

Atomically Dispersed Ru Catalysts for Polychlorinated Aromatic Hydrocarbons

Oxidation

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General Information

Chemicals

WO₃ (Aladdin, 99.8%), WCl₆ (Aladdin, 99%), NbCl₅ (Aladdin, 99%) and ethanol (AR) were purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. (Tianjin, China), RuCl₃, H₂PtCl₆·6H₂O and PdCl₂ (Kemat Chemical Technology Co. Ltd., 99%). *o*-DCB and Toluene (Rhawn, 99.8%). All the chemicals were used as-received without further purification.

Experiments

In X-ray diffraction (XRD), the instrument was operated in the continuous mode at 40 kV and 100 mA to collect data in the 2θ range of 5° to 90° with a step size of 0.02°, and the scanning speed was 15°/min. TEM and HRTEM images were obtained from a JEM-2100 transmission electron microscope under the acceleration voltage of 200 kV. ac-HAADF-STEM images and Ce M4,5-edge EELS spectra were collected from FEI Titan 80-300 electron microscope equipped with a Gatan Enfium camera system. The XAS of Ce L3-edge was collected on the beamline 7-3 in Stanford Synchrotron Radiation Lightsource (SSRL). PALS spectra were recorded using a fast108 slow coincidence system at room temperature. X-Ray photoelectron spectroscopy (XPS) was tested by ThermoFischer, ESCALAB250Xi with the excitation source was Al Kα ray (HV = 1486.6 eV). All the spectra were calibrated using C 1s = 284.6 eV. H₂-temperature-programmed reduction (H₂-TPR) was carried

as the following procedure: 100 mg sample was pretreated at 300 °C and was then purged by He for 2 h. After cooling to 50 °C, 10% H₂/Ar mixture (50 ml/min) was used for 0.5 h until the baseline is stable. The sample was then treated at 850 °C at a heating rate of 10 °C /min in the 10% H₂/Ar flow. In CO-temperature-programmed desorption (CO-TPD), 100 mg sample was firstly pretreated at 200 °C and was then purged by He flow (30 ml/min) for 1 h. After cooling to 50 °C, 10% CO/He mixture (30 ml/min) was used for adsorption for 1 h until saturated followed by purging for another 1 h by He flow, and the desorption gas was detected by a thermal conductivity detector (TCD). Inductive coupled plasma (ICP) was tested by Agilent ICP-OES 700. Before testing, 5 mL concentrated nitric acid and 2 mL hydrochloric acid were added to the sample and heated at 180 °C for about 8 h.

In situ FT-IR on *o*-DCB reaction was recorded on a Bruker TENSOR II equipped with MCT detector and supported. All spectra were collected with a resolution of 4 cm⁻¹ in a CRCP-7070 IR cell. The sample was in the form of a thin self-supported wafer, approximately 10 mg in weight. The samples were pre-treated in vacuum before collecting background spectrum at 300 °C. During each test, *o*-DCB with 10% O₂/N₂ was introduced, and the spectra were recorded at 100, 150, 200, 250, 300 °C. All the spectra were analysed by subtracting the background.

Kinetic study

The conversion of *CB* (*x*) (the abbreviation of *o*-DCB) can be calculated by the following equation:

$$x (\%) = \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}}\right) \times 100\% \quad (1)$$

Where C_{in} is the initial concentration of *CB*, C_{out} is the *CB* concentration in the outlet gas.

The rate of catalytic oxidation of *CB*, r , can be expressed by the following equation:

$$r = -\frac{d[CB]}{dt} = k[CB]^n [O_2]^p \quad (2)$$

Where $[CB]$ and $[O_2]$ are the concentration of *o*-DCB and O₂, respectively; k is the

apparent rate constant of the reaction. Since $[O_2] \gg [CB]$, the Eq. (3) can be rewritten as follows:

$$r = -\frac{d[CB]}{dt} = k_{ap}[CB]^n \quad (3)$$

Suppose this reaction obeys a first-order rate law, combining Eq. (1) and Eq. (3), and solving the resulting differential equation leads to Eq. (4):

$$\ln[1/(1-x)] = k'_{ap}\tau \quad (4)$$

Where τ is the space time (s) and is defined as the reciprocal of the space velocity.

The apparent activation energy of the catalytic oxidation of *CB* over the two catalysts as calculated according to the Arrhenius equation (Eq. (5)):

$$\ln \frac{k'_{ap1}}{k'_{ap2}} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (5)$$

Where k'_{ap1} and k'_{ap2} are the apparent rate constants at T_1 and T_2 , respectively, s^{-1} ; E_a is the apparent activation energy, kJ/mol; and T_1 and T_2 are the reaction temperatures, K.

