# Photoactivation of CO in Ti Silicalite Molecular Sieve

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Irradiation at 266 nm of Ti silicalite (TS-1) molecular sieve loaded with CO and $CH_3OH$ gas at 173 K gave methyl formate as the main product. The photoreaction was monitored in situ by FT-IR spectroscopy and was attributed to reduction of CO at LMCT-excited framework Ti centers under concurrent oxidation of methanol. Infrared product analysis based on experiments with $C^{18}O$, $^{13}CO$, and $^{13}CH_3OH$ revealed that carbon monoxide is incorporated into the ester as a carbonyl moiety. It is proposed that CO is photoreduced by transient $Ti^{3+}$ to HCO radical in the primary redox step. This finding opens up the possibility for synthetic chemistry of carbon monoxide in transition metal materials by photoactivation of framework metal centers.

## I. Introduction

The constrained environment of microporous solids, combined with the unique properties of framework transition metals as robust chromophores and redox centers, offers a new approach for accomplishing demanding photosynthetic transformations. A most interesting case is the photoreduction of $CO_2$ in Ti silicate sieves reported recently by Anpo.[1,2] In situ FT-infrared spectroscopy of the photoreduction of $CO_2$ by the excited Ti−O ligand-to-metal charge-transfer (LMCT) state of titanium silicalite sieve (TS-1) using methanol as the electron donor allowed us to detect the two-electron reduction product.[3] To explore further the photoredox properties of this prototypical framework LMCT center, we have attempted the photoactivation of CO using $CH_3OH$ as the donor. Carbon monoxide has a much higher electron affinity than $CO_2$, and hence, it is expected to be activated at excited Ti centers by acting as an acceptor. Beyond its role as a probe molecule for determining the reactivity of excited framework metal atoms, activation of CO is of interest in its own right because of its commercially important role as a $C_1$ building block.[4,5] Elucidation of the interaction with excited Ti centers in TS-1 sieve might furnish important insights for selecting new microporous materials and metals for CO activation at longer photolysis wavelengths.

In this paper, we report the UV-light-induced photoreaction of CO and $CH_3OH$ gas mixtures loaded into TS-1 sieve at 173 K. The low temperature was chosen so that sufficient concentrations of adsorbed CO could be achieved. The chemistry was monitored in situ by FT-infrared spectroscopy. TS-1 is a crystalline silicate with a two-dimensional channel structure (5.5 Å in diameter)[6] and 1−2% of the Si isomorphically substituted by Ti.

## II. Experimental Section

Titanium silicalite sieve with the MFI structure (TS-1) was synthesized according to the literature procedure.[7] The chemicals tetraethyl orthosilicate (98%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 20% in $H_2O$, Fluka), and tetrabutyl orthotitanate (Fluka) were used without further purification. Most gels had a molar composition of $SiO_2/TiO_2 = 50$, $H_2O/SiO_2 = 35$, and $TPAOH/SiO_2 = 0.46$. Gels with composition $SiO_2/TiO_2 = 200$ and 100 were also prepared. Typically, gel preparation involved hydrolysis of 7.5 mL of tetraethyl orthosilicate and 0.24 mL of tetrabutyl orthotitanate in a solution containing 15 mg of tetrapropylammonium hydroxide as an organic template. The gel was kept at 343 K for 2 h under stirring. Water was added periodically to compensate for evaporation. The final gel was crystallized in a 50-mL Teflon-lined autoclave at 443 K for 48 h. The product was mixed with 0.5 M aqueous ammonium acetate solution and separated from the mother liquor by vacuum filtration. The material was washed repeatedly with distilled water, dried at 293 K for 4 h, and calcined at 723 K for 10 h in airflow.

Powder XRD patterns were recorded on a model Siemens D5000 diffractometer using Cu Kα ($\lambda = 1.5406$ Å) radiation. Data for the calcined samples were collected in the range $10° < 2\Theta < 50°$ at steps of 0.02° and a sampling time of 2 s. They agreed completely with literature XRD data for MFI structures.[8] Chemical analysis by ICP-AES indicated TS-1 samples with Ti contents of 1.4, 2.5, 3.8, and 5.7%. The samples were prepared by solubilization in HCl/HF solution.[9,10] The result of UV−vis diffuse reflectance measurements of calcined TS-1 (1.4% Ti) in ambient air is displayed in Figure 1. These data were recorded on a Shimadzu model UV-2100 spectrometer equipped with an integrating sphere (model ISR-260). For these measurements, the sample was prepared in the form of a pressed wafer, and $BaSO_4$ powder used as the reference. [The spectrum is presented as $1 - R$ ($R$ = reflectance) rather than as the Kubelka−Munk function because, in the case of pressed wafers of microporous crytallites, a substantial fraction (about 25%) of the light exits the rear of the pellet.[11] Hence, the physical assumptions of the Kubelka−Munk theory are not fulfilled (no light exiting the sample except from the front)].[12] The spectrum agrees with those of TS-1 materials reported in the literature[13−16] and is assigned to the LMCT transition of tetrahedrally coordinated Ti (open and closed sites).[17,18] Specifically, there is no sign of extraframework Ti-containing species, which give rise to absorption at wavelengths longer than 330 nm.[14,15] This indicates that, judging from the UV data, this TS-1 sample is a pure Ti framework-substituted material.

