Supporting Information

Exploring the formation of carbonates on La$_2$O$_3$ catalyst with OCM activity

Cairu Guan [a,b,c], Zebang Liu [a,b], Danyu Wang [a], Xiaohong Zhou [a,b], Yaoqi Pang [a,b,c], Na Yu [a], Alexander P. van Bavel [d], Evgeny Vovk [a],Yong Yang* [a]

[a] School of Physical Science and Technology, Shanghai Tech University, 393 Huaxia Middle Road, Shanghai, 201210, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

[d] Shell Technology Centre Amsterdam, P.O. Box 38000, 1030 BN Amsterdam, Netherlands.

* Corresponding author email: yangyong@shanghaitech.edu.cn

MS signal calibration of nearly pure (99%) CO_2 with low partial adsorption

The online CO_2 output flow rate during the adsorption experiment is generally estimated by the following equation:

$$[CO2\ out] = \frac{Sig\ CO2}{Sig\ Ar} \times [Ar]$$

(eq. 1)

Where [Ar] denotes the molar flow of Ar, which is its MFC setting value. [$CO_{2\ output}$] denotes that of the output CO_2, and CO_{2Sig} and Ar_{Sig} are the online MS signals of CO_2 and Ar output after fragmentation correction.

The MS sampling signal of amu 44 or amu 22 (double ionization of CO_2) will have no change upon 100% pure CO_2 adsorption experiment, since after partial adsorption the sampled output gas is still pure CO_2. However, if a low concentration (1%) of Ar dilution is added, the relative Ar signal will increase upon partial uptake. In this way, in this experiment with online MS, 1% of Ar is mixed with high concentration CO_2 input flow to simulate the pure CO_2 adsorption.

In the experiment in Figure 6, the highest CO_2 uptake is about 3%. At the highest adsorption uptake, the CO_2 concentration changed from 99% (no adsorption) to about $(\frac{99-3}{100-3})x$ 100%, or 98.97%. Its relative change is $(\frac{0.03\%}{99\%})$, which almost not affects the MS signal of amu 44. On the other hand, the Ar signal changes from 1% to $(\frac{1}{100-3})x$ 100%. Following the same calculation, the Ar signal relative change is $(\frac{0.03\%}{1\%})$, or about 3%. This relative signal change from Ar baseline is almost 100 times higher than CO_2 and can be captured by MS.

Since the MS signal of CO_2 remains almost constant in this case, the CO_2 uptake can be also directly estimated only by the Ar MS signal just converting from its relative change scale normalized with its background signal (no adsorption). The advantage of this second approach is that there is no ionization difference between Ar and CO_2 need be considered. Fig.6 is plotted from eq. S1 and the calibration result is also strongly confirmed by the 2nd calibration method.
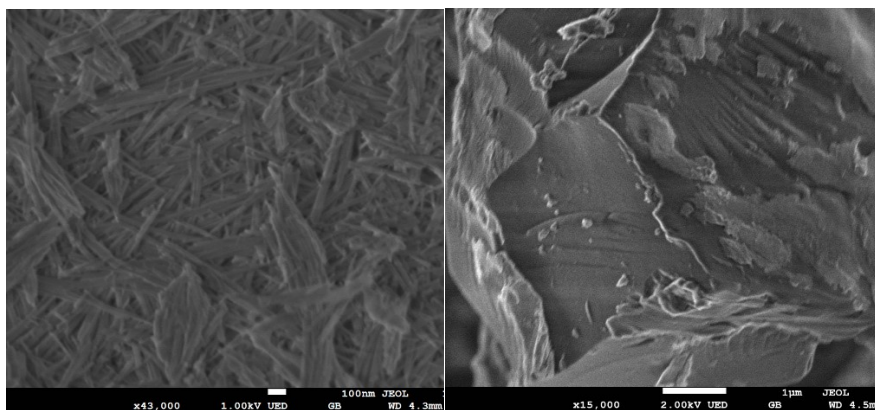

Figure S1. Nanorod (left) and commercial (right) La_2O_3 SEM image
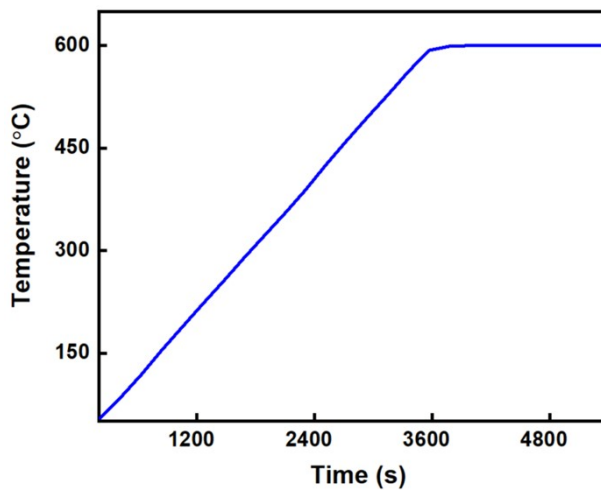