The specific rates, r_{CB} , of 0.2 Ru ADCs and 0.2 Ru NPs were also compared based on equation (6):

$$r_{CB} = \frac{X}{m_{NM}} \times f_{CB} \quad (6)$$

Where m_{NM} is the mass of precious metals obtained by ICP analysis, f_{CB} is the molar gas velocity, mol h⁻¹; x is the conversion rate of *CB*.

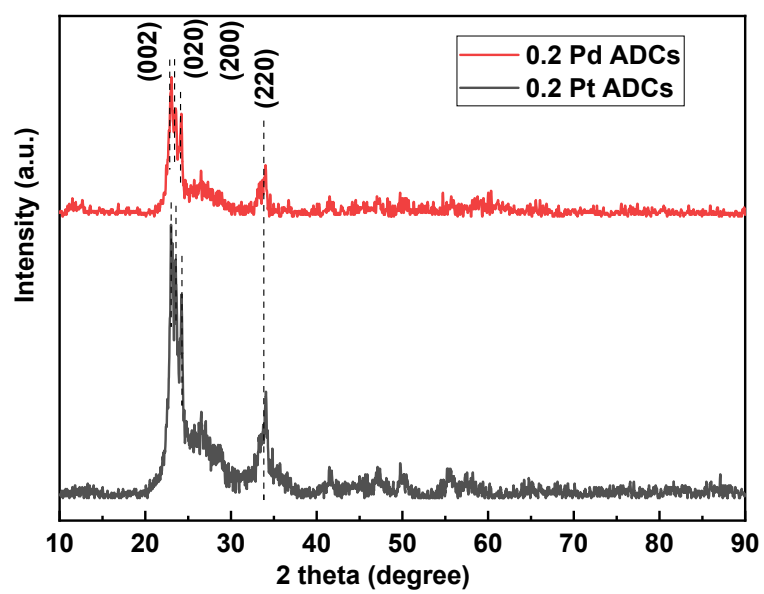


Fig. S1 XRD spectra of 0.2 Pd ADCs and 0.2 Pt ADCs.

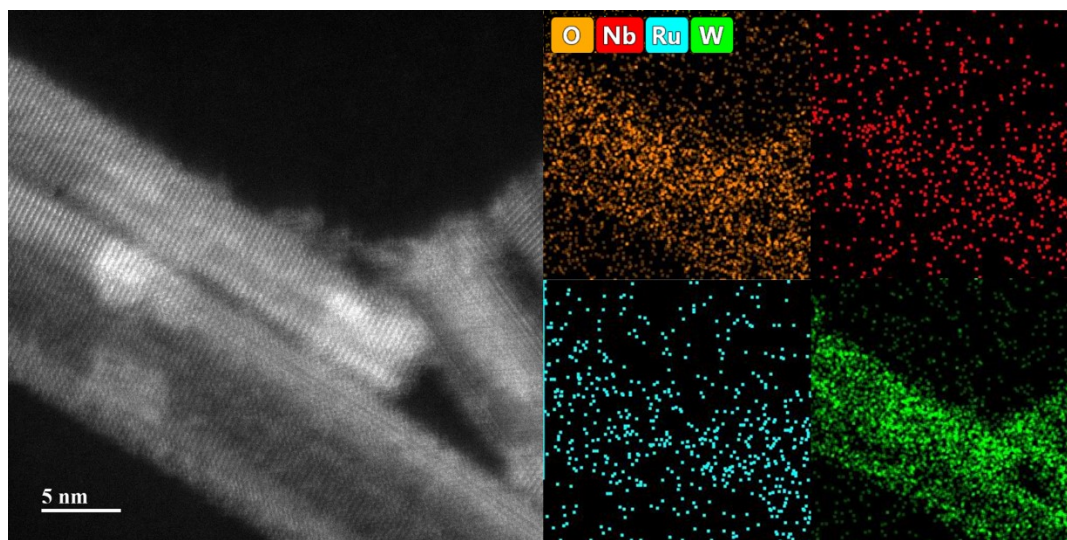


Fig. S2. ac-HAADF-STEM and EDS images of Ru NPs.

