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Supplementary Information

Enhanced hydrogen spillover to fullerene at ambient temperature

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Sample preparation

We have selected ketjenblack (KB; EC600JD, Lion) as a carbon support for Pt and C_{60}. KB is a well-known carbon black which is commercially available and widely used as a conductive additive. Unlike activated carbons with complicated structures and inorganic impurities, KB has a simple spherical shape free from inorganic impurities, which makes experiments reproducible and reliable.

First, Pt nanoparticles were dispersed in KB (Fig. 1a to b). Specifically, dried KB was impregnated with methanol (40 ml) under vacuum. After recovering normal pressure with N_2, a solution of $Pt(NH_3)_2(NO_2)_2/HNO_3$ (Tanaka Kikinzoku Kogyo Co. Ltd.) diluted with water (ca. 200 ml) was added, and the mixture was refluxed at 358 K for 6 h to reduce $Pt(NH_3)_2(NO_2)_2$ into Pt,[2, 3] at the form of dispersed nanoparticles with the size of ca. 1-3 nm (Fig. 1f). The weight ratio of Pt in the starting solution was adjusted to be Pt:KB = 1:99. The solid product was then filtered, washed with pure water, and dried at 423 K for 6 h under vacuum to obtain Pt-loaded KB (Pt/KB). Pt/KB indeed contains 0.89 wt% of Pt, which was determined by inductively coupled plasma-optical emission spectrometry. Next, C_{60} was dispersed on Pt/KB by liquid phase adsorption (Fig. 1b to c). Pt/KB (0.32 g) was mixed with a C_{60}/toluene solution (1 mg/ml, 40 ml) and the mixture was stirred at 298 K for 24 h. After filtration and drying at 423 K for 6 h under vacuum, C_{60}-loaded Pt/KB (C_{60}-Pt/KB) was obtained. The adsorption amount of C_{60} was determined to be 8.8 wt% (in C_{60}-Pt/KB), from the C_{60}/toluene concentration change monitored by UV-VIS measurement.

Hydrogen adsorption-desorption measurement

H_2 isotherms were measured on Pt-loaded samples at 273, 298, 323, and 353 K with a static volumetric technique using a MicrotracBEL BELSORP-max. The pressure range of the measurements was below 103 kPa, which is free from the problem of leaking. Though it is generally not easy to obtain reliable data of H_2 physisorption isotherms, we have developed a reliable protocol reported in our previous paper.[1] H_2 adsorption amount on a porous material is generally very small, and this causes a noticeable error. Therefore, a large amount of sample (ca. 300 mg) was used to increase the total adsorption amount. Before each measurement, degassing pretreatment was carried out at 423 K for 6 h, by using the BELSORP-max instrument, and after the degassing step, measurement was immediately started without exposure of the sample to any gas or air. This procedure is very important to avoid adsorption of gases other than H_2, such as N_2, O_2, H_2O, and He; otherwise desorption of these gases could affect the results. Therefore, the dead-volume of the sample vessel was measured with He-probe after finishing the H_2 measurement. We have previously demonstrated a good reproducibility of the isotherm measurement on a Pt-loaded carbon according to this procedure.[1]

Calculation for the amount of physisorption H_2 and spillover H to KB

Hereafter, Pt/KB and C_{60}-KB/Pt composites are denoted composite 1 and 2, respectively. Specific surface areas (S_α) of KB and these composites are denoted S_{KB}, S_{cp1}, and S_{cp2}, respectively.

