HESEB Research Stay Program

Ambient Pressure XPS and IRRAS Investigations of the CO_2 Hydrogenation Reaction

Amin Mohammadpour[1,2], Robert Temperton[3], Andrey Shavorskiy[3], Jonas Weissenrieder[4], Sarp Kaya[1,2]

[1]Department of Chemistry, Koç University, 34450 Istanbul, Turkey. [2]Koç University Tüpraş Energy Center (KUTEM), 34450 Istanbul, Turkey.
[3]MAX IV Laboratory, Lund University, Box 118, 221 00 Lund, Sweden. [4]Material Physics, School of Engineering Sciences, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden.

ABSTRACT

This report is a part of experiment I have done during HESEB Research Stay Program at HIPPIE beamline in MAXIV Laboratory, Lund, Sweden. Here we investigate hydrogenation of carbon dioxide on Cu_xO/Cu(211) surface in different hydrogen to carbon dioxide ratios.

INTRODUCTION

Carbon dioxide hydrogenation to methane, or methanation of carbon dioxide, also known as the Sabatier reaction, is the hydrogenation of carbon dioxide with hydrogen to form methane. The methanation of CO_2 is the conversion of carbon dioxide and hydrogen to methane and water through the following catalytic reaction[1]

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$$

CO_2 methanation is gaining interest due to its ability to utilize greenhouse gas in the atmosphere to produce clean and green fuel, to fulfill energy demand for the growing human population[1]. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful technique to study catalytic reactions, which can provide information about the chemical composition of the interface between solids and gases during the reactions.

EXPERIMENT

HIPPIE beamline at MAX IV is a soft x-ray beamline for Ambient pressure X-ray photoelectron spectroscopy (APXPS) equipped with a Bruker Vertex 70v FTIR spectrometer. Therefore, we can carry out in situ XPS and Infrared reflection absorption spectroscopy (IRRAS) measurements in the presence of a controlled gaseous atmosphere at pressures up to 30 mbar [1 mbar = 100 Pa] as well as under ultra-high-vacuum conditions. The photon energy range is 250 to 2200 eV in planar polarization and with photon fluxes $>10^{12}$ photons s^{-1} (500 mA ring current)[2].

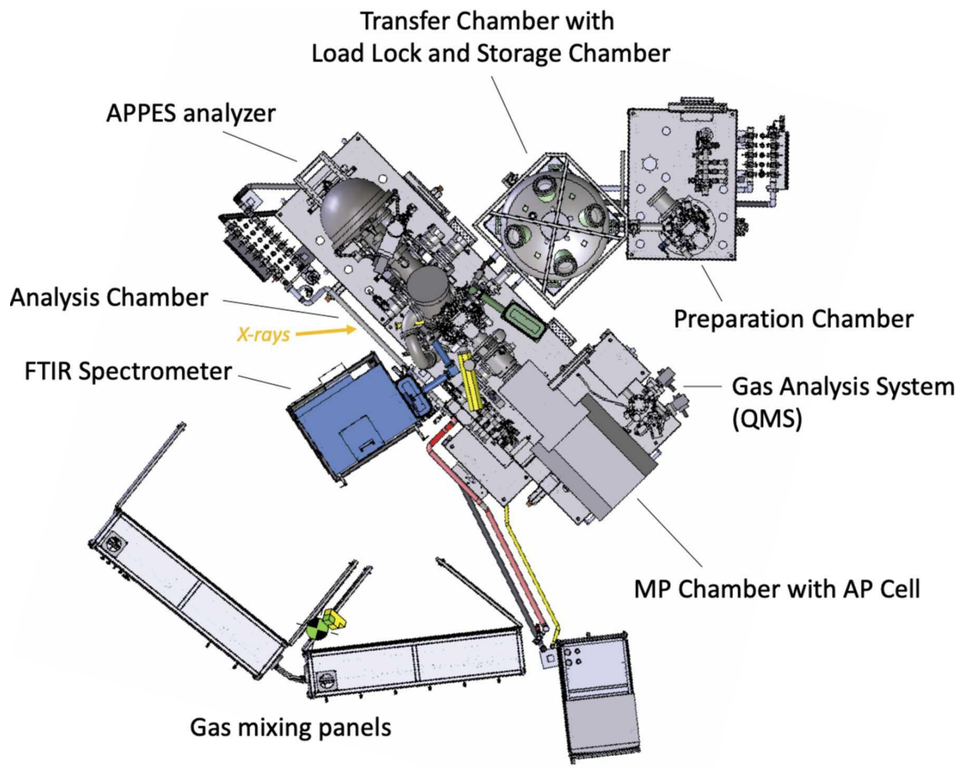

Fig. 1. APXPS endstation at HIPPIE beamline.

