Supplementary Information

CO Dissociation Induced by Adsorbed Oxygen and Water on Ir(111)

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Experimental Section

All experiments were conducted in a supersonic molecular beam surface scattering apparatus in which the ultrahigh vacuum scattering chamber has a base pressure less than 2×10^{-10} Torr. The scattering chamber is equipped with an Auger electron spectrometer (AES), low energy electron diffraction optics (LEED), and a quadrupole mass spectrometer (QMS). A detailed description has been previously reported by our group[1] but particularly pertinent details are described here. The circular Ir(111) sample with a diameter of ~1 cm can be resistively heated to 1550 K and rapidly cooled to 77 K by liquid nitrogen. Research purity $^{16}O_2$, $H_2{}^{16}O$, and isotopically labeled reagents (i.e., $H_2{}^{18}O$ and $^{13}C^{18}O$) were employed in this study. A molecular beam of each of the reagents (other than $^{13}C^{18}O$) was introduced into the scattering chamber using a device consisting of separated nozzles, each with the same aperture size and separate plumbing to insure reagent purity as delivered to the sample. $^{13}C^{18}O$ was backfilled into the scattering chamber and adsorbed on Ir(111). The coverage of each gas (CO and O_2) was estimated based on LEED measurements for saturated coverages that are in agreement with those reported previously.[2, 3] Water was dosed on the sample at a rate of 0.067 monolayer (ML)/s. Referring to the water structure on Pt(111), the density of 1 ML water was estimated to be 1.23×10^{15} molecules/cm^{-2}.[4] The sample was cleaned by Ar ion sputtering followed by annealing in gaseous oxygen.

CO Dissociation on Clean Ir(111)

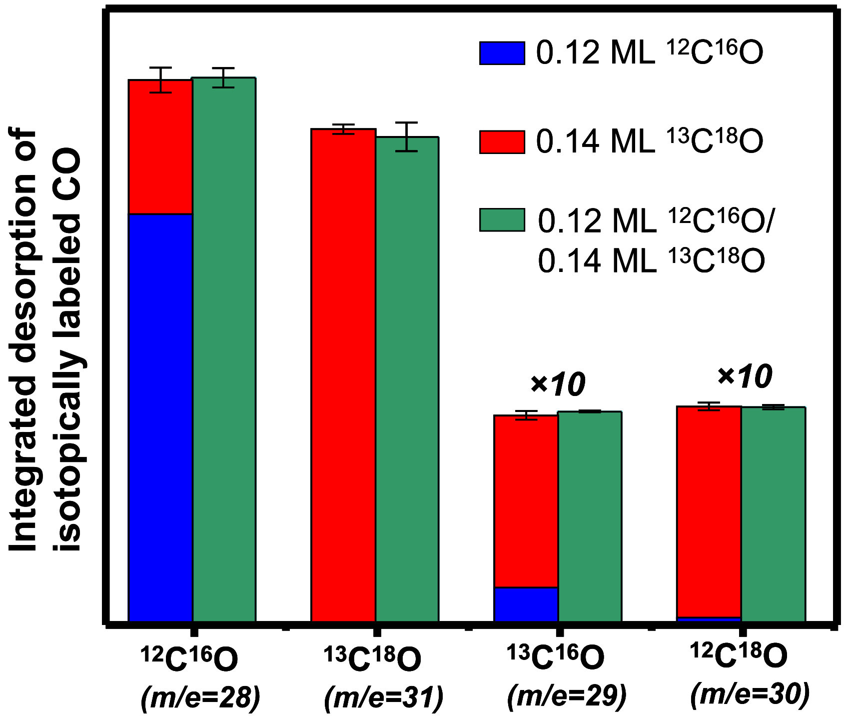

Fig. S1. Integrated desorption of $^{12}C^{16}O$, $^{13}C^{18}O$, $^{12}C^{18}O$, and $^{13}C^{16}O$ from Ir(111) covered by 0.12 ML $^{12}C^{16}O$ (blue column), 0.14 ML $^{13}C^{18}O$ (red column) and co-adsorbed 0.12 ML $^{12}C^{16}O$/0.14 ML $^{13}C^{18}O$ (green column). All species were dosed onto the surface between 89 and 77 K. The heating rate during TPD was 10 K/s.

