Supporting Information

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S1. Oxygen isotope exchange (OIE) and equilibrium techniques

As shown in figure S1, the OIE apparatus consists of a vacuum pump, a circulation pump, a heating furnace, a U-shaped microreactor, $^{18}O_2$ gas source, $^{16}O_2$ gas source, and quartz gas pipelines. The gas circulation volume is 70 cm^3, with a circulation rate of 170 cm^3/s. The gas signals are recorded by a quadrupole mass spectrometer (MS, Omnistar, Pfeiffer Vacuum). About 30 mg of the sample is placed in the reactor and pre-treated at 300 ºC for 30 min in an $^{16}O_2$ atmosphere, followed by cooling to 50 ºC. Under dynamic vacuum conditions, vacuum pumping is conducted for 30 min to remove excess $^{16}O_2$. Approximately 65.0 ± 1.5 millibars of pure $^{18}O_2$ is introduced into the reaction system. The catalyst is then subjected to a temperature programmed heating up to 600 ºC, while recording changes in the partial pressures of $^{18}O_2$ (P_{36}), $^{16}O_2$ (P_{32}), and $^{16}O^{18}O$ (P_{34}) using mass spectrometry. Additionally, N$_2$ (m/z=28) changes are recorded to detect potential leaks in the vacuum system.
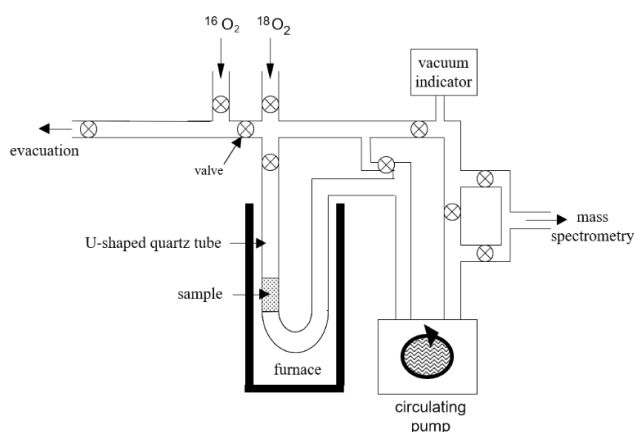
Figure S1. Schematic diagram of the oxygen isotopic exchange experiment

According to Royer[S1] and Martin[S2], the rate of exchange (Re, atom/(g s)) is calculated from the rate of disappearance of ^{18}O from the phase gas at time t :

$$R_e = -2N_g \cdot \frac{d\alpha_g^t}{dt} = 2N_s \cdot \frac{d\alpha_s^t}{dt} \qquad (S1)$$

where N$_g$ and N$_s$ are respectively the total number of oxygen atoms in gas phase and the number of exchangeable oxygen atoms at the oxide surface.

α_g^t and α_s^t are the ^{18}O atomic fraction in the gas phase and the ^{18}O atomic fraction

at the surface at each time.

α_g^t is calculated from the partial pressure of $^{18}O_2$, $^{16}O_2$ and $^{16}O^{18}O$ at each time:

$$\alpha_g^t = \frac{\frac{1}{2} \cdot P_{34}^t + P_{36}^t}{P_{32}^t + P_{34}^t + P_{36}^t} \tag{S2}$$

and N_g is obtained as follows:

$$N_g = \frac{N_A P_t}{R}\left(\frac{V_r}{T_r} + \frac{V_c}{T_c}\right) \tag{S3}$$

where N_A is Avogadro's number, P_T is total pressure, R is the gas constant, V_r and V_c are the volumes of the heated and nonheated parts of the system, T_r and T_c are the temperatures of the heated and nonheated parts of the system.

In the test conditions, the initial rate of exchange was calculated from the initial slopes with respect to time of the partial pressure of $^{18}O_2$ $\left(\frac{dP_{36}^0}{dt}\right)$ and $^{16}O^{18}O$ $\left(\frac{dP_{34}^0}{dt}\right)$:

$$R_e = -\frac{N_A}{R}\left(\frac{V_r}{T_r} + \frac{V_c}{T_c}\right)\left(2\frac{dP_{36}^0}{dt} + \frac{dP_{34}^0}{dt}\right) \tag{S4}$$

The number of exchanged atoms at each time is calculated from the number of ^{18}O atoms at time t:

$$N_e^t = \left(\alpha_g^0 - \alpha_g^t\right)N_g \tag{S5}$$

S2. N$_2$ adsorption-desorption isotherms and BJH pore-size distributions of different samples
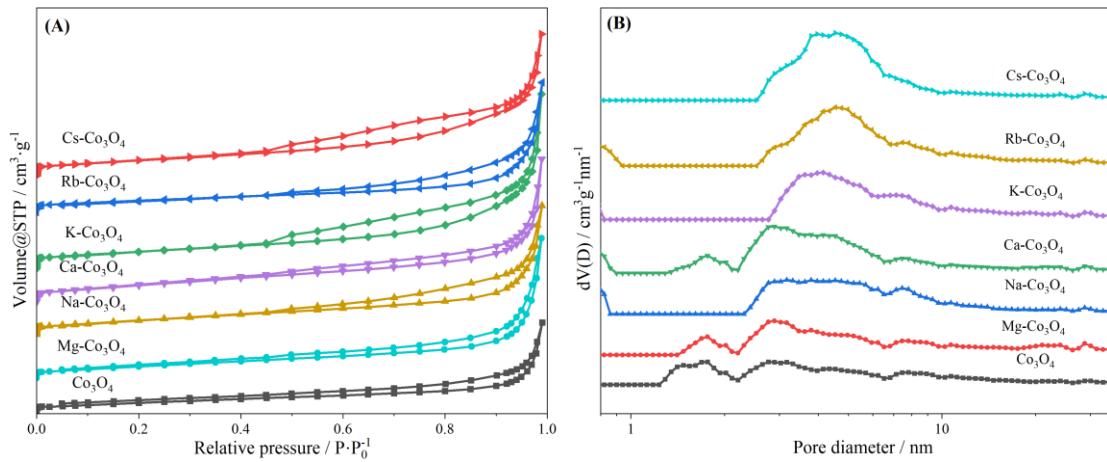
Figure S2. N$_2$ adsorption-desorption isotherms (A) and BJH pore-size distributions

(B) of different samples

References

S1. D. Martin and D. Duprez, *J. Phys. Chem.*, 1996, **100**, 9429-9438.

S2. S. Royer, D. Duprez and S. Kaliaguine, *J. Catal.*, 2005, **234**, 364-375.