The Cu(211) crystal substrate cleaned by using cycles of Ar^+ ion sputtering (1 keV) followed by anneaing in vacuum at 500 °C. The crystallinity of the surface was confirmed by low energy electron diffraction (LEED) which showed a sharp LEED pattern (fig. 1 a). Copper oxide surface was prepared by annealing Cu(211) crystal at 380 °C in the oxygen pressure of 5×10^{-7} mbar. Then surface annealed at 500 °C in vacuum. Then time resolved APXPS and IRRAS measurements have been done on Cu_xO/Cu(211) surface exposed to CO_2, CO_2 /H_2 (1:1), (2:1) and (1:2) at different temperatures.

RESULTS AND DISCUSSION

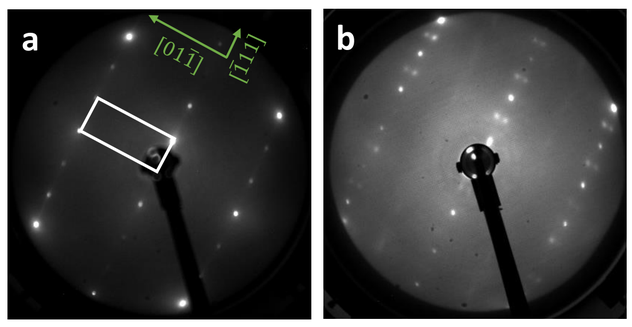

Fig. 2. LEED pattern of (a) clean surface of Cu(211), (b) oxidized Cu(211)surface(Cu_xO/Cu(211)).

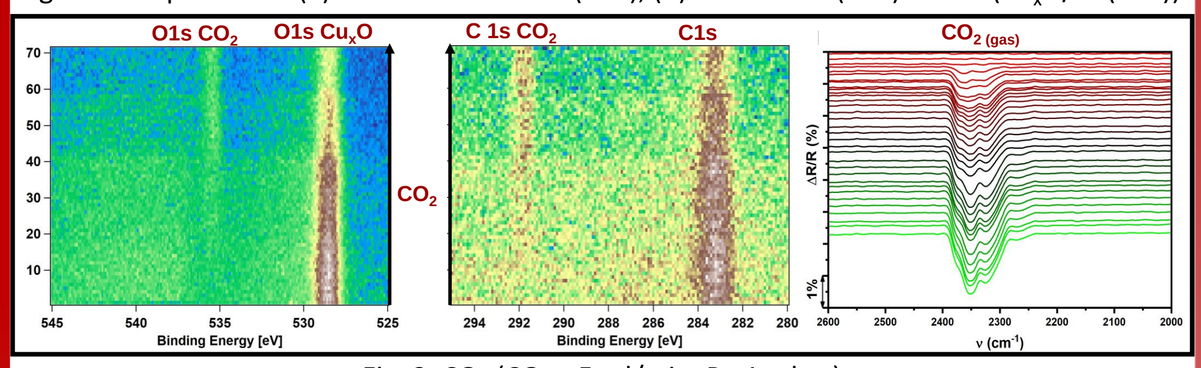

Fig. 3. CO_2 (CO_2 = 5 ml/min, P= 1 mbar)

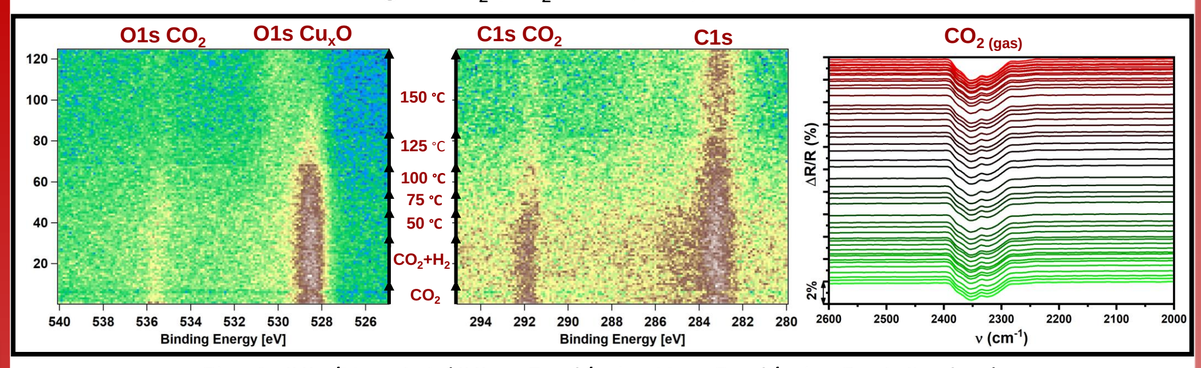

Fig. 4. CO_2/H_2 = 1:1 (CO_2 = 5 ml/min, H_2 = 5 ml/min, P= 1.6 mbar)

