



Design, implementation and production upscaling of novel, high-performance, cluster-based catalysts for CO<sub>2</sub> hydrogenation

## Deliverable D4.4

IR spectra of CO<sub>2</sub> adsorption structure on free clusters



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## 1. IR spectra of bimetallic clusters

The team of RU (ESR4 Mr. Deepak Pradeep) has, with the aid of KUL, commissioned a dual-target, dual-laser ablation source (July 2022) and have produced bimetallic clusters containing cobalt and vanadium, both easy clustering materials and monoisotopic, which facilitates mass spectral analysis, and reacted them with CO<sub>2</sub>. The team, strengthened by ESR4 Ms. Barbara Zamora Yusti (on secondment from BME), then recorded IR spectra for these complexes and for the simultaneously formed complexes with pure cobalt clusters (Figure 1). Strikingly, the spectra for the doped cobalt clusters differ dramatically from those for the pure clusters, where the bands are characteristic for intact CO<sub>2</sub>: the  $\nu_2$  CO<sub>2</sub> bending mode around 650 cm<sup>-1</sup> or the Fermi resonance between the  $\nu_2$  overtone and the symmetric stretch mode  $\nu_1$  around 1400 cm<sup>-1</sup> are visible for all pure cobalt clusters. In contrast, these have largely disappeared for the vanadium doped clusters. Especially for n=5, the spectrum of the doped cluster complex exhibits a wealth of new bands, where for instance the band at 2113 cm<sup>-1</sup> is diagnostic for the stretching vibration of CO, formed upon the dissociation of CO<sub>2</sub>. Similarly, bands in the 1500-2000 cm<sup>-1</sup> spectral range are indicative of distorted (bent) CO<sub>2</sub> (see Figure 3). This appears to indicate that the inclusion of an early transition metal (TM) atom (vanadium) in a cluster of middle-to-late TM atoms (cobalt) can significantly reduce the CO<sub>2</sub> activation barrier, and significantly change the reactivity of a cluster.

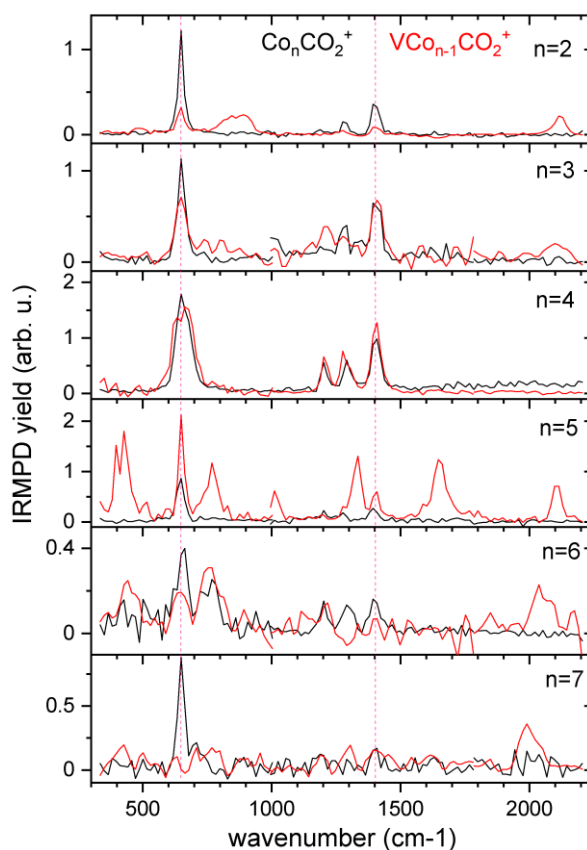


Figure 1: IR MPD spectrum for CO<sub>2</sub> adsorbed on cationic pure (black) and V-doped Co (red) clusters. The vertical dashed lines indicate the frequencies of the free CO<sub>2</sub> molecule.

Because many other modes are not as easily rationalized as the carbon monoxide CO stretch, Mr Pradeep, when on secondment at FETI, performed DFT calculations on cationic vanadium-doped cobalt clusters (in particular the  $VCo_4^+$  cluster). Different spin multiplicities (1-21) were considered for the geometry optimizations and to determine the harmonic vibrational frequencies of all structures. The CALYPSO structure prediction method was used to search for the different bare cluster geometries. (1; 2) Subsequently, to generate inputs for geometry optimization, we used an in-house code to systematically investigate carbon dioxide adsorption in different binding modes to low-energy bare metal clusters. In the binding modes considered,  $CO_2$  was either activated (indicated by the bending of the  $CO_2$  moiety and by increased bond lengths), intact or dissociated. The harmonic vibrational frequency results of the different binding modes will aid in the identification of the  $VCo_4^+-CO_2$  spectrum.