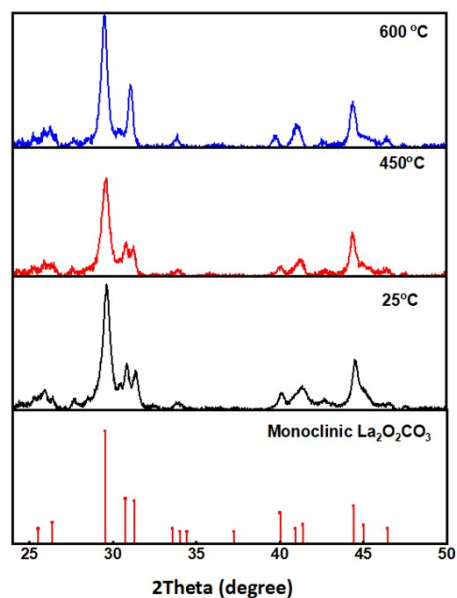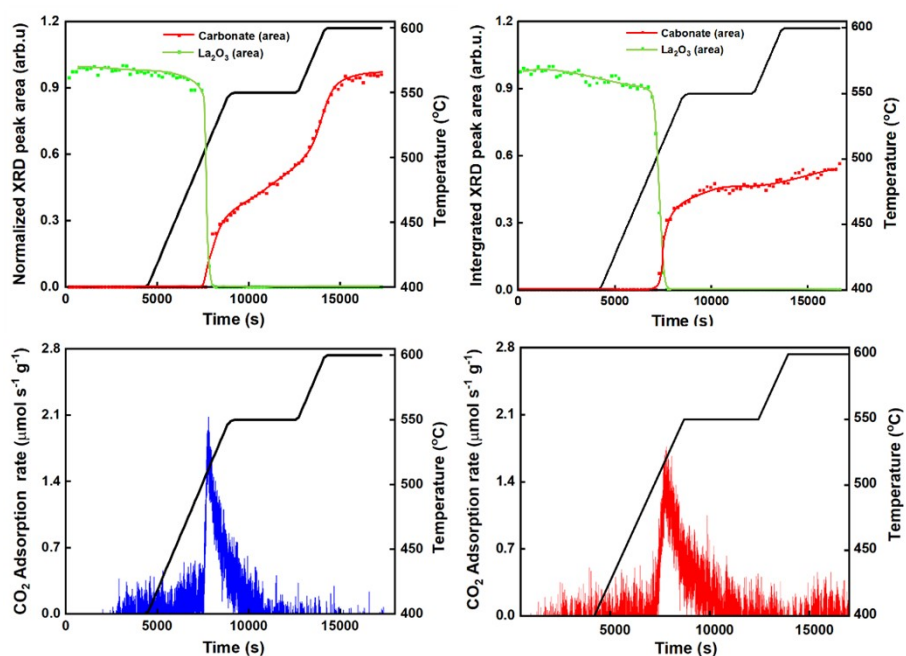Figure S2. The actual temperature profile of Figure 3

Figure S3. Heating in CO_2 to 600 °C, survey at 25 °C, 450 °C, 600 °C

Figure S4. Simultaneous obtained online MS and *in situ* XRD analysis of a) *M*-La_2O_3 and b) *n*-La_2O_3 samples during exposure to 99% CO_2 /1% Ar (10 sccm) flow for behavior comparison of CO_2 uptake and phase change. The phase changes from La_2O_3 (green) to $La_2O_2CO_3$ (red) are plotted by tableted XRD peak intensity curves in upper panels; the CO_2 uptakes are plotted in lower panels. The temperature profiles are plotted in all panels.

