of acetaldehyde onto the catalyst surface is dependent on the nature of the supporting oxide, in all cases, discernable spectral differences were observed following the addition of Cu (Figure 2b). For TiO_2 , the spectral features of adsorbed acetate species intensified following Cu addition. In the case of Cu/CeO_2 , acetate species in different geometries formed as indicated by the preferential growth of the signal at 1444 cm^{-1} . The general intensification relative to the bare oxides may indicate that a higher proportion of the adsorbed ACA is oxidatively adsorbed. Interestingly, the crotonaldehyde feature detected at 1380 cm^{-1} over the bare supports, was absent over all materials following Cu addition (Figure 2b), which raises the possibility that Cu ions or CuO clusters somehow prevent or retard the aldolization process at 298 K . Little or no changes were recorded in the spectra of pure and 4 wt.% $\text{Cu/Al}_2\text{O}_3$.

As mentioned earlier, SiO_2 and Cu/SiO_2 have distinctly different behaviors and did not appear to perform partial ACA oxidation following room temperature exposure. Weak signals that are possibly due to $\tilde{\nu}(\text{C=O})$ and $\delta_{\text{as}}(\text{CH}_3)$, along with a lack of detectable bands from carboxylate groups, are congruent with the limited physisorption of ACA, though this region is also likely to contain contributions from hydroxy groups. In Cu/SiO_2 , a red shift of 22 cm^{-1} in the OH stretch region (not shown) may indicate the formation of hydrogen bonds between the lone pair electrons of the carbonyl oxygen and adjacent surface silanol groups.^[25]

Adoption of the bidentate configuration requires the partial oxidation of ACA^[21] (Scheme 1). This process occurs by reaction with either O_2 from the air supply or oxygen species from the



Scheme 1. Mechanism of ACA adsorption on a metal oxide surface giving a bidentate configuration.

support surface. The lack of acetate formation by SiO_2 and Cu/SiO_2 indicates that the presence of gaseous oxygen alone is insufficient for acetate formation and oxygen from the substrate surface must participate in the oxidative adsorption reaction. During ACA adsorption, no H_2 was detected, which suggests that the H remains on the surface as part of the acetate complex.

The low-temperature conversion of ACA to acetate can be explained by relating the electronic distribution of the ACA molecule, or more specifically that of its C=O bond, to the relative surface basicity of the different metal oxides. In ACA, the electronegativity of O relative to C results in a withdrawal of electron density from the C nucleus, creating an electrophilic site which is potentially susceptible to attack from nucleophiles, such as coordinately unsaturated surface oxygen^[26] (Scheme 1).

The Lewis acidity of each metal oxide will dictate whether sufficient electron density is available for the partial oxidation of ACA to acetate to occur. Auroux et al.^[27] reported that acidic oxides displayed comparatively more covalent bond-like character at the catalyst surface, whereas basic oxides were more ionic. Prior measurements^[28,29] suggested that the surface basicity decreases in the order $\text{CeO}_2 > \text{TiO}_2 > \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$, which is identical to the order detected for catalytic activity (Figure 1). From these findings it is proposed that, during adsorption, basic oxides such as CeO_2 present electron-rich oxygen groups at the surface which readily donate electron density to ACA, allowing for its conversion to acetate. Amphoteric supports, such as TiO_2 , ZrO_2 , and Al_2O_3 , appear capable of promoting this reaction. This process also favors formation of enol species and therefore condensation reactions, producing undesired products, such as crotonaldehyde.

The comparative covalency of SiO_2 surface bonding results in a higher degree of Lewis acidity, eliminating the potential for nucleophilic attack and endorsing physisorption as the exclusive mode of adsorption. The reversible nature of this adsorption mechanism partially explains the low levels of catalytic activity for SiO_2 -based samples, as it implies that ACA is more likely to desorb intact from the surface at lower tempera-

tures. This also suggests that any oxidation reactions which can occur must do so purely at the CuO sites,^[30] with the overall reaction rate being significantly lower than over the materials in which support cations can also participate.

Comparing these results with the catalytic activity studies, it is apparent that the tendency of basic oxides (CeO₂, TiO₂, and ZrO₂) to convert ACA to acetate, along with the strength of the subsequent configuration with the surface, is the underlying basis for the activity series for both bare oxides and 4 wt.% Cu catalysts.

Temperature Programmed Oxygen Desorption (O₂-TPD)

O₂-TPD was conducted over each of the bare and Cu-containing metal oxides (SiO₂, Al₂O₃, ZrO₂, TiO₂, CeO₂) to identify the different states of O species and their quantities. The bare metal oxides display no significant O₂ desorption, even up to 1273 K (Figure 3). However, the addition of Cu dramatically enhances O desorption, in particular O at high temperature related to the lattice oxygen, β -(O). Surface chemisorbed oxygen, α -(O), generally desorbs at a lower temperature than β -(O).