By the method explained in Fig. 3d, the net physisorption amount of H_2 in the composite 1 at 100 kPa and T [K], $M_{\mathrm{phys\text{-}cp1}}(100,T)$ [μmol-H_2 g^{-1}-composite1], can be obtained as follows.

$$M_{\mathrm{phys\text{-}cp1}}(100,T) = M_{\mathrm{phys\text{-}KB}}(100,T) \times (S_{\mathrm{cp1}}/S_{\mathrm{KB}}) \qquad (1)$$

where $M_{\mathrm{phys\text{-}KB}}(100,T)$ is experimentally obtained physisorption amount of H_2 on KB at 100 kPa and T [K]. As shown in the following section, the contribution of the Pt surface in Pt/KB is negligible. Therefore, the number of physisorbed H_2 on a 1 nm^2 area of KB surface, $N_{\mathrm{phys\text{-}KB}}(100,T)$ [nm^{-2}], can be estimated by the following equation.

$$N_{\mathrm{phys\text{-}KB}}(100,T) = \{M_{\mathrm{phys\text{-}cp1}}(100,T)\times 10^{-6}\}\times N_{\mathrm{A}} \,/\, \{S_{\mathrm{cp1}}\times 10^{18}\} \qquad (2)$$

At T = 298 K, $N_{\mathrm{phys\text{-}KB}}(100,298)$ is obtained as 0.014 nm^{-2}.

On the other hand, the spillover storage amount in the composite 1 at 100 kPa and T [K], $M_{\mathrm{spill\text{-}cp1}}(100,T)$, can be obtained as follows.

$$M_{\mathrm{spill\text{-}cp1}}(100,T) = M_{\mathrm{total\text{-}cp1}}(100,T) - M_{\mathrm{chem\text{-}cp1}}(T) - M_{\mathrm{phys\text{-}cp1}}(100,T) \qquad (3)$$

where $M_{\mathrm{total\text{-}cp1}}(100,T)$ and $M_{\mathrm{chem\text{-}cp1}}(T)$ are experimentally obtained total H_2 uptake amount at 100 kPa and chemisorption amount, respectively, on the composite 1 at T [K]. Since the contribution of the Pt surface in Pt/KB is negligible, the number of spillover H on a 1 nm^2 area of KB surface, $N_{\mathrm{spill\text{-}KB}}(100,T)$ [nm^{-2}], can be estimated by the following equation.

$$N_{\mathrm{spill\text{-}KB}}(100,T) = \{2M_{\mathrm{spill\text{-}cp1}}(100,T)\times 10^{-6}\}\times N_{\mathrm{A}} \,/\, \{S_{\mathrm{cp1}}\times 10^{18}\} \qquad (4)$$

At T = 298 K, $N_{\mathrm{spill\text{-}KB}}(100,T)$ is obtained as 0.0041 nm^{-2}. Thus, it is found that the spillover amount is much lower than the physisorption amount on KB at 100 kPa and 298 K.

Surface area of Pt

To estimate the surface area of Pt in composite 1, we first determined areal H_2 chemisorption amount on Pt (μmol m^{-2}). Platinum black (PT-354011, Nilaco) was used as a standard material. N_2 adsorption-desorption isotherms and H_2 adsorption isotherm were measured at 77 K and 298 K, respectively, on an automatic adsorption analyzer (BELSORP MAX, Microtrac BEL Corp.), as shown in Fig. S1. The Brunauer-Emmett-Teller (BET) surface area was calculated form the adsorption branch of Fig. S1a to be 18.3 $m^2\ g^{-1}$. The chemisorption amount of H_2 was obtained to be 0.157 mmol g^{-1}, as the intercept of the plots above 10 kPa in Fig. S1b. By dividing the chemisorption amount by the surface area, the areal H_2 chemisorption amount on Pt, $A_{\text{chem-Pt}}$, was obtained as 8.6 μmol-H_2 m^{-2}-Pt.

The chemisorption amount of H_2 on composite 1 at 298 K ($M_{\text{chem-cp1}}$) is obtained to be 9.5 μmol-H_2 g^{-1}-composite1 by taking an intercept of the isotherm plots ranging above 10 kPa. Therefore, the surface area of Ptin the composite 1 ($S_{\text{Pt-cp1}}$) is calculated as follows:

$$S_{\text{Pt-cp1}} = M_{\text{chem-cp1}}/A_{\text{chem-Pt}} = 1.1\ \text{m}^2\text{-Pt g}^{-1}\text{-composite1} \tag{5}$$

It is very small compared to the total surface area of composite 1 (1192 $m^2\ g^{-1}$).