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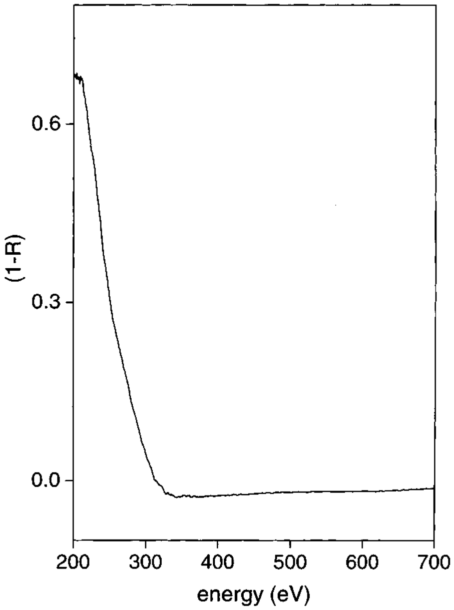


**Figure 1.** UV−vis reflectance spectrum of TS-1 calcined at 823 K. R = reflectance, $BaSO_4$ as the reference.

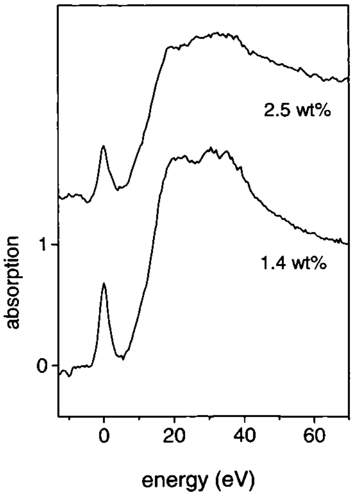


**Figure 2.** Ti K-edge XANES spectra of TS-1. Absorption scale is normalized to the plateau between the K-edge and the onset of the extended region.

XANES spectra at the Ti K-edge were recorded at beamline 9.3.1 of the Advanced Light Source at LBNL. The beamline is equipped with a Si(111) double-crystal monchromator, and the ring ran at 1.9 GeV with beam current in the range of 200−400 mA. Measurements were conducted in transmission mode using a Si photodiode detector (Hamamatsu model S2744-08). For energy calibration, a 5$\mu$ Ti foil was used and the beam intensity was monitored by the current generated at an Al foil. TS-1 samples were used in the form of pressed wafers (50 mg) and mounted on an OFC holder that can simultaneously hold 12 samples. The holder was mounted on a liquid $N_2$ dewar equipped with a programmable heater, and the entire assembly was inserted into the high vacuum end station ($2 \times 10^{-7}$ Torr). The temperature of the wafers can be varied between 77 and 700 K. XANES spectra of the dehydrated wafers (250 °C overnight) were recorded at room temperature at sampling intervals of 0.5 eV and a recording time of 3 s per data point. Figure 2 shows spectra of TS-1 (1.4% Ti) and TS-1 (2.5% Ti). The preedge peak at 4968 eV (taken as the origin of the scale in Figure 2) is assigned to the $A_1$−$T_2$ absorption of Ti centers in the tetrahedral substitutional sites of the silicalite framework. The intensity of this sharp band is known to be sensitive to the degree of Ti substitution in tetrahedral framework sites.[16,19,20] The peak height relative to the height of the plateau between the K-edge and the onset of the EXAFS region[21] is 0.69 compared to 0.75 for TS-1 material reported by Bordiga et al.[19] The slightly lower height is expected in view of the lower energy resolution of our experiment (0.5 eV steps compared to 0.2 eV intervals for the literature spectrum).[19] Hence, although not furnishing sufficient evidence for complete framework substitution on its own, the XANES result is consistent with that of pure TS-1 samples reported in the literature.