The type of metal oxide support influences the desorption temperature range of β -(O). In this study, the β -(O) tempera-

ture ranges for Cu/SiO₂ (700–1100 K), Cu/Al₂O₃ (800–1273 K), Cu/ZrO₂ (950–1273 K), Cu/TiO₂ (920–1130 K), and CeO₂ (920–1200 K) generally agree with the reported values for lattice oxygen desorption.^[12,31–33] With the exception of Cu/TiO₂, the amount of surface chemisorbed O₂ was low (< 10%) compared with the lattice oxygen. α -(O) constitutes 21% of the total desorbed O₂ for Cu/TiO₂.

It is well established that doping foreign cations in metal oxides lowers the energy for lattice oxygen release.^[34] In particular, the coprecipitation of Cu and the metal oxide phase during flame synthesis should engender some degree of homogeneous mixing and solid-state miscibility, beyond which the CuO phase is enriched and surface-dispersed on the metal oxide supports. In the instances of the two most active catalysts, Cu/CeO₂ and Cu/TiO₂, evidence of substitutional lattice doping (on top of the highly dispersed surface states) was supported from the enhanced bulk oxygen vacancies^[11] and phase transformation, respectively.^[13] Substitutional doping of Cu ions in lattice sites induces structural and valence defects, which in turn create oxygen vacancies and lower the surface energies. As a result, more lattice oxygen is accessible, as evident in Figure 3. The possibility also exists for provision of some of the oxygen by the dispersed CuO. However, as shown in the ensuing temperature-programmed ACA studies of TiO₂- and CeO₂-based catalysts, these lattice oxygen species are only available at elevated temperatures and are thus unlikely to be involved in the oxidation reaction at low temperatures (<573 K).

Temperature Programmed Acetaldehyde Desorption (ACA-TPD)

On the basis of the ACA oxidation results (Figure 1), four catalysts were selected for temperature-programmed desorption and surface oxidation studies to identify the influence of surface reactivity variations on the detected activities. The TiO₂-based catalysts were selected as an example of the additive activity effect upon Cu addition. CeO₂ and 4 wt.% Cu/CeO₂ were selected based on their superior activity levels compared with the other metal oxides.

TiO₂ and Cu/TiO₂

The desorption of saturated ACA from TiO₂ was accompanied by a mixture of other anaerobically decomposed fractions (Figure 4a), that is, H₂, CH₄, CO, CO₂, and H₂O as well as the C₃₊ fractions acetone, butane, and butadiene. In general, the desorption profile from TiO₂ can be divided into three desorption windows, 350–440, 440–800, and > 900 K. Desorption within the low-temperature window (350–440 K) can be attributed to the decomposition of adsorbed ACA. A relatively minor amount of CO₂ was liberated in this case, as well as a mixture of CO, CH₄, and H₂. Desorption of unreacted ACA was also detected in this temperature range, in agreement with the desorption of ACA over TiO₂/carbon molecular sieve fibers.^[35] Crotonaldehyde, which is formed by aldol-condensation during

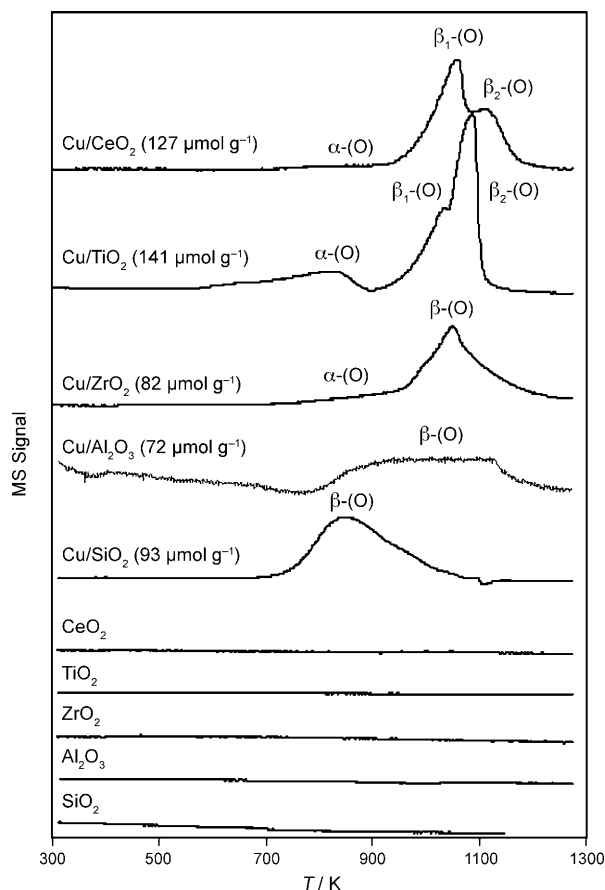


Figure 3. Temperature-programmed O₂ desorption profiles. Desorption performed under Ar atmosphere at temperature ramping rate of 15 K min⁻¹. Value in brackets indicates amount of O₂ desorbed. α -(O) corresponds to surface chemisorbed oxygen. β -(O) corresponds to lattice oxygen.

