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## **Methane synthesis from CO<sub>2</sub> and H<sub>2</sub>O using electrochemical cells with polymer electrolyte membranes and Ru catalysts around 120°C: comparative study to phosphate-based electrolyte cell.**

### **Electronic supplementary information**

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### **Characterization of Ru/ZrO<sub>2</sub> catalysts**

The Ru/ZrO<sub>2</sub> catalysts used in this study was prepared as same as those in our reference.<sup>8</sup> Transmission electron microscope (TEM) image for 10 wt%-Ru/ZrO<sub>2</sub> is shown in Fig. S1. This image was obtained by JEOL JEM-2100F TEM. While Zr and Ru are both elements in the fifth period of the periodic table, there is relatively weak contrast. Nevertheless, it is possible to observe the dispersion of Ru particles that are several nanometers in size on the ZrO<sub>2</sub> particles of about 20 nm in diameter. In the referennce<sup>8</sup> energy-dispersive-X-ray spectroscopy mapping and TEM images for Ru catalysts supported by other oxides are demonstrated. Considering all these results, it can be concluded that Ru nanoparticles are uniformly dispersed on ZrO<sub>2</sub>. Refer to the referennce<sup>8</sup> for details.

X-ray diffraction (XRD) measurements were conducted for a sample of 10 wt%-Ru/ZrO<sub>2</sub>, as shown in Fig. S2. The reference patterns for monoclinic- and tetragonal-ZrO<sub>2</sub> and metallic Ru are also shown in Fig. S2. These measurements were carried out using a Shimazu XRD-6100 instrument. The XRD pattern primarily displayed peaks corresponding to monoclinic and tetragonal ZrO<sub>2</sub> lattices, indicating that the ZrO<sub>2</sub> particles comprised a mixture of monoclinic and tetragonal phases. Notably, no discernible peaks associated with elemental Ru were observed, despite the catalyst containing 10 wt%-Ru. This absence of Ru peaks can be attributed to the formation of nanometer-sized Ru particles on the ZrO<sub>2</sub> support, resulting in broad and weak diffraction signals. It's important to note that the XRD measurements were performed after the catalysts were exposed to atmospheric air, and the oxidation of Ru surfaces hindered the clear observation of any diffraction patterns assignable to Ru.

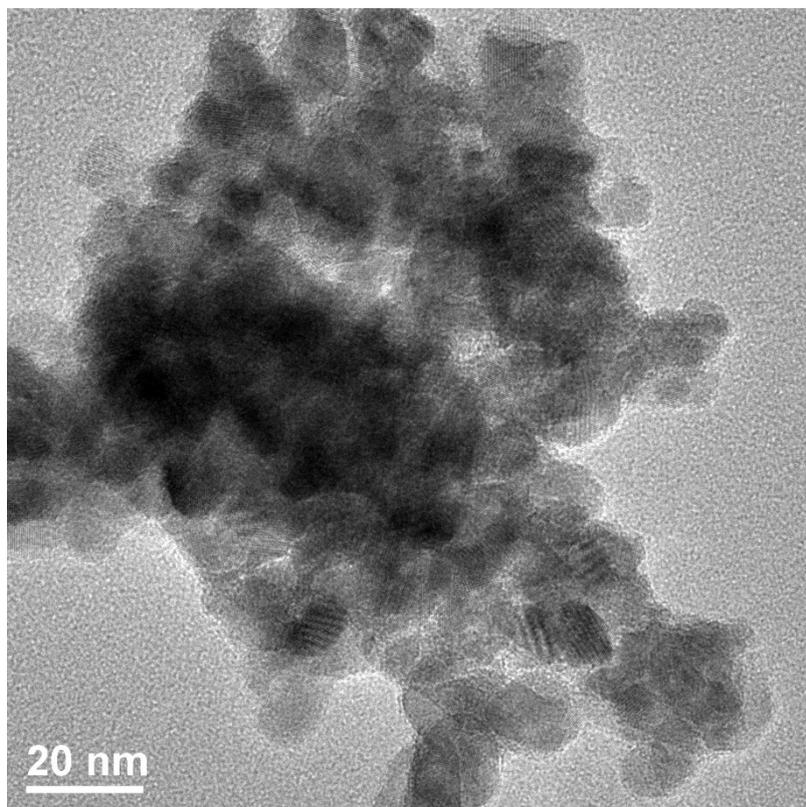


Fig. S1 Transmission electron microscope image of 10 wt%-Ru/ZrO<sub>2</sub>.

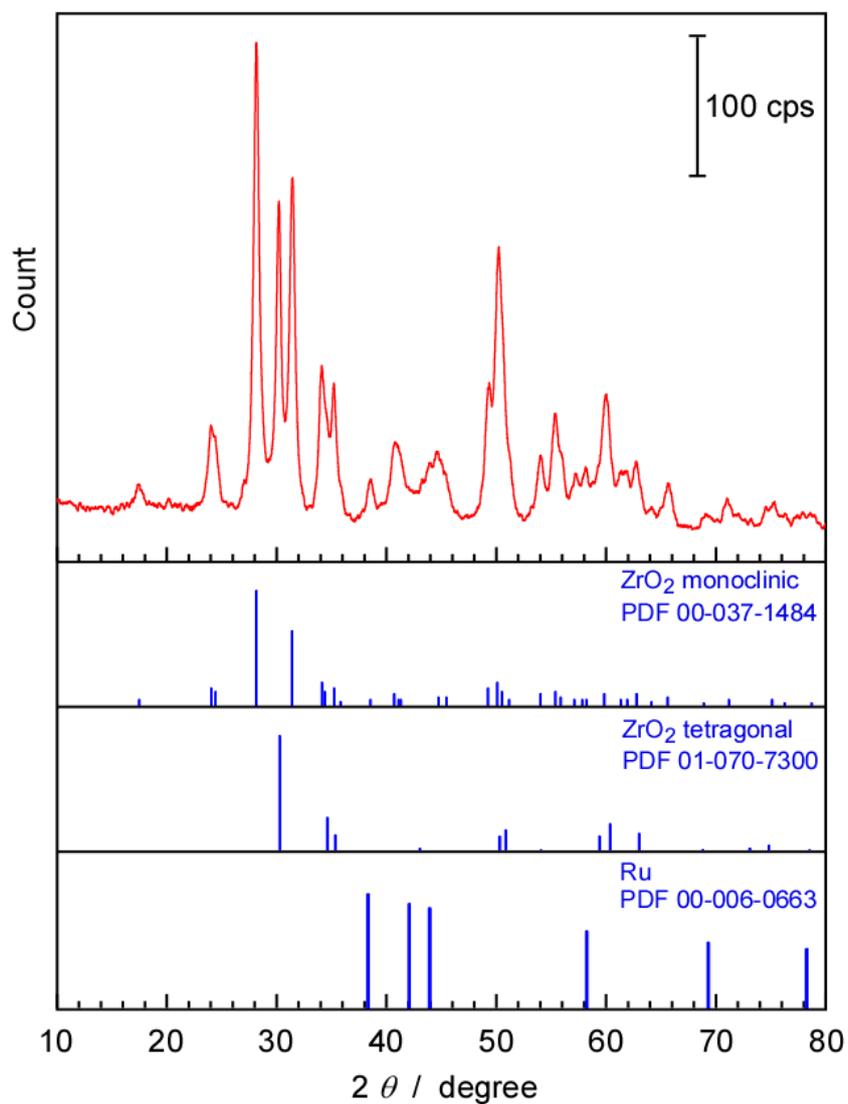


Fig. S2 X-ray diffraction pattern of 10 wt%-Ru/ZrO<sub>2</sub>.