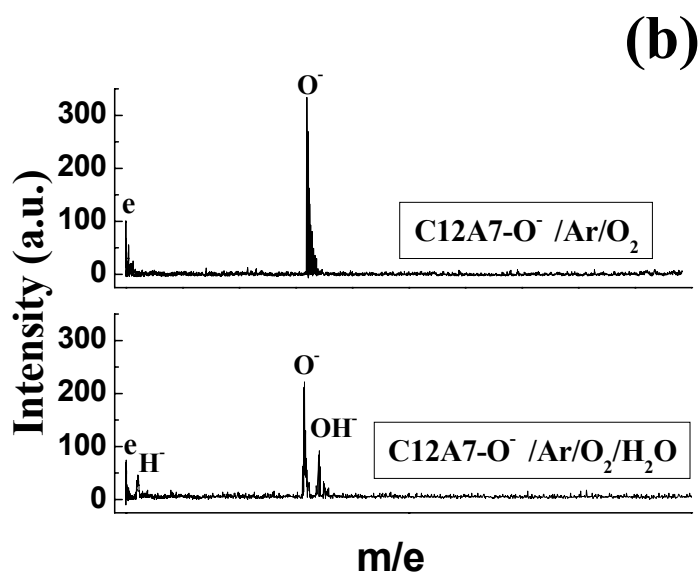
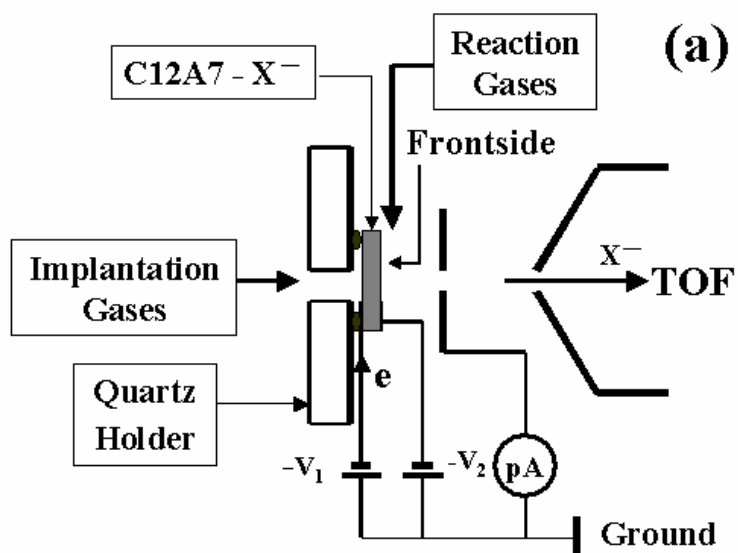
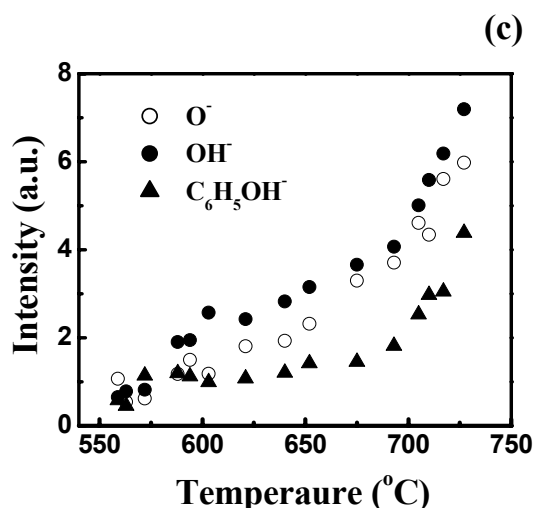