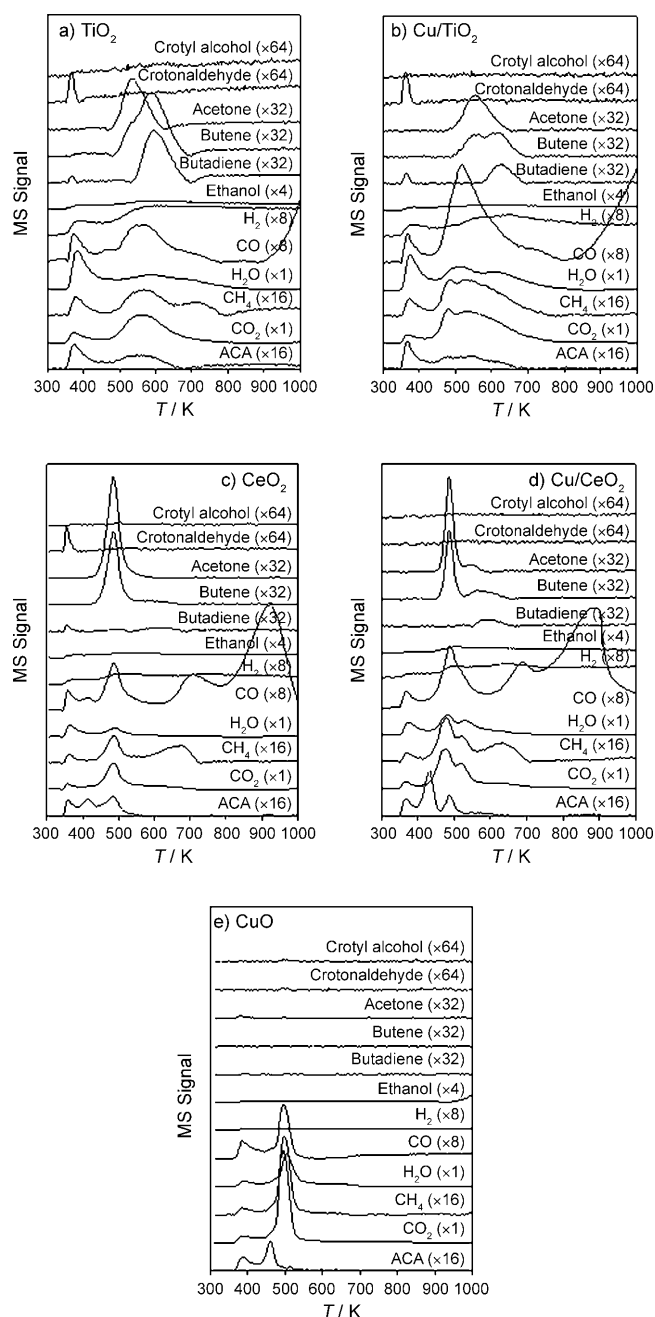


Figure 4. Temperature-programmed desorption spectra of ACA adsorbed on a) TiO_2 , b) Cu/TiO_2 , c) CeO_2 , d) Cu/CeO_2 , and e) CuO . Desorption performed under Ar atmosphere at temperature ramping rate of 15 K min^{-1} .

ACA adsorption, desorbed over this temperature range, in which a small amount of butadiene was also detected.

The mid-temperature desorption window (460–700 K) is associated with the decomposition of chemisorbed carboxylates through carbon–carbon bond cleavage, giving rise to further CO , CO_2 , CH_4 , and H_2 generation. Desorption of ACA, although in a lower amount than the low-temperature desorption, was evident and could originate from either the stronger surface-chemisorbed ACA or by the reforming of carboxylate species. Simultaneously, desorption of acetone, butane, and butadiene, which are formed by the coupling of ACA and/or carboxylates,

occurs at increasing peak temperatures of 520, 560, and 590 K, respectively. Compared with the desorption of saturated acetone for TiO_2 , which occurs at the lower temperature of 310 K,^[36] the comparatively high desorption temperature (Figure 4a) would suggest that acetone formed only during temperature ramping. Although it is difficult to distinguish the exact temperatures at which the coupling reactions (to form acetone, butane and butadiene) occur based purely on TPD, the desorption of these unsaturated C_{3+} species, along with the simultaneous desorption of H_2 , CO , CO_2 and CH_4 , suggests they were formed within this mid-temperature window.

