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Combined Infrared and Programmed Desorption Study of Methanol Decomposition on ZnO

INTRODUCTION

Methanol decomposition is the simplest catalytic reaction of an oxygenated hydrocarbon. Previous IR studies have shown convincingly that decomposition proceeds via sequentially formed methoxy and formate intermediates (*1, 2*). Similarly, several temperature-programmed decomposition studies have also demonstrated that the reaction proceeds via the formate intermediate, and that decomposition of the formate intermediate is the elementary step that has the highest free energy of activation within the overall mechanism (*3–6*).

Despite this well agreed upon qualitative understanding of the decomposition pathway, a quantitative kinetic study of these IR-active surface intermediates has not been reported. In part this reflects the difficulty of simultaneously obtaining IR and TPD spectra using conventional transmission cells, in which the sample is prepared as a self-supporting thin disk with relatively poor thermal conductivity.

Here we describe a new IR cell design that provides better temperature control for performing more accurate TPD studies of the sample under spectroscopic scrutiny. Combined IR and TPD experiments permit us to obtain a direct correlation between the time evolution of the observed surface intermediates and the desorption flux of their decomposition products. Using this new cell, we can now resolve the kinetics of both the methoxy and formate decomposition steps, in excellent agreement with recent results for CH_3OH decomposition on ZnO thin films (*3*).

PROCEDURE

The sample cell used in this work is shown schematically in Fig. 1. The sample powder is deposited as a thin layer onto a polished silver disk that serves as a mirror for reflecting the incident IR beam. The disk is silver-soldered onto the reentrant inner sleeve of the stainless-steel cell body. The sample can be heated to 873 K using a 50-W cartridge heater which is inserted into a silver heating well soldered to the backside of the sample disk. The sample can be cooled to 100 K by flowing chilled N_2 through $\frac{1}{16}$-in. stainless steel tubing also soldered to the back of the disk. An iron-constantan thermocouple is externally attached to the disk to monitor the sample temperature.

The cell body itself is assembled from stainless-steel tubing, welded onto a commercially available $2\frac{3}{4}$-in. Cu-gasket flange. Two gas inlet lines with bellow-sealed on–off valves are welded into the side of the cell body. After the sample layer is deposited onto the silver mirror, the cell is assembled by sealing the front face with a flange-mounted CaF_2 window (Harshaw).

The new cell configuration offers several advantages over our previous design for recording simultaneous IR and TPD spectra (*7*). The sample temperature can be controlled much more easily and accurately, especially during high-temperature pretreatment steps. For strongly adsorbing materials, an arbitrarily thin layer can be deposited onto the mirror, thus eliminating the constraint of preparing a thin, self-supporting thin layer. Finally, both the thermo-

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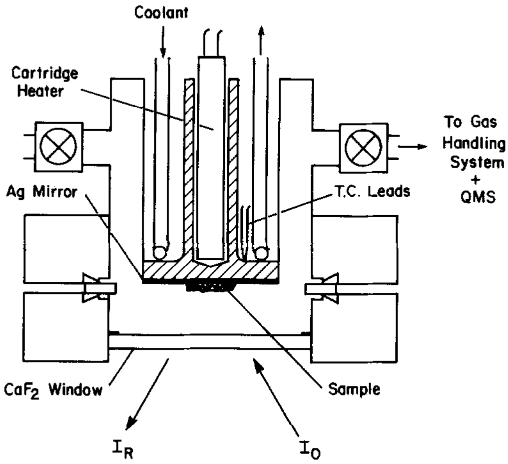

FIG. 1. Schematic diagram of sample cell used for combined temperature-programmed desorption and IR spectroscopy of catalyst powders.

couple and the cooling line are attached to the rear of the sample-mounting disk on the outside of the vacuum wall, thus eliminating the need for vacuum feedthroughs for these connections.