Only the pure CO_2 flow exposure results in complete phase changes for both n-La_2O_3 and M-La_2O_3. A much slower temperature profile is performed to obtain the details of these processes on the two samples by collecting the simultaneously La_2O_3 phase change (*in situ* XRD) and CO_2 loss (online MS) signals (Figure S4). To obtain relative CO_2 loss signal in MS, 1% Ar is mixed with pure CO_2 (99% CO_2 balanced with 1% Ar). The real time CO_2 loss rate is converted from the relative Ar signal intensity during this process. A brief description of this method is in the supporting information. Sample is first linearly heated in the CO_2 flow from room temperature to 400°C with the rate of 5°C/min. The heating rate is thus reduced to 2°C/min until the temperature reaches 550°C. After holding at 550°C for 1 hour, the sample is linearly heated to 600°C at the low heating rate of 2°C/min.

The phase change related CO_2 uptake is divided into three major steps for both samples. In the 1st step, both samples remain the original pure hexagonal La_2O_3 phases. Close inspect of MS data indicates a small CO_2 uptake as slight increase of signal from background. This indicates that there is a small CO_2 adsorption undergoing in this step but the formed carbonates grains are not large enough to be observed by XRD instrument, probably only surface carbonates species. The 2nd step of CO_2 uptake starts as the temperature approaches about 500°C. For both samples, three obvious changes correlating with transformation to bulk $La_2O_2CO_3$ phase initial in this step. These are including a sudden increase of the CO_2 uptake rates, a quick drop of La_2O_3 phase signal, and the rising of XRD intensity of $La_2O_2CO_3$. Interestingly, for both samples, the time points that XRD peak intensity of both La_2O_3 sample intensity reduce to zero also coincide with that the CO_2 uptake rates reach maximum level. So far the behavior of to $La_2O_2CO_3$ on both samples seems very similar. The CO_2 uptake and bulk $La_2O_2CO_3$ formation are not complete after the clearance of peaks in XRD patterns of La_2O_3. When the samples are hold at 550°C and heating to higher

temperature, the 3rd step observes the continued rising of XRD signal of $La_2O_2CO_3$ and the slow decrease of CO_2 uptake rates. In the third step, the CO_2 uptake over both samples are almost identical, the MS decay curves lasting about 3000 s before decreasing to zero, which is about 20 min before the finish of temperature holding at 550°C. The samples phase change behaviors are rather different. For n-La_2O_3 (figure 6), the XRD intensity of tetragonal (200) peak reaches ~50% of its maximum when La_2O_3 fully decomposes. Its intensity keeps increasing during the whole heating process, although relatively slowly. For M-La_2O_3 (Figure 6), the XRD intensity of hexagonal (110) peak reaches only about 25% of its maximum when La_2O_3 fully decomposes. The intensity keeps strongly increasing as the sample is heated to 550°C and hold for 1 hr. During the 2nd heating step to 600°C, the slope of XRD intensity is even sharper and the phase change is only stopped after the sample is hold at 600°C.
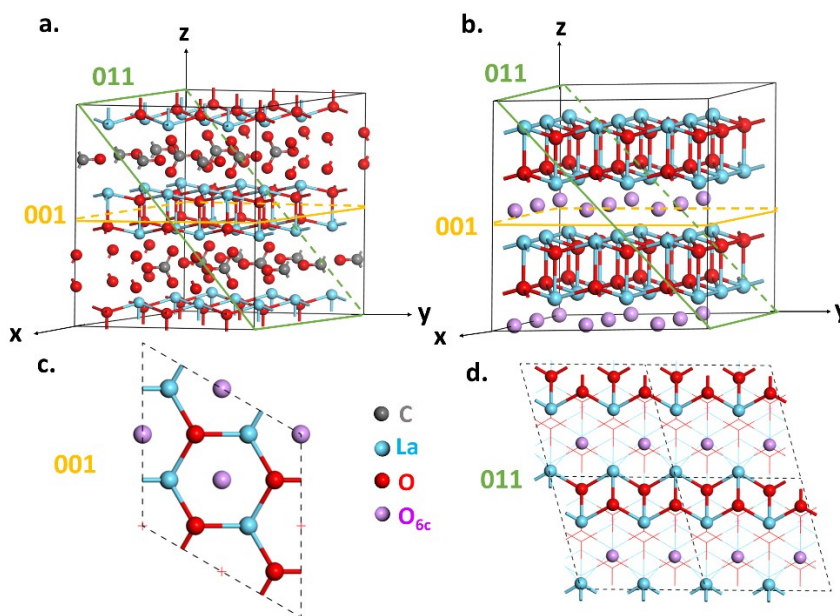
Figure S5. a) The bulk structure diagrams of $La_2O_2CO_3$ (hexagonal) and b) La_2O_3, together with the c) La_2O_3 (011) and d) La_2O_3 (011) surface. The O_{6c} atom is the purple one.