Within the high temperature window ($> 900 \text{ K}$), continuous liberation of CO was detected. In this case, the powder sample was visibly blackened at the TPD conclusion (up to 1000 K), indicating that a large portion of carbon remained on the catalyst surface. Part of the carbon was oxidized to CO at above 900 K as a result of activation by TiO_2 lattice oxygen species.

In the presence of Cu (Figure 4b), a similar ACA-TPD spectra was observed as for neat TiO_2 , but with additional desorption peaks at 450–550 K for ACA as well as its decomposed fractions H_2 , CH_4 , CO , CO_2 , and H_2O . These additional peaks coincide with the TPD signals of bare CuO (Figure 4e), inferring that they are associated with desorption from the well-dispersed and supported CuO phase. This finding rules out a synergistic relationship between Cu and the TiO_2 support, which was also suggested by the activity investigations (Figure 1). It can be deduced by directly comparing the TPD spectra of H_2 , acetone, butane and butadiene on TiO_2 , Cu/TiO_2 , and CuO , that the C_{3+} species are formed only on the TiO_2 surface, with CuO hindering these coupling reactions. Quantitative measurements indicated that butadiene formation over CuO and Cu/TiO_2 was only 8% and 27% of that observed over TiO_2 , respectively (see the Supporting Information, Table S2). This is in further agreement with the decreased C_{3+} and increased CO intensities for Cu/TiO_2 compared with bare TiO_2 . The high CO intensity at the high temperature range is attributed to the more accessible TiO_2 lattice oxygen species as a result of Cu doping (Figure 3). The amount of ACA adsorbed on TiO_2 and Cu/TiO_2 is similar (Table 1), ruling out the possibility that the higher CO evolution is due to disparity in the initial adsorbed carbon content.

Table 1. Specific surface areas and ACA adsorption capacities of neat and Cu-loaded TiO_2 and CeO_2 .

Catalyst	Specific Surface Area [$\text{m}^2 \text{g}^{-1}$]	ACA Adsorption Capacity [$\mu\text{mol m}^{-2}$]
TiO_2	85	7.2
Cu/TiO_2	109	5.4
CeO_2	112	7.9
Cu/CeO_2	78	7.1

CeO_2 and Cu/CeO_2

Pre-adsorbed ACA was decomposed anaerobically on the bare CeO_2 surface to CO_2 , CO , and CH_4 within the low temperature window (Figure 4c), with approximately 25% less H_2 and H_2O

being liberated compared with TiO_2 (Figure 4a and the Supporting Information, Table S2). Crotonaldehyde, formed by aldolization of ACA, and a small amount of butadiene also desorbed at low temperatures. These chemisorbed species were most likely formed during the room temperature ACA adsorption as suggested by the earlier FTIR spectra (Figure 2). A distinct ACA desorption characteristic was observed for CeO_2 (three peaks at 375, 420, 490 K), which differed to that for TiO_2 . The first peak (375 K) originates from the desorption of unreacted ACA. On a prereduced CeO_2 surface, the desorption of unreacted ACA occurs at a marginally higher temperature (390 K), but is accompanied by a significant amount of ethanol production.^[19] This can be attributed to the more basic surface of reduced CeO_2 , whereas for the current pre-oxidized CeO_2 surface, only subtle ethanol desorption occurred with ACA desorption. The ACA desorption coincides with a significant level of CO and CO_2 desorption, which was absent in the case of reduced CeO_2 .^[19] Assignment of the second ACA desorption peak (420 K) is unclear and may be due to strongly adsorbed ACA.

The third ACA peak (490 K) evolves in the mid-temperature region along with the liberation of acetone and butene, as well as H_2 , CH_4 , CO, CO_2 , and H_2O . Unlike TiO_2 , the desorption of acetone and butane was better defined on CeO_2 as exemplified by the relatively sharp Gaussian peaks. Close inspection of the TPD spectra found small desorption peaks of acetone, butene, and butadiene at 560, 580, and 590 K, respectively. Further anaerobic decomposition of carboxylates and other recalcitrant hydrocarbons results in desorption of CH_4 , CO, and CO_2 up to 720 K. Beyond this temperature, the remaining carbon is oxidized by lattice oxygen in CeO_2 to form CO. In the process, Ce^{4+} is reduced to Ce^{3+} through a facile redox exchange.^[37,38] This change was visually evident at the conclusion of the TPD experiment in which the dark grey catalyst (Ce^{3+}) reverted to the original pale yellow pigment (Ce^{4+}) when exposed to air. No carbon remained on the CeO_2 surface as the oxidation was completed by 1000 K (Figure 4c).