Supplementary Information

(1) The setup of TOF measurements and emission features of C12A7-O⁻





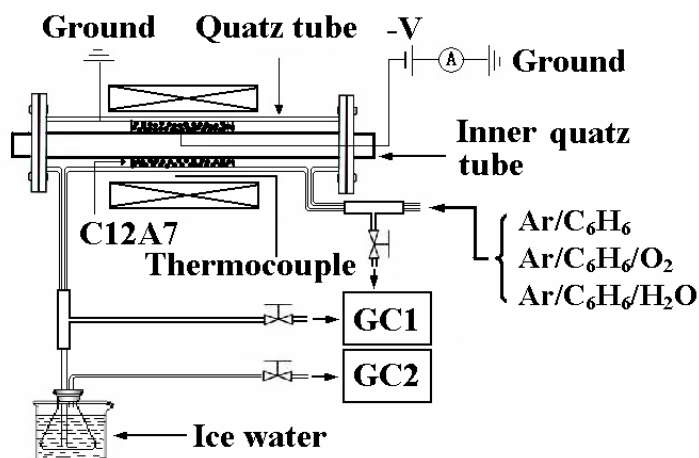
(a) Schematic diagram of the experimental setup for measuring the emitted anionic species from the C12A7-O⁻ surface and the anionic intermediates in the phenol synthesis. Sustainable anions X⁻ (X=O and OH) were obtained by implanting mixed-gas (Ar/O₂ or Ar/O₂/H₂O) and electrons to the backside of the C12A7-O⁻ sample (backside: opposite to TOF spectrometer). The emitted anionic species were analyzed by a time of flight (TOF) spectrometer. Absolute emission intensity of anions was determined by the relative intensity distribution of anions and total emission current measured by a picoammeter. The reactant of benzene was fed onto the front-side surface (the side facing the TOF spectrometer) of C12A7-O⁻ by a nozzle. The anionic intermediates formed by the surface reactions were detected by the TOF spectrometer.

(b) Anion emission spectra from C12A7-O⁻. The upper panel: implanting the mixed-gas (Ar/O₂=0.95:0.05) and electrons to the backside of the

C12A7-O⁻ sample; the bottom panel: implanting the mixed-gas (Ar/O₂/H₂O=0.75:0.05:0.20) and electrons to the backside of the C12A7-O⁻ sample. Implantation pressure: 2.0 torr; implantation current: 0.3 ± 0.1 mA; sample temperature: 923 K. When we implanted the mixed-gas Ar/O₂ and electrons to the backside of the C12A7-O⁻ sample, there are two peaks with the respective mass number of 16 and 0, which correspond to strong O⁻ and weak electrons, as shown in the upper panel. When we implanted the mixed-gas Ar/O₂/H₂O and electrons to the backside of the C12A7-O⁻ sample, the anionic species emitted from the C12A7-O⁻ sample are quite different, as shown in the bottom panel. Besides the peaks of O⁻ and electrons, two new peaks appear around the respective mass number of 1 and 17, which are attributed to the anions of H⁻ and OH⁻.

(c) The relative intensity of the anions O⁻, OH⁻, C₆H₅OH⁻ as a function of the sample surface temperature in the reaction system C₆H₆/O₂/H₂O/Ar/C12A7-O⁻. The mixed-gas (O₂/H₂O/Ar=0.05:0.20:0.75) was implanted to the backside of the C12A7-O⁻ sample. The reaction gas (benzene: 3 × 10⁻⁴ torr) was fed onto the frontside surface of the C12A7-O⁻ by a nozzle. With increasing the sample temperature, the intermediate C₆H₅OH⁻ formed increased significantly, which was similar to the temperature effects on the benzene conversion.

(2) The setup of the double-tube type reactor used for phenol synthesis.



A double-tube type reactor for phenol synthesis, operated in continuous flow condition at 1 atm. Typically, the reactor, containing 3 g of the C12A7-O⁻ sample on the surface of an inner quartz tube (16 mm of o.d.), was connected to an ice-cooling condenser. Benzene bubbled by argon gas or other mixed-gas was fed to the sample between the inner and outer tubes (the gap: 2.5 mm). The temperature was measured by a thermocouple placed near the heater around the outer tube and the temperature had been calibrated by another thermocouple placed in the catalyst. The reactants and products were analyzed by two gas chromatograms (GC1 and GC2). Benzene before and after reaction and the products beside CO and CO₂ were detected by GC1. Products of CO and CO₂ were detected by GC2. In order to continuously form O⁻ and OH⁻, Ar/O₂ and Ar/O₂/H₂O together with electrons (supplied by a negative dc

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power with a current of 0.3-0.4 mA) were fed to the sample.