The FT-IR instrumentation, vacuum equipment, and experimental details of photolysis experiments were similar to those described previously.[22] Briefly, TS-1 powder was pressed into 10 mg of self-supporting wafers with 12-mm diameters. These wafers were dehydrated at 473 K under high vacuum for 10 h inside a miniature stainless steel cell equipped with $CaF_2$ windows. The cell was mounted in a temperature-programmable Oxford cryostat (model DN1714). Methanol (4 Torr) was loaded into the TS-1 pellet from the gas phase at room temperature. Carbon monoxide (220 Torr) was added, and the temperature of the pellet was lowered to 173 K in order to increase the loading of CO. After 2 h was allowed for equilibration of the gases, a FT-infrared spectrum was recorded with a Bruker model IFS88 spectrometer. Photolysis was conducted with the 266-nm emission of a Coherent Nd:YAG laser (model Infinity) or a Quanta-Ray Nd:YAG laser (model DCR-2A, GCR-3 upgrade). The beam intensity was typically 10 mJ pulse$^{-1}$ at a repetition rate of 10 Hz. Spectra were taken at 1 cm$^{-1}$ resolution. The photochemical results were the same for experiments with TS-1(1.4%) and TS-1(2.5%).

Methanol (99.8%, EM Science) and methyl formate (99%, Aldrich) were purified by trap-to-trap distillation before use. Methanol-$^{13}$C (99% $^{13}$C, Aldrich), methanol-$D_4$ (99% D, Aldrich), carbon monoxide (99.99%, Matheson), carbon monoxide-$^{13}$C (99% $^{13}$C, ISOTEC), and carbon monoxide-$^{18}$O (95% $^{18}$O, ISOTEC) were used as received.

## III. Results

When 5 Torr of methanol gas was loaded into the dehydrated TS-1 sieve at 295 K and the temperature was then lowered to 173 K, infrared absorptions were observed at 1350, 1450, 1463, 1471, 2840, 2950, 3350 (broad), and 3632 cm$^{-1}$ (Figure 3). The last two mentioned bands are assigned to $\nu$(OH) of $CH_3OH$ with a free OH group (3632 cm$^{-1}$) or H-bonded to the pore surface (3350 cm$^{-1}$). Subsequent adsorption of CO gas (between 200 and 600 Torr) did not influence the $CH_3OH$ absorptions or induce reaction. The low matrix temperature assured a sufficient concentration of CO, which adsorbs poorly at room temperature. Irradiation of the matrix with 266-nm light at 200 mW cm$^{-2}$ led to depletion of the reactants with concurrent growth of the signals at 1371, 1435, 1455, 1466, 1684, 1718, 1734, 2870, 2900, and 2956 cm$^{-1}$. An infrared difference spectrum taken after 3.5 h of photolysis is shown in Figure 4. In the absence of CO, irradiation of a $CH_3OH$-loaded TS-1 pellet gave only small growth in the signals at 1734 and 1718 cm$^{-1}$. It was limited to the initial 30−60-min irradiation period and represented less than 10% of the yield in the presence of CO. No photoreaction was observed in S-1 sieve (neat silicalite), confirming that the chemistry is initiated by excited Ti centers. All bands (except for those at 1466 and 2900 cm$^{-1}$ and a small nonreproducible peak at 1757 cm$^{-1}$) agree with the infrared spectrum of an