In the case of Cu/CeO_2 , crotonaldehyde and butadiene desorption at low temperature (< 400 K) was absent (Figure 4d), corroborating the earlier FTIR results and indicating that the formation of these compounds was hindered during ACA adsorption at room temperature. The additional effect of CuO is clearly evident by the ACA desorption peak at 460 K, as well as the CH_4 , CO, CO_2 , and H_2O desorption maxima at 515 K. More interestingly, the secondary desorption amounts of acetone, butene, and butadiene over Cu/CeO_2 increased compared with bare CeO_2 , whereas these C_{3+} compounds were absent from the TPD over neat CuO samples (Figure 4e). This result suggests a higher extent of reductive coupling over the more reducible reaction sites of Cu/CeO_2 .^[11] The skewed high-temperature desorption of CO over Cu/CeO_2 towards a lower temperature is due to the more readily accessible lattice oxygen species. The CeO_2 lattice distortion induced by the Cu^{2+} presence lowers the energy for bulk oxygen release^[34] as was clearly demonstrated by the O_2 -TPD findings.

Temperature-Programmed Acetaldehyde Surface Reactions (TPSR)

To gather additional insight into the reactivity characteristics of the catalysts, samples presaturated with ACA were subject to temperature ramping under O_2/Ar . Unlike ACA-TPD, where only anaerobic desorption and reactions can be studied, in TPSR investigations, the aerobic characteristics of surface reactions can be monitored as a function of temperature.

TiO_2 and Cu/TiO_2

Low-temperature desorption (350–440 K) of ACA, CO, CO_2 , CH_4 , H_2O , butadiene, and crotonaldehyde, which was similarly detected during the anaerobic TPD studies on TiO_2 (Figure 4a), was present during TPSR (Figure 5a). The desorption profiles for these compounds are similar under both conditions, which indicate the low-temperature desorption is not associated with O_2 consumption. That is, desorption of these compounds in this temperature range is driven primarily by thermal effects and not catalyzed by O_2 -induced oxidation.

Within the mid-temperature window (440–800 K), stark contrasts between the TPSR and TPD profiles for TiO_2 are apparent. Within this temperature window, much of the surface adsorbed ACA and carboxylates (precursor to coupling reactions) are combusted during TPSR, resulting in significant amounts of CO, CO_2 , and H_2O being produced. This process is accompanied by a simultaneous consumption of O_2 whereas the liberation of CH_4 indicates that the thermal decomposition of acetates may be occurring to some extent, in parallel with the oxidative combustion. It is interesting to note that, despite the excess amount of O_2 provided during TPSR, the desorption of oxygenated fractions occurs across a temperature band similar to that observed for the TPD study. This further infers ACA oxidation is limited by the thermal decomposition of surface adsorbed species. No C_{3+} compounds were formed within the mid-temperature range, as the combustion/decomposition of ACA and carboxylates is more favorable under aerobic conditions.

As shown in Figure 5b, the TPSR characteristics of Cu/TiO_2 were similar to those of TiO_2 at low temperatures, comprising ACA, CO, CO_2 , CH_4 , H_2O , butadiene, and crotonaldehyde desorption. Conversely, a pronounced catalytic effect is distinctly evident at around 485 K. In this case, instead of the broad decomposition band seen during anaerobic TPD, rapid simultaneous desorption of ACA, CO, CO_2 , CH_4 , and H_2O occurred, as exemplified by the narrow desorption peaks. This can be readily likened to the TPSR profile of CuO (Figure 5e) and clearly demonstrates the additive catalytic effect of CuO on TiO_2 . Simultaneous consumption of O_2 reaffirms the catalytic combustion-type reaction, while CO liberation forms only a fraction of that detected over bare TiO_2 . The significantly higher CO_2 and O_2 signals that indicate oxidation on Cu/TiO_2 was accelerated by a factor of 200 by the presence of Cu. This process increased total CO_2 production by a factor of 3.4 and reduced CO production by a factor of 5 (see the Supporting Information, Table S3). Both the enhanced activity and autocatalytic