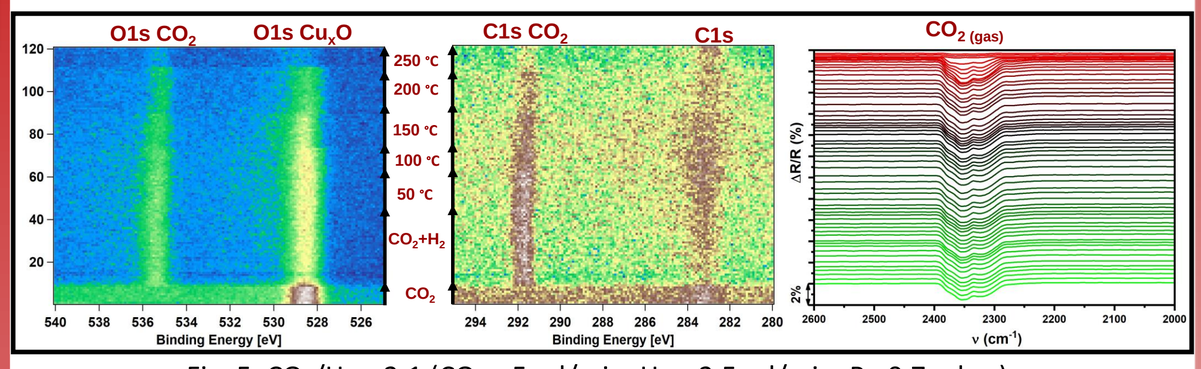

Fig. 5. CO_2/H_2 = 2:1 (CO_2 = 5 ml/min, H_2 = 2.5 ml/min, P= 0.7 mbar)

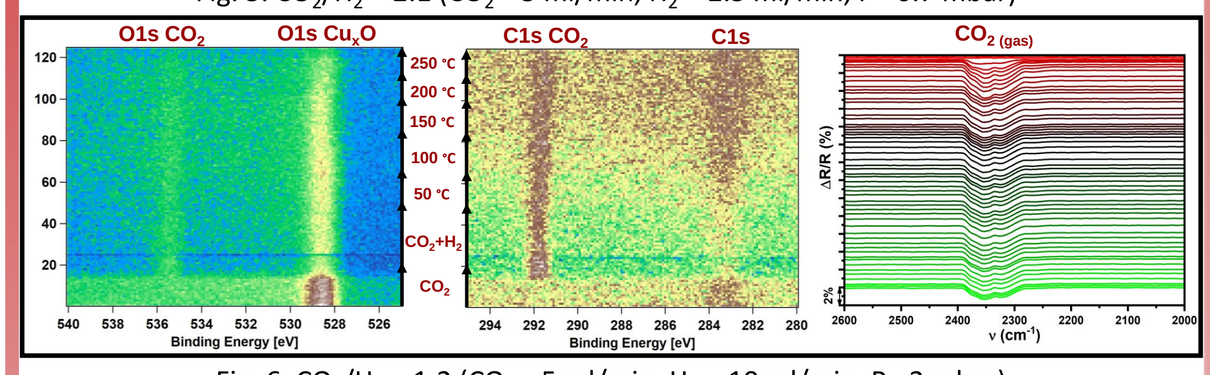

Fig. 6. CO_2/H_2 = 1:2 (CO_2 = 5 ml/min, H_2 = 10 ml/min, P= 2 mbar)

LEED pattern shows reconstruction of the Cu(211) surface after annealing in oxygen (Fig. 1 b). APXPS and IRRAS results shows there is not any CO_2 chemisorption on Cu_xO/Cu(211) surface in CO_2 atmosphere after increasing pressure to P(CO_2) = 1 mbar at room temperature (Fig. 2). Observed peak in the IRRAS is related to CO_2 gas phase. After exposing the sample to H_2 and CO_2 atmosphere in different ratios from CO_2 rich to H_2 rich region, we did not observe any carbonate/bicarbonate formation or hydrocarbon intermediates of the carbon dioxide hydrogenation.

Increase in the temperature of the sample results in the reduction of the copper oxide in the presence of hydrogen which starts at T>100 °C .

Since Cu_xO/Cu(211) surface can not activate CO_2, it is not an active surface for carbon dioxide hydrogenation.

ACKNOWLEDGMENT

The HESEB research stay programme is funded by the Helmholtz-SESAME Soft X-Ray Beamline for SESAME (HESEB) project. I would like to thank them for their support.

REFERENCES

[1] W. K. Fan et al, Journal of Environmental Chemical Engineering, vol. 9, no. 4, Aug. 2021
[2] S. Zhu et al., J Synchrotron Rad, vol. 28, no. 2, Art. no. 2, Mar. 2021