Preliminary computational results suggest two energetically favored binding modes for the  $CO_2$  adsorbate on the  $VCo_4^+$  cluster. We found an activated  $CO_2$  moiety (Fig. 2D) with a tridentate binding motif (carbon  $\eta^2$  bound to V-Co, and oxygen only bound to V), that with bands at 741, 1184 and 1707  $cm^{-1}$  ( $CO_2$  bending, symmetric and antisymmetric stretch modes) favourably compares to the experimental spectrum. Two structures with dissociated  $CO_2$  (Fig. 2B-C) present a V-O stretch at 633 and 878  $cm^{-1}$ , and a C-O stretch at 2091 and 2087  $cm^{-1}$ , respectively. These outcomes suggest the presence of both activated and dissociated  $CO_2$  entities. However, the proposed assignments have yet to undergo verification and different binding modes shall be explored. A publication on these results is currently in preparation.

## 2. IR spectra of oxidized clusters

The teams of UU and RU (ESR 3 Mr. Pavol Mikolaj and Mr. Pradeep) have investigated the activation of  $CO_2$  by cationic and anionic copper oxide clusters as well the activation of  $H_2$  by cationic copper oxide clusters. These data show a substantial cluster charge effect for the activation of  $CO_2$ . In particular, we found that anionic copper oxide clusters activate  $CO_2$  more readily than cationic clusters, while  $H_2$  activation is more favorable by cationic clusters.

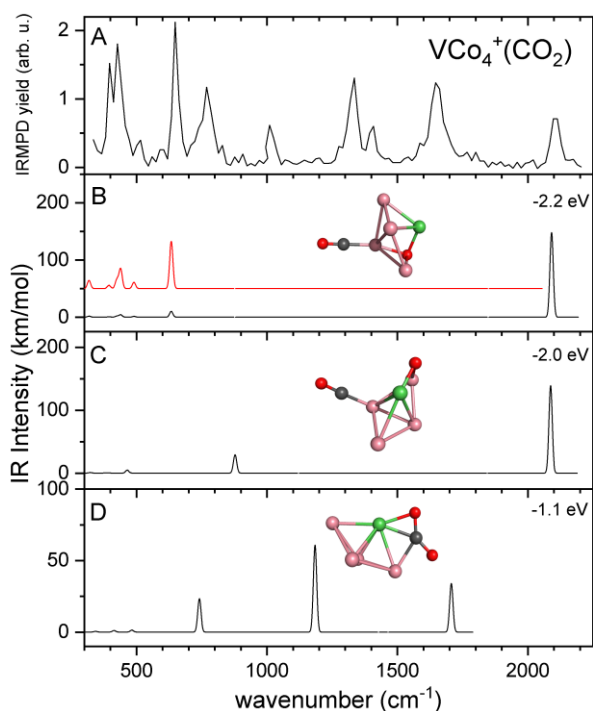


Figure 2: Experimental IRMPD spectra of  $[VCo_4CO_2]^+$  (panel A) compared to the calculated vibrational spectra of three low-energy structures of dissociated (panel B and C) and activated  $CO_2$  (panel D) adducts. Relative energies with respect to the reactants (cluster+ $CO_2$ ) are shown in eV. The red trace in panel B is a 10 times enlargement of the black trace.

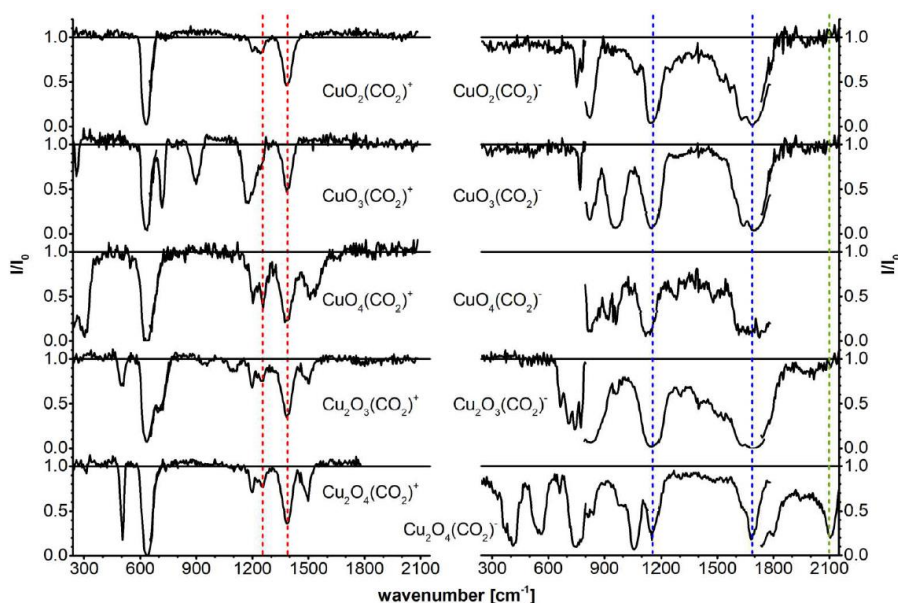


Figure 3: IR-MPD spectra of selected cationic (left) and anionic (right)  $\text{Cu}_n\text{O}_x(\text{CO}_2)$  complexes. Red-dashed lines indicate the Fermi dyad characteristic for a linear non-activated  $\text{CO}_2$  molecule, the blue dashed lines indicate characteristic modes of an activated bent  $\text{CO}_2$  molecule, and the green dashed line indicate the characteristic C-O stretch of a carbon monoxide molecule.