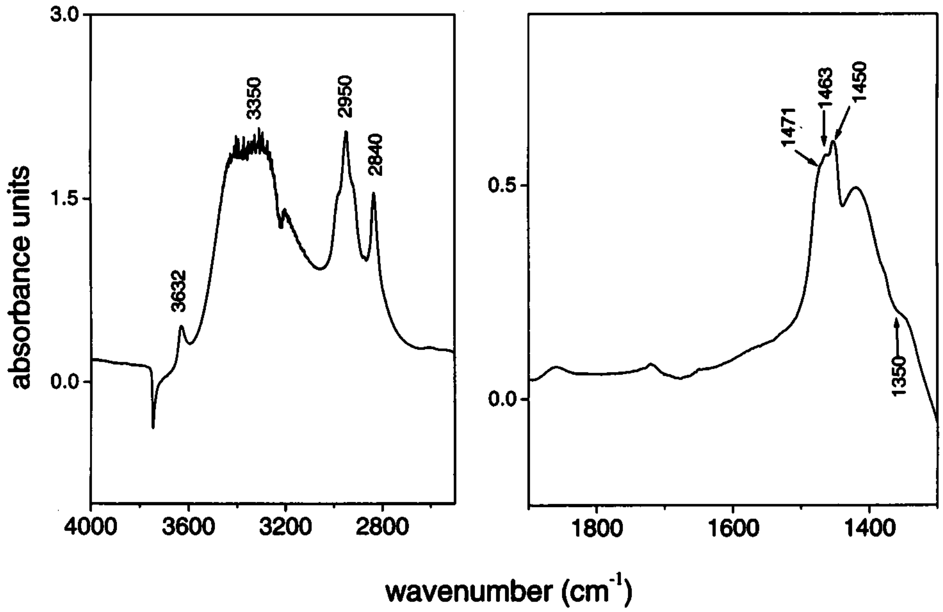


**Figure 3.** Infrared difference spectrum of TS-1 loaded with 4 Torr of $CH_3OH$ and 221 Torr of CO at 173 K.

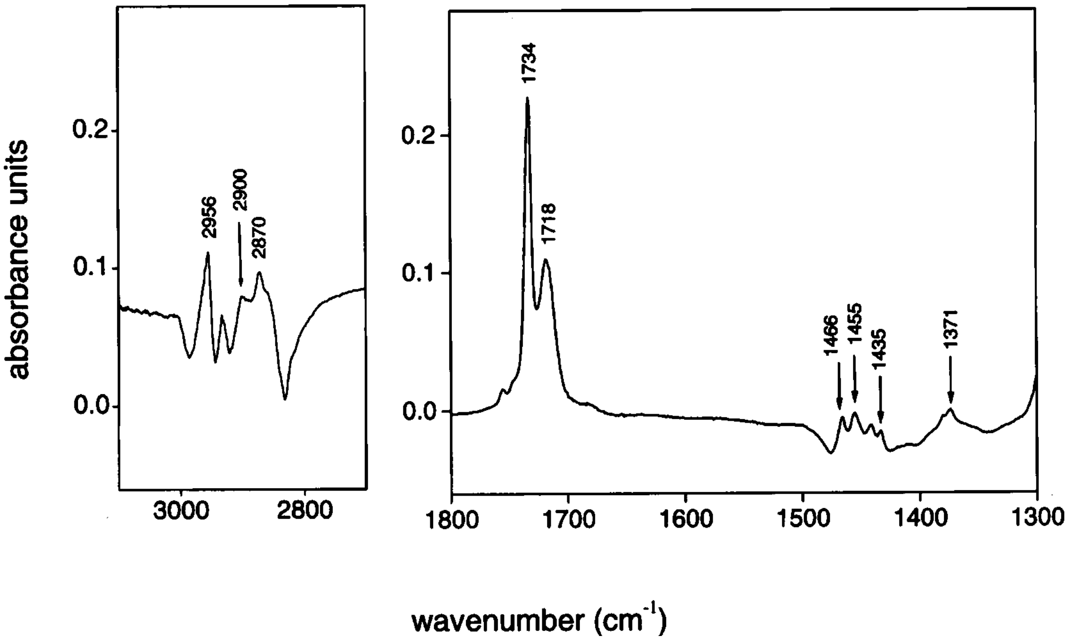


**Figure 4.** Infrared difference spectrum after 266-nm irradiation at 200 mW cm$^{-2}$ for 3.5 h.

authentic sample of $HCO_2CH_3$ in TS-1 at 173 K and with the spectrum in solid Ar reported in the literature.[23] Spectral overlap with methanol absorptions explain shifts of up to 10 cm$^{-1}$ in the CH stretching region. When the CO + $CH_3OH$ photoreaction is conducted at room temperature, only one C=O stretch band is observed at 1734 cm$^{-1}$. This indicates that the 1718 (strong) and 1684 (very weak) cm$^{-1}$ absorptions are methyl formate sites in TS-1 sieve formed at low temperature. For a given matrix temperature, the relative intensities of the 1734 and 1718 cm$^{-1}$ bands varied by as much as 50% from experiment to experiment.

Yet-unassigned bands at 1466 and 2900 cm$^{-1}$ signal the presence of an additional product. The frequencies indicate that these absorptions originate from CH modes. Because there is no unassigned product band in the 1700 cm$^{-1}$ region, the molecule does not feature a C=O group. In light of the proposed intermediacy of formaldehyde upon $CH_3OH$ oxidation (see below), a likely candidate is the hemiacetal $CH_3OCH_2OH$ formed by addition of $CH_2$=O to $CH_3OH$.

$$CH_2{=}O + CH_3OH \rightarrow CH_3OCH_2OH \tag{1}$$

Indeed, when 0.5 Torr $CH_2$=O gas was adsorbed into TS-1 sieve loaded with 0.5 Torr $CH_3OH$ at 220 K, the formaldehyde was spontaneously consumed under concurrent product growth of the signals at 1466, 1454, and 1411 cm$^{-1}$, as shown in Figure 5. Vibrational analysis based on partial deuteration[24] allowed us to assign the spectrum to $CH_3OCH_2OH$. These bands, superimposed on the $HCO_2CH_3$ product spectrum and the decreasing $CH_3OH$ spectrum, fully account for peaks and intensities of the photolysis difference spectrum shown in Figure 4.