By the similar method, the surface area of Pt in the composite 2 ($S_{\text{Pt-cp2}}$) is obtained as 0.4 m^2-Pt g^{-1}-composite2. Therefore, we ignore the surface area contribution of Pt in composite 1 and 2, in the following discussion.

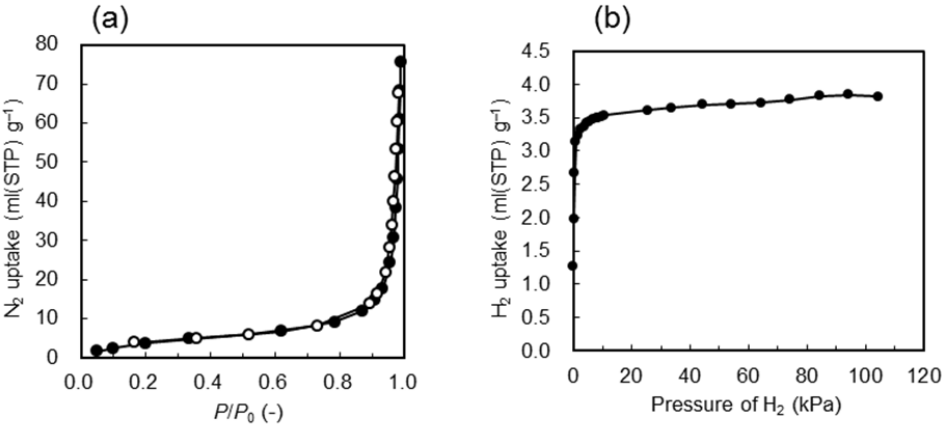

Fig. S1 (a) N_2 adsorption-desorption isotherms of Pt black measured at 77 K. (b) The corresponding H_2 adsorption isotherm measured at 298 K.

Calculation for the amount of spillover H to C_{60} in C_{60}-Pt/KB

The diameter of C_{60} including van der Waals radius is 1.0 nm. Therefore, the specific surface area of a single C_{60} molecule (S_{C60}) can be calculated to be 2625 m^2 g^{-1}, by dividing the surface area of a 1-nm-diameter sphere with the weight of a C_{60} single molecule. Since 0.088 g of C_{60} is included in 1 g of the composite 2, the total molecular surface area of C_{60} ($S_{C60\text{-}cp2}$) in the composite 2 is estimated as follows:

$$S_{C60\text{-}cp2} = 0.088 \times S_{C60} = 231\ \mathrm{m^2\text{-}C_{60}\ g^{-1}\text{-}composite2} \qquad (6)$$

Note that this is the entire value for all the C_{60} existing in the composite 2 regardless of its dead-surface areas generated by attaching to substrate and aggregations of C_{60}. The actual surface area of C_{60}, which can be measured by the N_2 adsorption technique, is much lower than $S_{C60\text{-}cp2}$. This can be understood by the following calculation. If C_{60} occupies 231 m^2 g^{-1} of surface area in the composite 2, KB occupies 962 – 231 = 731 m^2 g^{-1}. It is too smaller than the original surface area of 1273 m^2 g^{-1}, and such a large drop cannot be explained by the mild conditions for Pt-loading as well as for C_{60}-loading. Thus, the actual surface area occupied by C_{60} should be much smaller than $S_{C60\text{-}cp2}$. Nevertheless, using $S_{C60\text{-}cp2}$ as the maximum surface area of C_{60} can yield an interesting estimation, as shown later.