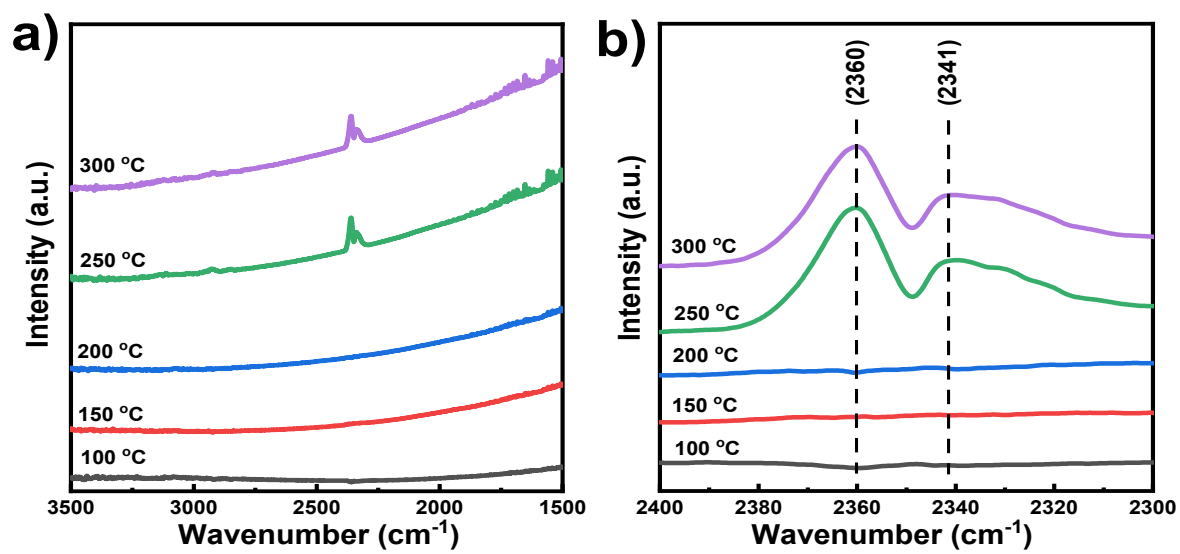


Fig. S3. *In-situ* FT-IR spectra of 0.2 Ru ADCs at different temperatures after 30 min.

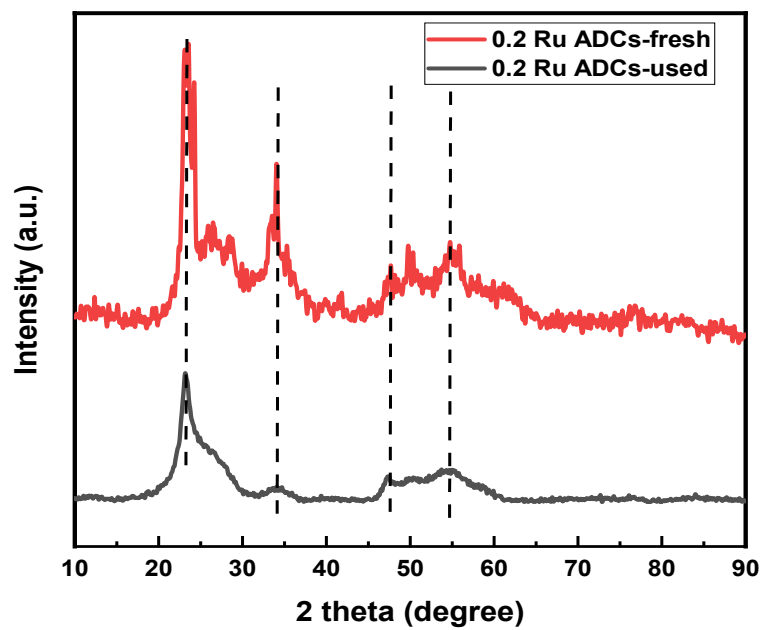


Fig. S4. XRD spectra of fresh 0.2 Ru ADCs and used 0.2 Ru ADCs.

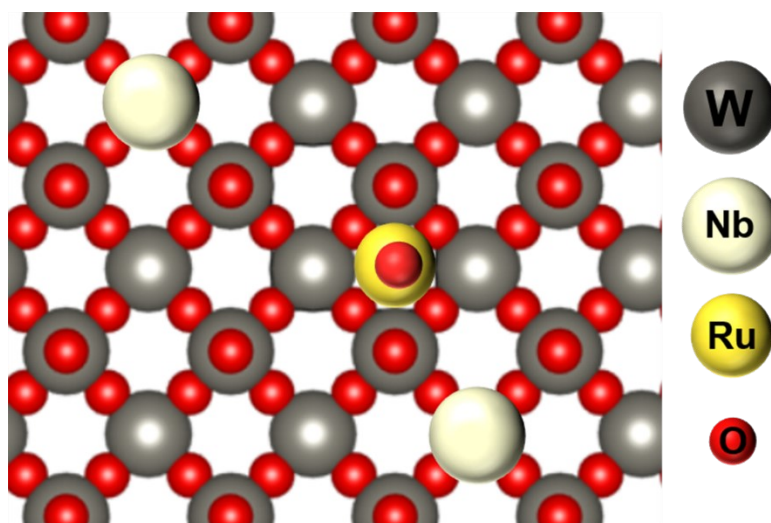


Fig. S5. Proposed crystal structure of atomically dispersed Ru supporting on Nb-WO_x.