The sample used in these studies consisted of 100 mg of ZnO (Kadox 25—Gulf Western Natural Resources) deposited uniformly over the 1-in.-diameter silver mirror from an aqueous slurry. After the layer had dried and the front window had been attached, the cell was connected to an ion-pumped stainless-steel gas handling system. The sample was then evacuated at 673 K for 3 h to desorb H_2O and CO_2, cooled to 573 K while still under vacuum, and finally cooled to room temperature in 1 Torr of O_2 to maximize the IR transmission of the sample.

Temperature-programmed decomposition experiments were performed by initially admitting 2 μmol of CH_3OH vapor to the cell at 300 K. About 90% of this dose was adsorbed, as measured by the finite residual pressure. After pumping away this remaining vapor, the TPD experiment was performed by heating the sample (heating rate = 0.2 K/s) and monitoring the desorption products using a quadrupole mass spectrometer mounted on the gas-handling system.

Infrared spectra were recorded using an FTIR spectrometer (Nicollet 60-SX). The IR beam was reflected off the silver mirror, thus traversing the sample layer twice. The spectra shown here were recorded during the TPD warmup using 50 interferometer scans at 4 cm^{-1} resolution and a scan rate of 2 scans/s, with a TGS detector. The spectra are reported as recorded, without background subtraction.

RESULTS AND DISCUSSION

Figure 2 shows the IR spectra obtained over the temperature range 300–670 K. The spectra have been vertically displaced along the absorbance axis for clarity. In general, the sample absorbance increased with heating. For example, at 3000 cm^{-1} the absorbance increased from 1.55 to 1.59 between 300 and 670 K, while at 1500 cm^{-1} the change was from 1.21 to 1.57. This increase is largely reversed upon cooling, indicating that it is primarily caused by the increase in conduction band electron density with temperature due to ionization of intrinsic Zn donor levels in bulk ZnO (*8*).

The 300 K spectrum (bottom curve) was recorded immediately after adsorption of CH_3OH, and shows bands at 2936 and 2818

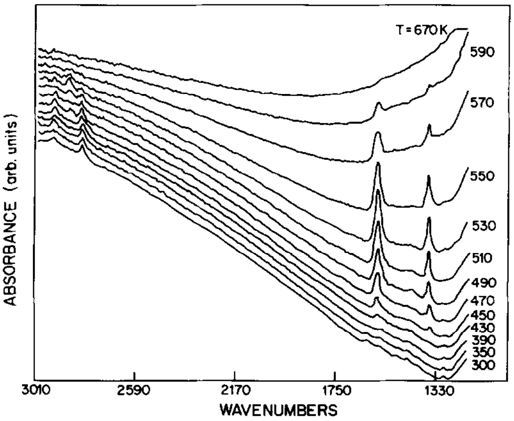

FIG. 2. Infrared spectra recorded during decomposition of preadsorbed CH_3OH on ZnO powder (initial coverage ≈20 μmol/g).

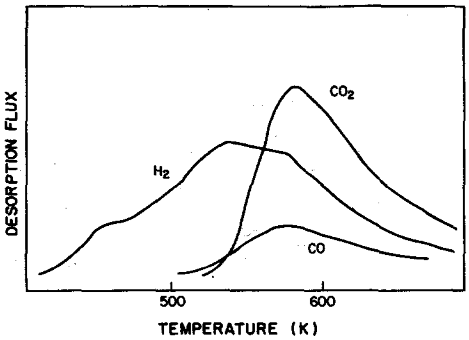

FIG. 3. Evolution of H_2, CO, and CO_2 during temperature-programmed decomposition of CH_3OH on ZnO (recorded simultaneously with IR spectra shown in Fig. 2).

cm^{-1}, assigned to the asymmetric and symmetric C–H stretches of adsorbed methoxy species, respectively (*1*). The C–H deformation mode that should be observed at 1470 cm^{-1} is largely obscured by residual carbonate features in this frequency region.