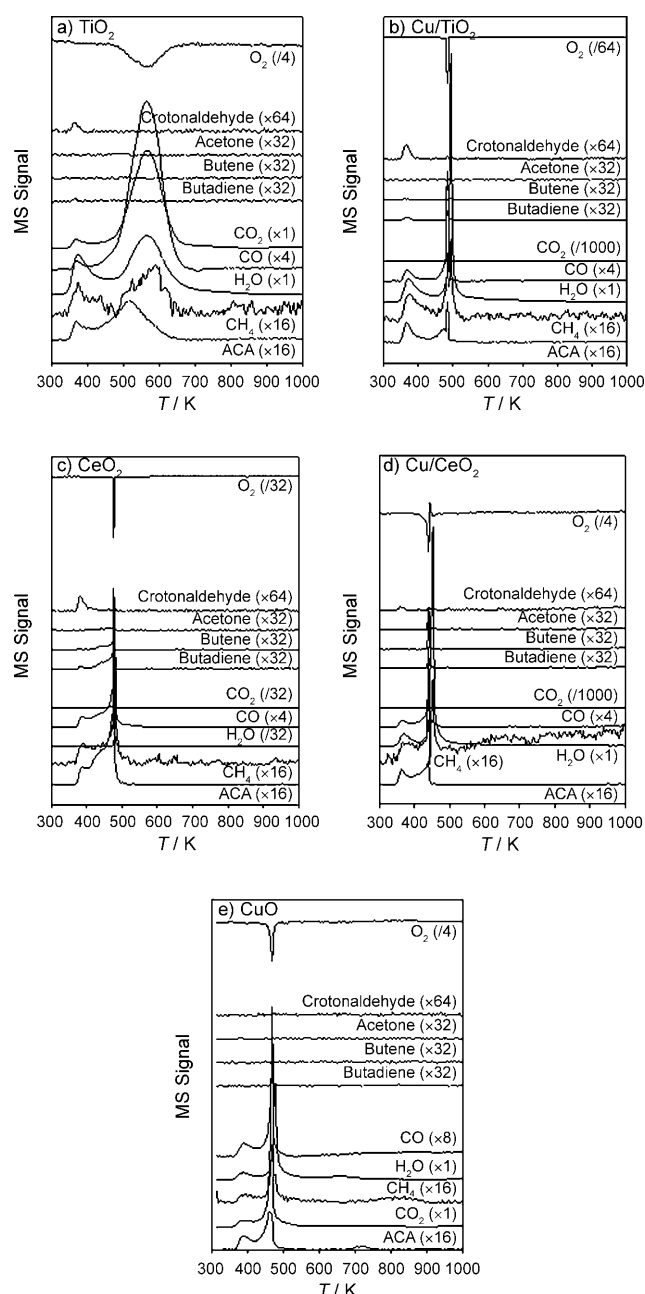


Figure 5. Temperature-programmed surface reaction spectra of ACA adsorbed on a) TiO_2 , b) Cu/TiO_2 , c) CeO_2 , d) Cu/CeO_2 and e) CuO . Desorption performed under 20 vol.% O_2/Ar at temperature ramping rate of 15 K min^{-1} .

oxidation temperature of Cu/TiO_2 agree strongly with the ACA oxidation assessment (Figure 1). The absence of desorption products at higher temperatures ($> 485 \text{ K}$) indicates complete oxidation of all surface adsorbed ACA and its derivative species.

CeO_2 and Cu/CeO_2

The TPSR of CeO_2 and Cu/CeO_2 are interesting as these two samples demonstrated the highest catalytic activity for ACA oxidation. Within the low temperature range, the bare CeO_2 TPSR profile (Figure 5c) is similar to the corresponding CeO_2

ACA-TPD. Initial desorption peaks of ACA, CH_4 , H_2O , CO , CO_2 , butadiene, butene, and crotonaldehyde are again detected between 370 and 400 K, with their origin discussed in the earlier CeO_2 TPD findings. The secondary TPD desorption peak of ACA ($\sim 420 \text{ K}$) is still apparent for the TPSR profile; however, the third ACA TPD desorption peak ($\sim 490 \text{ K}$), along with the corresponding desorption peaks for CH_4 , H_2O , CO , and CO_2 , are swamped by the autocatalytic oxidation at $\sim 480 \text{ K}$. The autocatalytic oxidation temperature agrees well with the steady-state reaction (Figure 1), and is 25 K lower than the autocatalytic temperature of CuO . It is unlikely that the rapid oxidation on CeO_2 is catalyzed by the release of the lattice oxygen, which would otherwise be evident at the same temperature or lower, under the more reducing condition of ACA-TPD. From the ACA-TPD studies, it was only at high temperatures ($> 700 \text{ K}$) that the release of lattice oxygen was evident. On the other hand, the autocatalytic oxidation activity of CeO_2 may originate from the high oxygen mobility on CeO_2 , which is in turn related to its surface basicity as well as the oxygen vacancies.^[28] These effects, coupled with the high affinity for surface acetate formation, offer a possible explanation for the high intrinsic catalytic effect demonstrated by neat CeO_2 in the mid-temperature range.

