Supporting Information

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

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MS signal calibration of nearly pure (99%) CO\textsubscript{2} with low partial adsorption

The online CO\textsubscript{2} output flow rate during the adsorption experiment is generally estimated by the following equation:

$$[\text{CO}_2\text{ out}] = \frac{\text{Sig CO}_2}{\text{Sig Ar}} \times [\text{Ar}]$$

(eq. 1)

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

The MS sampling signal of amu 44 or amu 22 (double ionization of CO\textsubscript{2}) will have no change upon 100% pure CO\textsubscript{2} adsorption experiment, since after partial adsorption the sampled output gas is still pure CO\textsubscript{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\textsubscript{2} input flow to simulate the pure CO\textsubscript{2} adsorption.

In the experiment in Figure 6, the highest CO\textsubscript{2} uptake is about 3%. At the highest adsorption uptake, the CO\textsubscript{2} concentration changed from 99% (no adsorption) to about $\frac{99 - 3}{100 - 3} \times 100\%$, 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 $\frac{1}{100 - 3} \times 100\%$. 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\textsubscript{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 2$^{nd}$ calibration method.

Figure S1. Nanorod (left) and commercial (right) La$_2$O$_3$ SEM image

Figure S2. The actual temperature profile of Figure 3
Figure S3. Heating in CO₂ 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-La₂O₃ and b) n-La₂O₃ samples during exposure to 99% CO₂/1% Ar (10 sccm) flow for behavior comparison of CO₂ uptake and phase change. The phase changes from La₂O₃ (green) to La₂O₃CO₃ (red) are plotted by tableted XRD peak intensity curves in upper panels; the CO₂ 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$_2$O$_3$ and $M$-La$_2$O$_3$. A much slower temperature profile is performed to obtain the details of these processes on the two samples by collecting the simultaneously La$_2$O$_3$ 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 1$^{st}$ step, both samples remain the original pure hexagonal La$_2$O$_3$ 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 2$^{nd}$ 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$_2$O$_2$CO$_3$ phase initial in this step. These are including a sudden increase of the CO$_2$ uptake rates, a quick drop of La$_2$O$_3$ phase signal, and the rising of XRD intensity of La$_2$O$_2$CO$_3$. Interestingly, for both samples, the time points that XRD peak intensity of both La$_2$O$_3$ sample intensity reduce to zero also coincide with that the CO$_2$ uptake rates reach maximum level. So far the behavior of to La$_2$O$_2$CO$_3$ on both samples seems very similar. The CO$_2$ uptake and bulk La$_2$O$_2$CO$_3$ formation are not complete after the clearance of peaks in XRD patterns of La$_2$O$_3$. 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$_2$O$_2$CO$_3$ 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$_2$O$_3$ (figure 6), the XRD intensity of tetragonal (200) peak reaches \(~50\%\) of its maximum when La$_2$O$_3$ fully decomposes. Its intensity keeps increasing during the whole heating process, although relatively slowly. For \( M \)-La$_2$O$_3$ (Figure 6), the XRD intensity of hexagonal (110) peak reaches only about 25\% of its maximum when La$_2$O$_3$ 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$_2$O$_2$CO$_3$ (hexagonal) and b) La$_2$O$_3$, together with the c) La$_2$O$_3$ (011) and d) La$_2$O$_3$ (011) surface. The O$_{6c}$ atom is the purple one.