Next, the spillover storage amount of H on C_{60} is estimated. If the areal storage amounts of H on Pt/KB and C_{60}-Pt/KB are the same, the spillover storage amount should be proportional to their surface areas. Thus, from M_{spill}(100 kPa) in Pt/KB and the surface areas of the two composites, M_{spill}(100 kPa) in C_{60}-Pt/KB is estimated to be 3.26 μmol-H_2 g^{-1} at 298 K. However, the actual value is 12.26 μmol-H_2 g^{-1} as shown in Fig. 3f. Thus, the difference of these two values, $M_{spill\text{-}C60}(100,298)$ = 9.00 μmol-H_2 g^{-1}, can be considered the H uptake on C_{60} at 100 kPa and 298 K.

The areal storage amount of spillover H on C_{60} at 100 kPa and T [K], $N_{spill\text{-}C60}(100,T)$, can be obtained by the following equation.

$$N_{spill\text{-}C60}(100,T) = \{2N_{spill\text{-}C60}(100,T)\times10^{-6}\}\times N_A\ /\ \{S_{C60\text{-}cp2}\times10^{18}\} \qquad (7)$$

At T = 298 K, $N_{spill\text{-}C60}(100,298)$ is 0.047 nm^{-2}. Note that this is the minimum estimation obtained with the probable maximum surface area of C_{60}, $S_{C60\text{-}cp2}$. In the actual surface area of C_{60} is lower than $S_{C60\text{-}cp2}$ because there is dead-surface area caused by attaching KB or aggregation of C_{60}. Additionally, there are two pathways for hydrogen spillover to C_{60}: directly [Fig. 1d (2)] and by the secondary spillover[4] [Fig. 1d(2')]. If the latter is much less active than the former, $N_{spill\text{-}C60}(100,298)$ could be further underestimation.

Since the diameter of C_{60} is 1.0 nm, the surface area of a single C_{60} atom can be calculated as $S_{single\text{-}C60}$ = 0.785 nm^2. By multiplying $N_{spill\text{-}C60}(100,298)$ by $S_{single\text{-}C60}$, the number of spillover H atoms on one C_{60} molecule is calculated as 0.037.

TOF-MS measurements

A small amount of C_{60}-Pt/KB was dispersed in ethanol with sonication, and the dispersion was dropped on a thin stainless plate. After drying in air, the stainless plate was heat-treated under vacuum, and D_2 was dosed. Note that we applied the same manner for the heat treatment and D_2 dose as that for hydrogen adsorption-desorption measurements (Figs. 3c). Specifically, the stainless plate was evacuated at 423 K for 6 h in a closed chamber. Then, the sample chamber was kept at 353 K for 30 min with dosing D_2 gas (101.3 kPa). 353 K was chosen because Fig. 3f shows that the spillover amount is highest at 353 K among 273-353 K. After cooling down to room temperature, the stainless plate was attached on a sample holder for the TOF-MS instrument (Bruker Daltonics, autoflex Speed-S1), and the measurement was performed. During the period for attaching the stainless plate onto the sample holder, the sample was exposed to air for about 5 min. Fullerene is easily ionized by laser, and a matrix was not used in the present experiments. The generated negative ions were analyzed by the TOF-MS instrument.

From Fig. 3c, it is found that hydrogen is not completely desorbed from C_{60}-Pt/KB even at a very low pressure, indicating that spillover hydrogen is strongly attracted by the sample. This result suggests that D species can remain in C_{60}-Pt/KB even when the sample is inserted in the highly-vacuumed chamber of the TOF-MS instrument. At such a condition, the strongly attached D would be slowly desorbed as D_2 by reverse-spillover,[5] and it causes the slight pressure increase of the vacuum chamber. For hydrogen adsorption-desorption measurements shown in Figs. 3b and c, each sample was exposed to air after the measurement at each temperature, and evacuated for 6 h at 423 K. We have confirmed that the reproducibility of the adsorption-desorption isotherms by this pre-treatment, indicating that all the hydrogen stored in a sample can be removed by this pre-treatment.

References

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