Photolysis experiments with $^{13}CO$, $C^{18}O$, and $^{13}CH_3OH$ were conducted to determine the fate of each reactant. Isotopic frequency shifts are most pronounced and easiest to interpret in the C=O stretching region, and the results are presented in Figure 6 and Table 1. When the photoreaction is conducted with $C^{18}O$, two new peaks appeared at 1702 and 1685 cm$^{-1}$ (trace

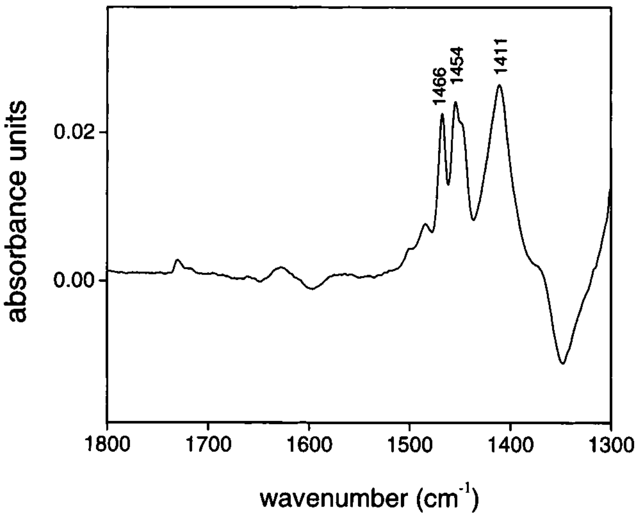


**Figure 5.** Infrared difference spectrum taken immediately after adsorption of 0.5 Torr of $CH_2{=}O$ gas into TS-1 sieve loaded with 0.4 Torr of $CH_3OH$ at 220 K. Bands at 1729 and 1501 $cm^{-1}$ are due to as-yet-unreacted formaldehyde.

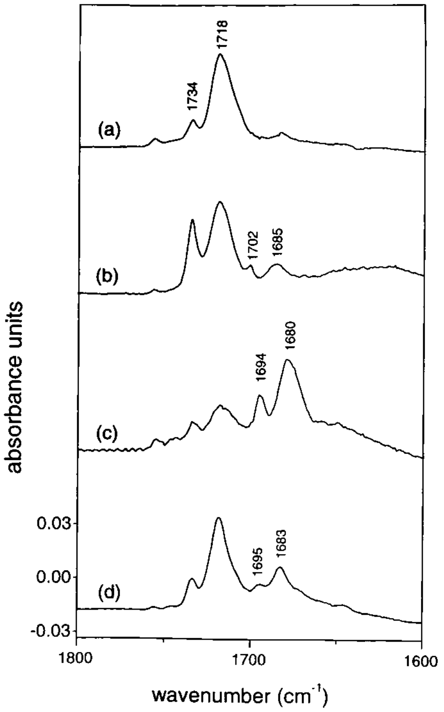


**Figure 6.** Photoinduced reaction of carbon monoxide and methanol in TS-1 at 173 K. Shown are the infrared difference spectra upon 266-nm irradiation for 2 h at 100 mW $cm^{-2}$ of (a) CO + $CH_3OH$, (b) $C^{18}O$ + $CH_3OH$, (c) CO + $^{13}CH_3OH$, (d)$^{13}CO$ + $CH_3OH$.