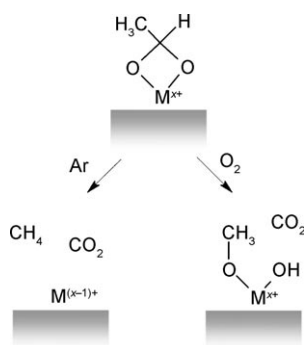
The autocatalytic oxidation profile of Cu/CeO_2 (Figure 5d) is similar to that of the bare CeO_2 . It appears that the catalytic effect of Cu is overwhelmed by the more active intrinsic catalytic effect of CeO_2 . This effect is illustrated by the autocatalytic oxidation temperature of both CeO_2 and Cu/CeO_2 occurring at $\sim 460 \text{ K}$, while the effect of Cu takes place at $\sim 485 \text{ K}$. Cu/CeO_2 produced approximately 30% more CO_2 and 20% less CO , relative to pure CeO_2 (see the Supporting Information, Table S3). These TPSR profiles are in excellent agreement with the steady state ACA oxidation profiles (Figure 1), in which the activity trend decreases in the order of $\text{Cu/CeO}_2 \approx \text{CeO}_2 > \text{Cu/TiO}_2 > \text{TiO}_2$.

Acetaldehyde Oxidation Mechanism

Based on the bidentate acetate species detected by FTIR and the results of the ACA-TPD and TPSR studies, several key intermediates and structural parameters would appear to govern the ACA oxidation activity. Firstly, the ACA undergoes spontaneous oxidation to form surface-chemisorbed carboxylates (Figure 2; Scheme 2). The extent to which oxidation occurs appears to be governed by the basicity of the metal oxide.

At sufficiently high temperatures, the C–C bond within the acetate undergoes cleavage, generating a carbonate and a methyl radical ($\text{CH}_3\cdot$). Under anaerobic conditions (Figure 4), the carbonate will desorb from the surface as CO_2 and $\text{CH}_3\cdot$ may react with the allyl H to form CH_4 as observed over all materials during TPD.

Conversely, if acetate formation occurs under an aerobic environment (Figure 5), CH_4 evolution from the surface is significantly curtailed. Following CO_2 desorption, oxygen vacancies in metal oxides will tend to localize electrons to form negatively charged F-centers^[39] that, in the presence of O_2 , will encourage the formation of O_2^- , especially at the basic sites.^[40]



Scheme 2. Mechanism of ACA decomposition and oxidation.

At elevated temperatures, these O_2^- species could then undergo rapid dissociation to restore the original oxidation state of the surface cations. The monoatomic oxygen species generated in this process may react with the allyl H, allowing for the evolution of surface hydroxy groups and H_2O .

Reoxidation of the support would also encourage reaction of the $\text{CH}_3\cdot$ radical from the decomposing acetate with surface oxygen to form a metal-methoxy species. Such species have been shown to be the dominant intermediate in the low-temperature total oxidation of CH_4 and their formation was favored over supports such as CeO_2 which could readily undergo the necessary surface reductive reaction.^[39]

The heightened reducibility of the bare metal oxides following the addition of Cu,^[41,42] would provide a higher concentration of sites for the formation of methoxy groups. These methoxy groups are then likely to undergo a series of oxidations to form formic acid, which can then decompose to CO_2 and H_2O . The TPSR results support the notion that total oxidation of $\text{CH}_3\cdot$ groups occurs in the presence of O_2 following the decomposition of the parent acetate, with the apparent rapidity of this event effectively discounting it as a possible rate determining step in the overall oxidation.

Conclusions

Bare metal oxides and 4 wt.% Cu catalysts were prepared and tested for acetaldehyde oxidation to elucidate the role of support and the effect of copper on the overall reaction mechanism. ACA conversion by neat metal oxides decreased in the order $\text{CeO}_2 > \text{TiO}_2 \approx \text{ZrO}_2 \gg \text{Al}_2\text{O}_3 > \text{SiO}_2$. The addition of 4 wt.% Cu markedly improved the activity of all the metal oxides, apart from CeO_2 , with its influence appearing to be additive rather than synergetic. For CeO_2 , the high activity of the original neat material beset any benefits imparted by the Cu.