As the warmup proceeds, the first changes in the IR spectra are observed at 450 K. Two new bands appear at 1577 and 1364 cm^{-1}, which are assigned to the asymmetric and symmetric O–C–O stretching vibrations, respectively, of the bidendate surface formate species (*1*). The C–H stretching mode of this species can also be observed at 2870 cm^{-1}, while the in-plane C–H bending mode is resolved as a shoulder at 1379 cm^{-1}. The intensities of the formate bands continue to increase up to a temperature of 550 K. The intensities of the methoxy stretching features also decrease over this temperature range. The formate features finally begin to decrease in intensity at 550 K, and have essentially disappeared by 670 K.

The TPD spectra which accompany these IR spectra are shown in Fig. 3. Spectra are shown for the three major decomposition products H_2, CO, and CO_2. No significant desorption of H_2O or CH_4 was observed (≤ 0.01 μmol). In addition, a small amount of nondissociated CH_3OH desorbs with a peak temperature at 440 K (not shown). Separate experiments with different amounts of absorbed CH_3OH showed that this nondissociatively absorbed CH_3OH signal is absent for initial coverages lower than about 10 μmol CH_3OH/g ZnO.

The desorption of H_2 begins at 430 K and increases steadily but nonexponentially to an overall maximum near 530 K. The fact that about one-half of the total H_2 desorption signal occurs before the onset of CO and CO_2 evolution indicates that an independent H_2 evolution process is occurring over the temperature range 450 to 550 K. Comparison with the IR results in Figs. 2 and 3 shows conclusively that this H_2 evolution process is due to the decomposition of the methoxy groups as they convert to formate species.

The desorption spectra of CO and CO_2 show simultaneous maxima at 580 K. A well-resolved slope change in the H_2 desorption flux is also observed at this temperature. The fact that all three events occur simultaneously suggests that all three are due to the rate-limiting decomposition of a single intermediate. Comparison with Figs. 2 and 3 shows that this process is the decomposition of the formate intermediate.

Another significant feature of these results is the large CO_2 signal. The absence of CH_4 desorption indicates that the extra oxygen atom must be supplied by the ZnO lattice. However, repeating the experiment several times without intermediate reoxidation treatments revealed that the CO : CO_2 ratio is not greatly affected by repeated experiments, despite the removal of lattice oxygen from the catalyst. This somewhat surprising result is supported by the additional observation that the baseline absorbance of the sample returned to the same value after cooling at the end of each experiment. As a tentative explanation, we propose that the removal of O^{2-} anions from the catalyst must be accompanied by the reduction of Zn cations to Zn metal, thus maintaining both charge neutrality and conduction band electron density.

To further demonstrate the capability of the new cell, a heating rate variation study was performed to resolve the activation energy and preexponential factor of the formate decomposition step. For a change in heating rate from 0.1 to 0.9 K/s, the peak temperature of the CO and CO_2 desorption fluxes shifted from 559 to 588 K. By applying the heating rate equation for a first-order decomposition,

$$2 \ln T_p - \ln \beta = E_a/RT_p + \ln(E_a/R\nu_0) \quad (1)$$

this shift yields values of $\nu_0 = 5 \times 10^{13}$ s^{-1} for the preexponential factor and $E_a = 40$ kcal/mol for the activation energy. This result is consistent with the value for the free energy of activation of formate decomposition on *c*-axis oriented thin films studied recently in our laboratory. Those results yielded a value of $E_a = 37$ kcal/mol, assuming a preexponential factor of 10^{13} s^{-1} (*3*).

In summary, we have described a new sample cell for combined IR and TPD measurements. The cell has been used to resolve quantitatively the kinetics of the methanol decomposition reaction on ZnO. The TPD spectra have resolved the H_2 desorption process which accompanies the methoxy decomposition step, as well as the CO : CO_2 selectivity of the formate decomposition step. Future work is intended to relate these elementary reaction steps observed under vacuum conditions to the methanol synthesis mechanism at higher pressure, where surface coverages are likely to be significantly different.

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