**TABLE 1: Isotopic Frequency Shifts of C═O Stretching Modes of Methylformate (in $cm^{-1}$)**

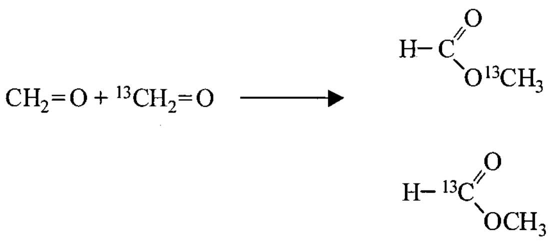
| frequency | | | | |
|---|---|---|---|---|
| $CH_3OH$ + CO | $C^{18}O$ + $CH_3OH$ | CO + $^{13}CH_3OH$ | $^{13}CO$ + $CH_3OH$ | species |
| | | 1680 | | $H^{13}COO^{13}CH_3$ |
| | | | 1683 | $H^{13}COOCH_3$ |
| | 1685 | | | $HC^{18}OOCH_3$ |
| | | 1694 | | $H^{13}COO^{13}CH_3$ |
| | | | 1695 | $H^{13}COOCH_3$ |
| | 1702 | | | $HC^{18}OOCH_3$ |
| | | 1717 | | $HCO_2{}^{13}CH_3$ |
| 1718 | 1718 | | 1718 | $HCO_2CH_3$ |
| | | 1732 | | $HCO_2{}^{13}CH_3$ |
| 1734 | 1734 | | 1734 | $HCO_2CH_3$ |

b) in addition to the 1734 and 1718 $cm^{-1}$ bands observed for the parent reaction (trace a). The $^{18}O$ shift of 33 $cm^{-1}$ of the 1734/1718 $cm^{-1}$ doublet is typical for a $\nu(C{=}O)$ mode. Hence, the 1702 and 1685 $cm^{-1}$ features are assigned to the $C{=}^{18}O$ mode of methyl formate. This implies that carbon monoxide is incorporated into the ester as a carbonyl group. When the photochemistry is conducted with parent CO and $^{13}CH_3OH$, bands at 1694 and 1680 $cm^{-1}$ appeared in addition to the absorptions at 1732 and 1717 $cm^{-1}$ (Figure 6, trace c). The 39 $cm^{-1}$ $^{13}C$ shift is again characteristic for the C═O group. Hence, the 1694/1680 $cm^{-1}$ doublet originates from $H^{13}C({=}O)OCH_3$ and/or $H^{13}C({=}O)O^{13}CH_3$. As a comparison with the $^{13}CO$ + $CH_3OH$ results will show (below), the latter isotopomer is the main contributor. Growth in the bands at 1732 and 1717 $cm^{-1}$ shows that CO is converted to the ester carbonyl group. The bands are shifted by 1−2 $cm^{-1}$ to the red of the parent $HCO_2CH_3$ absorptions, indicating that they originate principally from the $HC({=}O)O^{13}CH_3$ isotopomer. The 1695/1683 $cm^{-1}$ product of the $^{13}CO$ + $CH_3OH$ system (trace d) confirms that carbon monoxide becomes part of methyl formate. The frequency shift is a few wavenumbers smaller than that for the $^{13}C$ product of the CO + $^{13}CH_3OH$ reaction (1694/1680 $cm^{-1}$), indicating that the bands belong mainly to the $H^{13}C({=}O)OCH_3$ isotopomer. The 1734/1718 peaks of trace d originate predominately from parent $HC({=}O)OCH_3$. We conclude from the experiments with $^{18}O$-, and $^{13}C$-labeled carbon monoxide and $^{13}C$-labeled $CH_3OH$ that the photoreaction of CO with $CH_3OH$ in TS-1 sieve leads to incorporation of carbon monoxide into methyl formate. One pair of carbonyl stretch bands is attributed to the methyl formate isotopomer whose C═O group originates from carbon monoxide and methoxy group predominately from methanol. The second, more intense pair of absorption bands stems from methyl formate made up exclusively of atoms from methanol. The relative intensity of the two sets of product absorptions remains unchanged, within uncertainty limits, during the entire growth period.

Two spectroscopic findings indicate intermediacy of formaldehyde. One is the observation of a small but well-resolved product band at 1728 $cm^{-1}$ when the photoreaction of $^{12}C^{18}O$ is conducted with $^{13}CH_3{}^{16}OH$, in addition to the doublets of the expected $H{-}^{12}C({=}^{18}O)^{16}O^{13}CH_3$ (1699 and 1682 $cm^{-1}$) and $H^{13}C({=}^{16}O)^{16}O^{13}CH_3$ (1695 and 1680 $cm^{-1}$) products. The absorbance growth of the 1728 $cm^{-1}$ band exhibits an induction period not seen for other product bands in this or any other experiment. The band originates from $\nu(C{=}O)$ of a methyl formate $^{12}C{=}^{16}O$ group that is shifted slightly to the red from the 1734 $cm^{-1}$ band of the parent isotope, indicating the presence of a labeled methoxy group. Hence, the absorption is assigned to $H^{12}C({=}^{16}O)^{16}O^{13}CH_3$. A likely process by which $^{12}C{=}^{16}O$ moieties might be formed is O exchange involving the $^{12}CH_2{=}^{18}O$ intermediate, produced by $^{12}C^{18}O$ photoreduction, with residual $H_2{}^{16}O$ still remaining in the sieve after dehydration (0.2 au at 1630 $cm^{-1}$).