During the adsorption stage of reaction, the basicity of several oxides (CeO_2 , TiO_2 , ZrO_2) was sufficient to induce the conversion of ACA to surface-chemisorbed bidentate and bridging acetates. Over more acidic supports (Al_2O_3 , SiO_2) the absence of this mechanism resulted in negligible catalytic activity. ACA-TPD studies and ACA-TPSR findings correlated well with the catalytic activities observed under reaction conditions and indicated that high surface oxygen availability was critical to the oxidation process. Based on this work, it is concluded that the

ACA oxidation activity of these materials is determined by two main factors: the basicity of the metal oxide support (and its subsequent ability to convert ACA to carboxylates) and the availability of surface oxygen during acetate decomposition. It is proposed that a high concentration of reducible sites, either by Cu addition or naturally occurring on CeO_2 , accelerates the activation and provision of oxygen and also potentially provides sites for the stabilization of methoxy intermediates resulting from the acetate decomposition.

Experimental Section

Catalyst Synthesis and Characterization

Bare and Cu-loaded CeO_2 , TiO_2 , ZrO_2 , Al_2O_3 ,^[11–14] and SiO_2 catalysts were prepared by one-step flame spray pyrolysis (FSP).^[43,44] Metal-organic-based precursors, consisting of 0.5 M cerium 2-ethylhexanoate (Strem, 49% in 2-ethylhexanoic acid), titanium tetraisopropoxide (Aldrich, 97% in propanol), zirconium propoxide (Aldrich, 70% in propanol), aluminum *sec*-butoxide (Strem, 98%) or tetraethyl orthosilicate (98%) and a predetermined amount of Cu 2-ethylhexanoate (Aldrich, >99.9%) in xylene (Riedel de Haen, 96%) were delivered at 5 mL min^{-1} using a syringe pump (Inotech R232). At the nozzle tip, the liquid precursor was dispersed with O_2 (5 L min^{-1} , 1.5 bar) forming fine spray droplets. The spray was ignited by a surrounding premixed CH_4/O_2 ($1.5 \text{ L min}^{-1}/3.2 \text{ L min}^{-1}$) supporting flame. A sintered metal plate ring provided an additional 5 L min^{-1} of sheath O_2 . The product particles were collected on a glass fiber filter (Whatman GF/D) with the aid of a vacuum pump (SD series, Alcatel).

FTIR spectra were collected for fresh catalysts by using the KBr disk method on a Nicolet Avatar IR spectrometer. Prior to spectral collection, each sample was exposed to ACA (200 ppm, 30 mL min^{-1}) at 298 K. The specific surface areas of the prepared catalysts were analyzed by nitrogen adsorption at 77 K, using the BET isotherm measured on a Micromeritics Tristar 3000. ACA and O_2 temperature-programmed desorption (ACA-TPD and O_2 -TPD, respectively) and temperature-programmed surface reaction (TPSR) studies were conducted on a Micromeritics Autochem 2920. The catalyst (50 mg) was pretreated in oxygen at 598 K and then cooled to room temperature under flowing O_2/Ar (20 vol.%). During ACA-TPD and TPSR runs, ACA (500 ppm) in air was passed over the sample until saturation was reached. The sample was then purged under Ar to remove physisorbed ACA. The ACA adsorption step was not performed for the O_2 -TPD experiments. ACA-TPD and O_2 -TPD experiments were conducted in Ar while TPSR experiments were conducted in O_2/Ar (20 vol.%). The temperature ramping rate for all the experiments was 15 K min^{-1} to a maximum temperature of 1023 K. Desorption products were monitored by a Balzers Quadrupole mass spectrometer with a sampling interval of 15 s. Fragmentation spectra of pure compounds were collected to determine the relative intensities of different peaks.

Catalytic Activity Testing

Reaction studies were conducted in a glass U-tube reactor heated in a Shimadzu GC-8A oven. The reactor bed contained the catalyst (50 mg) between two quartz wool plugs. The gas stream was simultaneously analyzed by FID (Shimadzu) and CO_2 (Canary Company) detectors. Prior to the reaction, the catalyst bed was exposed to ACA in air (60 mL min^{-1} , 200 ppm) at 448 K. This temperature was selected as it was found to be the lowest temperature at

which all studied materials displayed negligible catalytic oxidation. Each sample was held at 448 K until the ACA concentration exiting the reactor was 200 ppm, indicating complete saturation. The temperature was then raised in 25 K increments at 30 min intervals over the range of 448 K < T < 548 K, and ACA and CO₂ concentrations were monitored. Thirty minutes was found to be suitable for the system to attain equilibrium at each temperature step. As a control, a reactor tube filled with quartz wool displayed less than 1% ACA conversion at temperatures less than 598 K, confirming the absence of homogeneous oxidation.

Keywords: aldehydes • copper • heterogeneous catalysis • surface chemistry • temperature-programmed desorption

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Received: April 16, 2009

Revised: June 3, 2009

Published online on August 24, 2009