Application of alkali metal-doped carbons for recovery and isotope separation of hydrogen gas

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Alkali metals are able to intercalate graphite expanding carbon-carbon interlayer distance along c-direction [1]. The resulting compound, for example RbC_{24}, has nanospace, whose size is comparable to those of small molecules such as hydrogen, nitrogen, methane, etc. Watanabe et al. [2,3] found out that MC_{24} (M = K, Rb, Cs) is able to absorb hydrogen up to saturated composition of $MC_{24}(H_2)_2$ at 77 K. In addition, they found a large isotope effect in the absorption of hydrogen (H_2) and deuterium (D_2) by potassium-intercalation compounds. Terai and Takahashi [4,5] claimed that potassium-doped carbons having disordered structure are advantageous for the hydrogen-isotope separation.

On the other hand, a variety of carbon allotropes such as fullerenes, carbon nanotubes, etc. has been discovered in recent 25 years. Particularly, multi wall carbon nanotube (hereafter abbreviated as MWCNT) has characteristic curved carbon layer stacking. Therefore, we can expect intercalation of alkali metals into MWCNT. This is already confirmed by several researchers [6-8]. For example, Suzuki and Tomita [6] obtained second-stage potassium intercalated MWCNT by contacting potassium to MWCNT at room temperature under ultra high vacuum such as 2×10^{-8} Pa. Therefore, we have expectation that alkali metal-doped MWCNT also absorb molecules in their nanospace. This paper describes H_2- and D_2-sorption behavior of Rb- and K-doped carbons with different graphitization degree and MWCNT at 77 K for promoting application of these materials as hydrogen-recovery and isotope-separation agent.

Three types of carbon materials were used: Grafoil (exfoliated graphite sheet, GrafTech Int. Ltd. Company), carbons derived from petroleum cokes heat treated at different temperatures of 1000 and 1500°C and MWCNT prepared at National Institute of Advanced Industrial Science and Technology Tsukuba, containing a few % of Co as impurity. Rubidium (Nacalai tesque with purity of 99.5%) was used without further purification and potassium (Nacalai tesque with purity of 98%) was used after distillation.

Alkali metal and carbon sample were weighed in the ratio of a target compound. They were placed in a glass tube separately and heat-treated at 230°C for several days under vacuum. Raman spectroscopy was used to check the structure change. The Raman experiments were performed at room temperature using a JASCO Corporation NRS-3000 series for E_{laser}=2.33eV (532nm) excitations. X-ray diffraction measurements (hereafter abbreviated as XRD measurements) were also performed for several samples using a Bruker AXS K. K. MXP3 system with CuKα radiation. In the hydrogen-sorption experiment a sample was set in the sorption equipment and the sorption isotherms for H_2 and D_2 were determined at 77 K by the constant volume method.

The H_2-sorption isotherm of RbC_{24} (Grafoil) is classified into the Langmuir type, as already reported by Watanabe et al. [2], characterized by the steep increase of sorption at very low equilibrium pressure. The observed values of equilibrium pressure, p_{eq}, at half coverage were 40Pa and 260Pa for RbC_{24}(Grafoil) and RbC_{24}(MWCNT), respectively. RbC_{24} (Grafoil) can be considered as a candidate for recovering agent of H_2 at low pressure.

The Raman spectra of MWCNT and carbons (HTT-1000 and -1500) are shown in Fig. 1, where those of derived KC_{10} samples are also shown comparatively. For the host carbons, large D band signals are observed at around 1360 cm^{-1} and the G band signals (at around 1580 cm^{-1}) are overlapped with D' band signal (at around 1620 cm^{-1}), indicative of random structure of these samples. The Raman spectrum of KC_{10} (MWCNT) was similar to that of starting MWCNT. The signals were observed at relatively lower wave number. It can be considered that almost no charge transfer interaction between potassium and MWCNT exists. On the other hand, Raman spectra of KC_{10} (carbons with HTT-1000 and -1500) are quite different from those of host carbons, i.e. typical step at around 1550 cm^{-1} can be seen. This signal is the same with that observed for stage 1 potassium-graphite intercalation compounds [9]. In addition, the difference of color of the KC_{10} samples supports the above observation. There was no change in color for MWCNT along with potassium-doping, but change from black to brownish black for carbon (HTT-1000) by the potassium-doping was confirmed. This color change is an indirect proof of charge transfer [10].

In the H_2- and D_2-sorption isotherms of KC_{10} samples, the isotope effect can be seen for all the samples. The isotope-separation coefficient was calculated according to the method reported by Terai and Takahashi [4]. A very large isotope effect was observed also for KC_{10} (MWCNT).

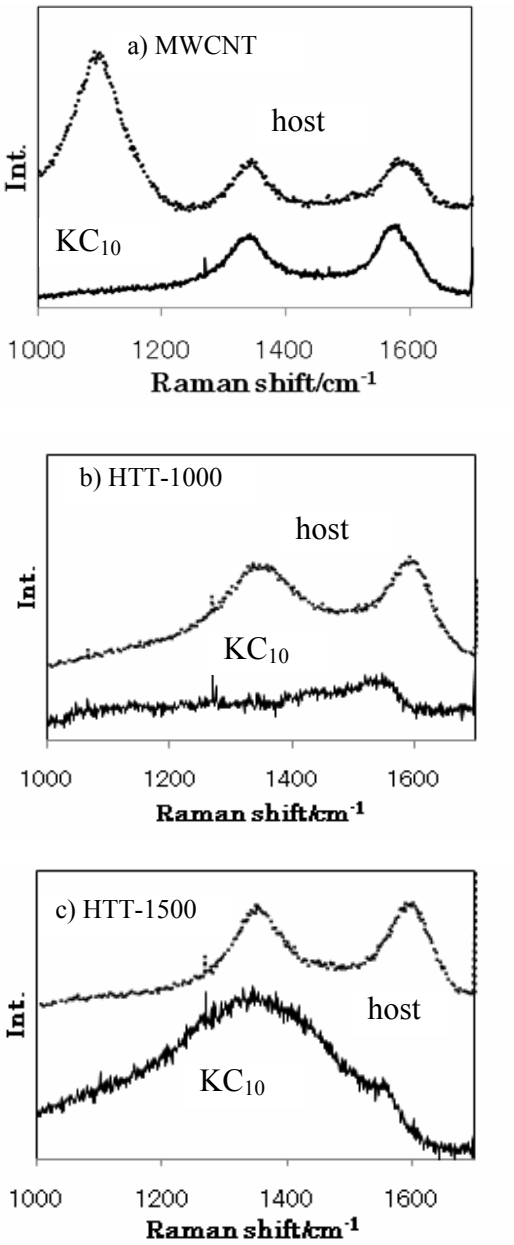

Fig. 1 Raman spectra of carbons and derived KC_{10} samples.

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