$$^{12}CH_2{=}^{18}O + H_2{}^{16}O \rightleftarrows {}^{12}CH_2(^{18}OH)^{16}OH \rightleftarrows {}^{12}CH_2{=}^{16}O + H_2{}^{18}O \quad (2)$$

Tishchenko disproportionation[25] of the $^{12}CH_2{=}^{16}O$ thus formed with $^{13}CH_2{=}^{16}O$ produced by $^{13}CH_3{}^{16}OH$ photooxidation would yield the observed $H{-}^{12}C({=}^{16}O)^{16}O^{13}CH_3$ isotopomer, as well as its $H{-}^{13}C({=}^{16}O)^{16}O^{12}CH_3$ counterpart.



(3)

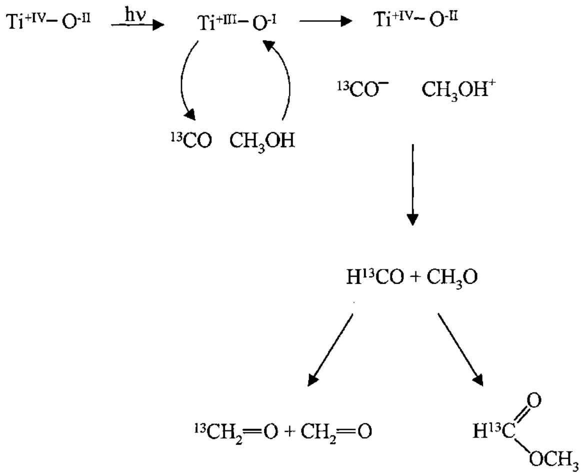
The absorption of the latter coincides with the intense $\nu(^{13}C{=}O)$ and $\nu(C{=}^{18}O)$ bands of the predominant $H-(C{=}^{18}O)O^{13}CH_3$ and $H-^{13}C({=}O)O^{13}CH_3$ products of the reaction. Tishchenko dimerization of formaldehyde in TS-1 to form methyl formate was described in detail in our previous report on the $CO_2 + CH_3OH$ system.[3] A recent spectroscopic study of $CH_2{=}O$ in Fe aluminophosphate sieve has shown that formaldehyde readily reacts with residual $H_2O$.[24] A second observation pointing to the intermediacy of formaldehyde is the apparent lower yield of the carbon monoxide insertion product for $C^{18}O + CH_3OH$ (Figure 6, trace b) compared to $CO + {}^{13}CH_3OH$ (trace c) or $^{13}CO + CH_3OH$ (trace d). Exchange of initially formed $CH_2{=}^{18}O$ with the $^{16}O$ of residual $H_2O$ by process 2 is a possible explanation for the reduced $HC({=}^{18}O)OCH_3$ growth.

## IV. Discussion

Our observation that excitation of the Ti−O LMCT state leads to reaction of $CH_3OH$ when CO is co-loaded into the sieve implies that carbon monoxide acts as an electron acceptor. CO has a relatively strong electron affinity (EA = 1.37 eV),[26] whereas the ionization potential is far too high for CO to be a donor (IP = 14.01 eV).[27] By contrast, methanol has a moderate ionization potential (IP = 10.84 eV)[27] and will therefore function as an electron donor when interacting with the excited LMCT state of the framework Ti center. Judging from these properties of the reactants, we propose the mechanism outlined in Scheme 1 to explain the observed reaction products. The initial step following excitation of the $Ti^{4+} - O^{2-} \rightarrow Ti^{3+} - O^{-}$ state is reduction of CO to $CO^-$ by the transiently reduced Ti under concurrent oxidation of $CH_3OH$ to the radical cation by the hole on the framework oxygen. Proton transfer from the highly acidic methanol radical cation[28] to $CO^-$ would yield HCO radical and $CH_3O$ radical (or the more stable $CH_2OH$ isomer).[29,30] Using enthalpies of formation[31−33] $\Delta H_f^o(CO) = -26.4$ kcal mol$^{-1}$, $\Delta H_f^o(CH_3OH) = -48.0$ kcal mol$^{-1}$, $\Delta H_f^o(HCO) = 43.5$ kcal mol$^{-1}$, $\Delta H_f^o(CH_3O) = 4.2$ kcal mol$^{-1}$, and $\Delta H_f^o(CH_2OH) = -2$ kcal mol$^{-1}$, we calculate an endothermicity of 122 kcal mol$^{-1}$ for the one-electron-transfer reaction $CO + CH_3OH \rightarrow HCO + CH_3O$ (or 116 kcal mol$^{-1}$ for $HCO + CH_2OH$). This is 10−15 kcal mol$^{-1}$ above the 266-nm photolysis photon energy (107 kcal mol$^{-1}$). However, the thermodynamic data refer to the free gas-phase radicals. Interaction of the transient radicals with the Ti center and pore walls could easily lower the endothermicity by tens of kilocalories per mole.

