## **Electronic Supplementary Information**

## **Coordination-Induced CO<sub>2</sub> Fixation into Carbonate by Metal Oxides**

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Fig. S1 Mass spectrum of the  $[YO(CO_2)_n]^+$  cluster ions produced by the reactions of the vaporized species with 2% O<sub>2</sub> seeded in CO<sub>2</sub>.



Fig. S2 Experimental IRPD spectrum of  $[YO(CO_2)_2]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S3 Experimental IRPD spectrum of  $[YO(CO_2)_3]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S4 Experimental IRPD spectrum of  $[YO(CO_2)_4]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S5 Experimental IRPD spectrum of  $[YO(CO_2)_5]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S6 Experimental IRPD spectrum of  $[YO(CO_2)_6]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S7 Experimental IRPD spectrum of  $[YO(CO_2)_7]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.



Fig. S8 Experimental IRPD spectrum of  $[YO(CO_2)_8]^+$  (bottom panel), with the calculated harmonic vibrational spectra, structures, and relative energies (kJ/mol) of the two lowest-energy isomers.

## The Method of Molecular Dynamics Simulations

The dynamic motion of the  $[YO(CO_2)_n]^+$  (n = 4-6) clusters are simulated by the Ab Initio Molecular Dynamics (AIMD) method, in which the atoms are treated as classical particles and the potential energy and forces on the atoms are calculated within the framework of density functional theory at each time step, as implemented in the CP2K package.<sup>1</sup> The wave functions are expanded in a double zeta Gaussian basis set, while the electron density is expanded in Gaussians and auxiliary plane waves (GPW) with an energy cut-off at 500 Rydberg for the electron density. The atomic cores are modelled by the Goedecker-Teter-Hutter (GTH) type pseudopotentials. The exchange and correlation energies are calculated by the PBE functional, with additional Grimme's dispersion corrections at the D3 level. A cluster ion is put at the center of a periodic cubic box, and the effects of the periodic charge density images are corrected by the decoupling technique developed by Martyna and Tuckerman.<sup>2</sup> The box length is at least 20 Å. The convergence criterion for the SCF electronic procedure is set to be  $10^{-7}$  a.u. at each time step. For molecular dynamics, the temperature is controlled by a Nose-Hoover thermostat, with a time step of 0.5 fs. An equilibration period of up to 5 ps is performed first, with the temperature scaled to an interval of at least 10 K around the intended value. A data collection run is then followed in the microcanonical ensemble. For different simulated temperature, the duration of a trajectory is more than 45 ps. Each trajectory is then cut into 15 ps interval for Fourier transformation and then added up to produce the dipole time-correlation function (DTCF) spectrum for a specific temperature.

The interactions of carbon atoms of  $CO_2$  between oxygen atoms of  $[YCO_3]^+$  core ion are electrostatic, which could be relatively weak and fairly flexible at finite temperature. Dynamic simulations are essential for sampling the solvated structures and for examining the thermal stability of a particular structure. More importantly, the electrostatic forces have strong effects on the vibrations of  $CO_2$  that can be captured by AIMD simulations. A vibrational spectrum can be directly simulated by the Fourier transform of the DTCF,<sup>3</sup>

$$\alpha(\omega) = \frac{2\pi\beta\omega^2}{3n(\omega)cV} \int_{-\infty}^{+\infty} dt \langle \vec{M}(t) \bullet \vec{M}(0) \rangle \exp(i\omega t)$$

where  $\beta = 1/kT$ ,  $n(\omega)$  is the refractive index, *c* is the speed of light in vacuum, *V* is the volume, and  $\vec{M}$  is the total dipole moment of the system, calculated by the

polarization including both ionic and electronic contributions.

## **References:**

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- 3 D. A. McQuarrie, Statistic Mechanics; Harper-Collins Publishers; New York. 1976.



Fig. S9 Comparison of experimental IRPD spectrum of  $[YO(CO_2)_4]^+$  (bottom panel) to the DTCF spectra of isomer 4C at 50 K, 150 K, and 250 K based on AIMD simulations.



Fig. S10 Comparison of experimental IRPD spectrum of  $[YO(CO_2)_5]^+$  (bottom panel) to the DTCF spectra of isomer 5C at 50 K, 150 K, and 250 K based on AIMD simulations.



Fig. S11 Comparison of experimental IRPD spectrum of  $[YO(CO_2)_6]^+$  (bottom panel) to the DTCF spectra of isomer 6C at 50 K, 150 K, and 250 K based on AIMD simulations.

$[\mathrm{YO}(\mathrm{CO}_2)_n]^+$	E <sub>diss</sub>	number of IR photon required for the dissociation	
n = 1	85.6	4	4
n = 2	77.9	4	3
<i>n</i> = 3	79.5	4	3
<i>n</i> = 4	76.6	4	3
n = 5	63.4	3	3
n = 6	53.5	3	2
n = 7	30.3	2	2
<i>n</i> = 8	28.1	2	1

**Table S1.** B2PLYP/def2-TZVP lowest dissociation energies ( $E_{diss}$ , kJ/mol) and the number of IR photon required for the dissociation of  $[YO(CO_2)_n]^+$  (n = 1-8).