**Supplementary:**

**In-situ high-temperature X-ray Diffraction studies of** **reduction of K2CrO4 and the formation of KxCrOy compounds**

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**Supplementary 1: Evolution of XRD patterns during the reduction of K2CrO4**

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Figure S1 (a) The XRD pattern of K2CrO4 at 30 °C; (b) The XRD pattern of K3CrO4 at 480 °C; (c) The XRD pattern of the amorphous intermediate at 520 °C; (d) The XRD pattern of KCrO2+KxCrO2 at 660 °C. (An Ni peak was attributed to the nickel (Ni) boat in the detection).

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Figure S2. Evolution of XRD patterns during the reduction of K2CrO4 in hydrogen at 500 °C for 270 min.

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Figure S3. (a) The XRD pattern of K2CrO4 at a reduction temperature of 30 °C; (b) The XRD pattern of K3CrO4 at a reduction temperature of 500 °C; (c) The XRD pattern of the amorphous intermediate at a reduction temperature of 600 °C for 2 min; (d), (e), (f), (g) The XRD pattern of KCrO2+K0.7CrO2 at a reduction temperature of 600 °C for 30 min, 60 min, 180 min, 270 min, respectively. (An Ni peak was attributed to the nickel (Ni) boat in the detection).

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Figure S4. Evolution of XRD patterns during the reduction of K2CrO4 in hydrogen at 700 °C for 240 min.

**Supplementary 2: The In-situ high-temperature X-ray Diffraction experiment**

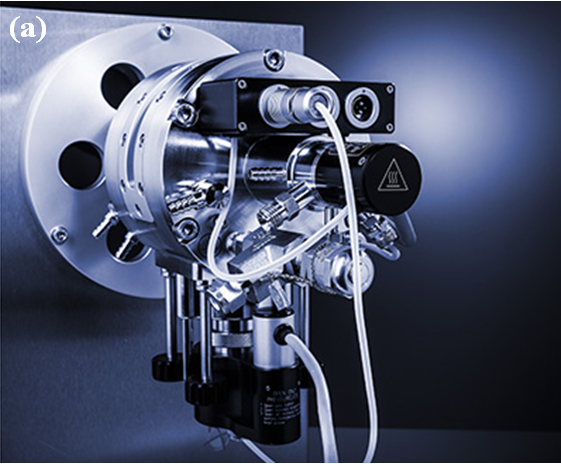
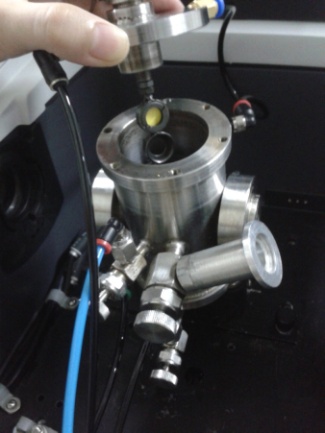
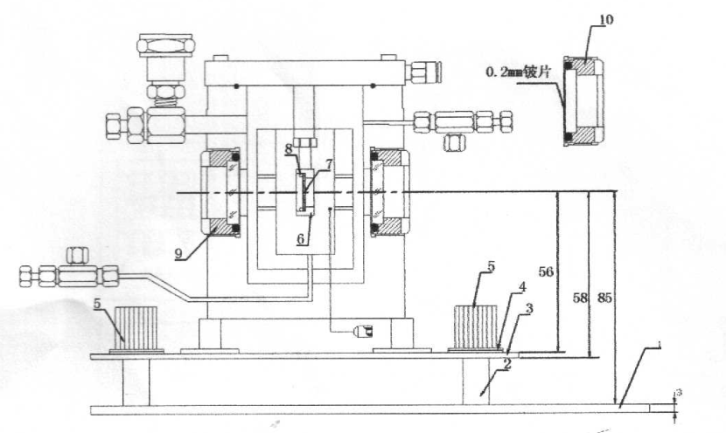
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Figure S5. (a) The In situ X-ray diffractometer; (b)The sample holder.

The In situ XRD experiments were carried out using a SmartLab X-ray diffractometer (a XRK-900 Anton Paar ). A mixture of gas was compose of 3.55% hydrogen and 96.45% helium. The temperature was ranging from 30 to 700 °C. The temperature rise rate was 10 °C /min or 1 °C /min. The holding time was 10min. The pressure was 1atm and the flow rate was 300mL/min.

A machinable “Macor” glass ceramic was used as a sample holder. A very small nickel (Ni) boat was placed on the top of the Macor to preventing the Macor contact with the molten reduction product KOH. The temperature was measured using a thermocouple contacting with the sample holder.