The most obvious explanation of the methyl formate isotopomer with the carbonyl group originating from carbon monoxide and the methoxy group from methanol is direct coupling of HCO and $CH_3O$ radical, as shown in Scheme 1. This requires that isomerization of $CH_3O$ to more stable $CH_2OH$ radical is slow on the time scale of $HCO + CH_3O$ coupling. The simultaneous appearance of methyl formate isotopomers with C=O groups not derived from carbon monoxide implies, however, that another reaction path is involved as well. This is most likely H-atom transfer from $CH_3O$ (or $CH_2OH$) to HCO to yield formaldehyde (Scheme 1), followed by Tishchenko reaction to produce methyl formate (eq 3). Random coupling of formaldehyde intermediates would produce methyl formate isotopomers with C and O from methanol only, from methanol and CO, and from CO only. Although we have not detected formaldehyde in these static FT-infrared experiments, its intermediacy is strongly suggested by the experimental observations presented in section III.

**SCHEME 1**



The HCO + $CH_3O$ radical coupling path and the H-transfer step followed by formaldehyde dimerization account for all observed methyl formate isotopomers, but not for the relative intensity of these products. Completely random reaction of formaldehyde molecules would lead to equal growth of each methyl formate isotopomer. However, a considerably higher intensity is found for the product with all atoms originating from methanol. Therefore, an additional process is operative that results in the oxidation of methanol to methyl formate apparently without concurrent reduction of CO. One possibility is that a species other than CO is acting as the electron acceptor. The constant intensity ratio during product growth implies that the acceptor concentration is stable over the entire photolysis period, which rules out a final product as the acceptor. The most likely candidate is the formaldehyde intermediate.

$$CH_3OH + {}^{13}CH_2{=}O \xrightarrow[\text{LMCT}]{h\nu} CH_2{=}O + {}^{13}CH_3OH \quad (4)$$

Formaldehyde is thought to be present at a small but steady concentration and has a reasonably good electron affinity of 0.65 eV.[34] The main reason it might be able to compete with CO as an electron acceptor is the low concentration of carbon monoxide in the sieve. Because half of the formaldehyde produced by the primary photoreaction of CO with $CH_3OH$ stems from carbon monoxide, the secondary photoreaction proposed here results in the net production of aldehyde from methanol under consumption of formaldehyde produced from CO. An alternative possibility is an additional channel for $HCO + CH_3O$ (or $CH_2OH$) coupling leading to $CO + H_2 + CH_2{=}O$. The result would be conversion of $CH_3OH$ to $CH_2{=}O$ without any additional accompanying changes in the (static) infrared spectrum. Detection and kinetic study of intermediates by time-resolved infrared spectroscopy will be needed to evaluate these mechanistic proposals.[35−37]

## V. Conclusions

In situ FT-IR monitoring of the reaction of a $CO/CH_3OH$ gas mixture loaded into TS-1 sieve induced by excitation of the Ti−O ligand-to-metal charge-transfer transition revealed activation of carbon monoxide and incorporation into methyl formate. This opens up the use of CO as a probe molecule for determining the excited-state properties of framework transition metals at the gas−micropore interface. Moreover, photoactivation of carbon monoxide in Ti silicalite sieve encourages exploration of synthetic chemistry of CO in new framework metal sieves that absorb at visible wavelengths.

On the basis of $^{13}C$- and $^{18}O$-labeling experiments, HCO radical is proposed as the one-electron reduction product of CO under concurrent oxidation of $CH_3OH$ to $CH_3O$ ($CH_2OH$). Direct coupling of the radicals to $HCO_2CH_3$ and H-atom transfer to form a formaldehyde intermediate followed by Tishchenko dimerization are the most likely paths leading to methyl formate. Time-resolved FT-IR spectroscopy will be employed to search for these intermediates and elucidate their interactions with the framework metal and the micropore environment.

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