Figure 3 shows the IR-MPD spectra of some selected cluster sizes. These spectra reveal that  $\text{CO}_2$  adsorbed on cationic clusters show the characteristic Fermi dyad (red dashed line in Figure 3 left column), indicating a rather weak cluster- $\text{CO}_2$  interaction without activation of  $\text{CO}_2$ . In contrast,  $\text{CO}_2$  adsorbed on anionic clusters shows two bands (blue dashed lines in Figure 3 right column) which are typical for the bent geometry of an activated  $\text{CO}_2$  molecule.

In a second set of experiments, we studied the interaction of cationic  $\text{CuO}$  clusters with  $\text{D}_2$ . As an example, Figure 4 displays the IR-MPD spectra of some selected cluster sizes. The rather complex nature of the spectra with an unexpected number of bands indicates the dissociation of hydrogen on these clusters. In addition, we obtained preliminary results on the for coadsorption of  $\text{CO}_2$  and  $\text{H}_2$  on anionic clusters, which we plan to study in more detail and different experimental conditions in this proposal. Theoretical simulations of the experimental IR-MPD data are currently in progress by the teams of FETI and BME (Ms Zamora Yusti with aid of Prof. Dr. Tibor Höltzl and Prof Laszlo Nyulászi)

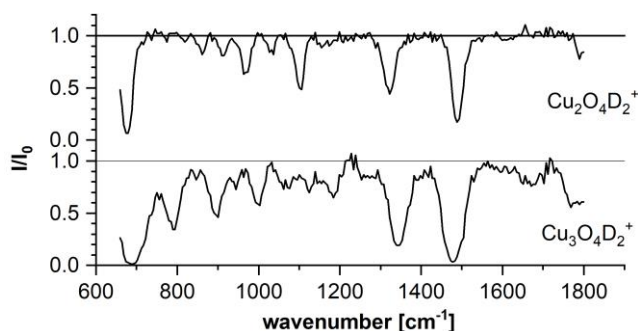


Figure 4: IR-MPD spectra of selected cationic  $\text{Cu}_n\text{O}_x\text{D}_2^+$  complexes

### 3. Conclusions

We have successfully produced IR spectra for complexes of free clusters with CO<sub>2</sub>. Such spectra show clear indications for whether the adsorption of the CO<sub>2</sub> on the cluster of interest leaves the CO<sub>2</sub> molecule unaffected, whether the CO<sub>2</sub> molecule gets weakened and distorted, or whether the CO<sub>2</sub> molecule gets dissociated. Overall, we identify the following trends:

- a) *Negatively charged* clusters are more active towards CO<sub>2</sub> than *positively charged* clusters. This both follows from comparison to the few studies known in literature (3-5), as well as from the internal studies on copper oxide clusters where a direct comparison between the charge states is made.
- b) *Substitution* of a single cobalt atom by a vanadium atom leads to a strong change in activity of the cluster towards CO<sub>2</sub>. Although it is still early for firm conclusions, we speculate that it is the much higher oxophilicity of vanadium that drives the dissociation, with known bond energies  $D(V^+-O)=5.68$  eV,(6) and  $D(Co^+-O)=3.25$  eV.(7)

### References

1. Lv J, Wang Y, Zhu L, Ma Y. 2012. Particle-swarm structure prediction on clusters. *J Chem Phys* 137:084104
2. Wang Y, Lv J, Zhu L, Ma Y. 2012. CALYPSO: A method for crystal structure prediction. *Computer Physics Communications* 183:2063-70
3. Yanagimachi A, Koyasu K, Valdivielso DY, Gewinner S, Schöllkopf W, et al. 2016. Size-Specific, Dissociative Activation of Carbon Dioxide by Cobalt Cluster Anions. *The Journal of Physical Chemistry C* 120:14209-15
4. Green AE, Justen J, Schollkopf W, Gentleman AS, Fielicke A, Mackenzie SR. 2018. IR Signature of Size-Selective CO<sub>2</sub> Activation on Small Platinum Cluster Anions, Pt<sub>n</sub><sup>-</sup> (n=4-7). *Angew Chem Int Ed Engl* 57:14822-6
5. Lushchikova OV, Szalay M, Tahmasbi H, Juurlink LBF, Meyer J, et al. 2021. IR spectroscopic characterization of the co-adsorption of CO<sub>2</sub> and H<sub>2</sub> onto cationic Cu<sub>n</sub><sup>+</sup> clusters. *Phys Chem Chem Phys* 23:26661-73
6. Aristov N, Armentrout PB. 1984. Bond energy-bond order relations in transition-metal bonds: vanadium. *Journal of the American Chemical Society* 106:4065-6
7. Fisher ER, Armentrout PB. 1990. Reactions of Co<sup>+</sup>, Ni<sup>+</sup>, and Cu<sup>+</sup> with Cyclopropane and Ethylene Oxide. Metal-Methylklene Ion Bond Energies. *The Journal of Physical Chemistry* 94:1674-83