In order to investigate CO dissociation on clean Ir(111), we co-adsorbed 0.12 ML $^{12}C^{16}O$ and 0.14 ML $^{13}C^{18}O$ on the Ir(111) surface between 89 and 77 K and searched for the production of scrambled recombination products, $^{13}C^{16}O$ and $^{12}C^{18}O$ ($^{12}C^{16}O+^{13}C^{18}O \rightarrow ^{13}C^{16}O+^{12}C^{18}O$), in temperature programmed desorption (TPD) spectra. First, two blank experiments were conducted with adsorption (separately) of either (i) $^{12}C^{16}O$ or (ii) $^{13}C^{18}O$. Figure S1 displays the integrated areas of TPD spectra with the red column denoting desorption of 0.14 ML $^{13}C^{18}O$, the blue column representing desorption of 0.12 ML $^{12}C^{16}O$, and the green column denoting desorption of the co-adsorbed carbon monoxides (0.12ML $^{12}C^{16}O$ and 0.14 ML $^{13}C^{18}O$). Note that the amount of desorbed $^{13}C^{16}O$ [an indicator of dissociation] from the co-adsorbed $^{13}C^{18}O$ and $^{12}C^{16}O$ on the Ir(111) surface is very similar to the sum of the mass 29 in the two blank experiments (i.e., the green column is very nearly equal to the sum of the red and the blue columns in the columns labeled $^{13}C^{16}O$ in Figure S1). Furthermore, similar phenomena were observed regarding desorbed $^{12}C^{18}O$ [also an indicator of CO dissociation in these experiments], indicating that the detected scrambled products ($^{13}C^{16}O$ and $^{12}C^{18}O$) are actually simply due to the impurities in reactant CO rather than due to CO dissociation. Additionally, the quantity of reactant gases $^{12}C^{16}O$ and $^{13}C^{18}O$ detected in the co-adsorption experiment [represented by the green column] is approximately equal to the sum of that in the blank experiments, further suggesting no mixing or dissociation. Therefore, we conclude that CO dissociation on clean Ir(111) is small and immeasurable by our techniques. We estimate that the smallest value of the CO dissociation probability that we would be able to measure is ~0.2%.

Calculation Method of CO Dissociation Probability

In this study, we can observe two indicators of CO dissociation on oxygen and/or water co-adsorbed Ir(111) surface, which are products from partial and full oxidation of carbon from CO dissociation. In general, we found that the main indicator is the product of partial carbon oxidation, which has a higher yield. Based on the TPD integrated areas of these two indicators, we can calculate the CO dissociation probability.

If we used $^{13}C^{18}O$ in experiments as shown in Figure 1 and 2, the indicators are $^{13}C^{16}O$ and $^{13}C^{16}O^{16}O$. We compared the TPD integrals of $^{13}C^{18}O$, $^{13}C^{16}O$ and $^{13}C^{16}O^{16}O$ on the clean surface (represented by A) and the O/OH modified surface (represented by B). Thus, the equation of CO dissociation probability is shown as follows:

$$\text{CO Diss. Prob. \%}=\frac{(B_{^{13}C^{16}O}-A_{^{13}C^{16}O})+(B_{^{13}C^{16}O^{16}O}-A_{^{13}C^{16}O^{16}O})}{A_{^{13}C^{18}O}}\times 100\%$$

Similarly, the indicators of CO dissociation are $^{12}C^{18}O$ and $^{12}C^{18}O^{18}O$ when we employed $H_2{}^{18}O$ (see Figure 3). Also, we used A and B to represent the integrated areas of TPD spectra of species desorbed from clean and OH modified surfaces, respectively. The equation is shown here:

$$\text{CO Diss. Prob. \%}=\frac{(B_{^{12}C^{18}O}-A_{^{12}C^{18}O})+(B_{^{12}C^{18}O^{18}O}-A_{^{12}C^{18}O^{18}O})}{A_{^{12}C^{16}O}-{}^{12}C^{16}O_{background}}\times 100\%$$

where background $^{12}C^{16}O$ was monitored by ramping the “clean” Ir(111) surface to 1550 K.

References

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