**Supplementary 3: The In-situ high-temperature FTIR experiment**

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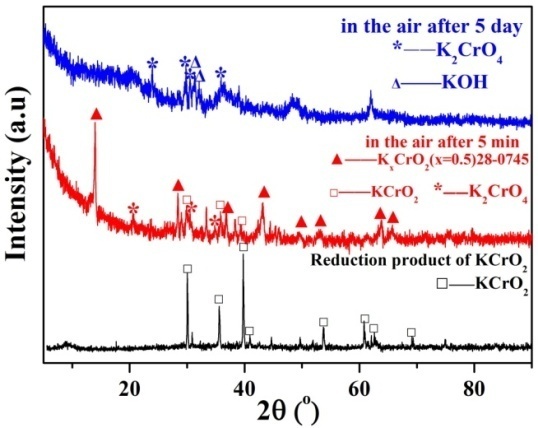
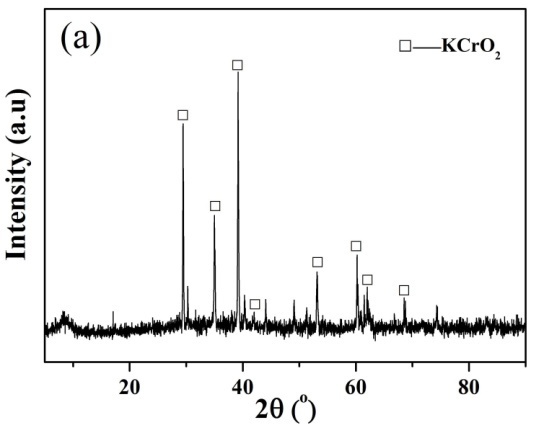
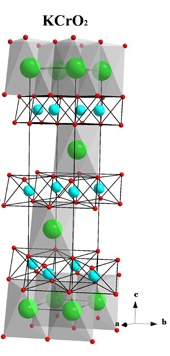
**(b)**

**(a)**

Figure S6. (a) The IR-X-01 In-situ pool; (b)The section view of IR-X-01.

The in situ FT-IR experiments were performed using a Nicolet 6700 FT-IR spectrometer. The pure K2CrO4 sample wafer was then sealed with stainless steel gaskets. A mixture of gas was compose of 3.55% hydrogen and 96.45% helium. From 30 °C to 600 °C, the temperature was increased at 10 °C per minute.

**Supplementary 4: the Characterization of KCrO2**



**(c)**

**(a)**

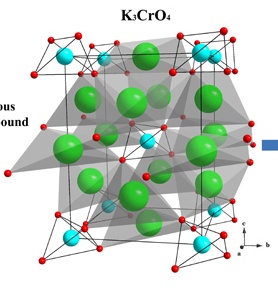
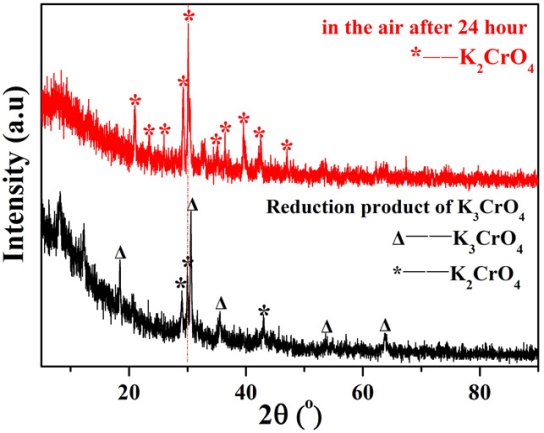
**(b)**

Figure S7. (a) The crystal structure of KCrO2, K (green spheres), Cr (blue spheres), O (red spheres); (b) The XRD data of KCrO2;

(c)The XRD data for the oxidation of KCrO2 in air at a room temperature after 5 min and 5 days.

As shown in Figure S.3 (b), the XRD spectra of the reduction product, shows that all diffraction peaks can be indexed to the rhombohedral KCrO2, indicating that the product has a single crystalline phase. Oxidation reaction of KCrO2 occur naturally at room temperature in air. Figure S. 3(c) shows the XRD results for the oxidation of KCrO2. After exposing to air for 5 min, the KCrO2 is converted to KxCrO2 (0.50≤ x ≤ 0.60) and K2CrO4. The phase transition from K0.5CrO2 to K2CrO4 was observed, and the complete conversion takes place after 5 days in air. Therefore, in an atmosphere of air, the most likely process is the conversion of KCrO2 to K0.5CrO2 and then K0.5CrO2 to K2CrO4. Research on the oxidation of the KCrO2 in air is important for guiding the whole process.

**Supplementary 5: The Characterization of K3CrO4**

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**(b)**

**(a)**

Figure S8. (a)The crystal structure of K3CrO4, K (green spheres), Cr (blue spheres), O (red spheres);

(b) The XRD data for the oxidation of K3CrO4 in air at a room temperature after 24 hours.

The dark-green K3CrO4 is also highly hygroscopic and sensitive, and it is spontaneous oxidation at room temperature. Figure S. 4 (b) shows the XRD results for the oxidation of K3CrO4 in air at room temperature. We found the oxidation of K3CrO4 is an easy process. The diffraction for K3CrO4 completely disappears, whereas the diffraction for K2CrO4 appears. After exposing the K3CrO4 and K2CrO4 system to air for 24 hours, only the K2CrO4 remained.