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Effect of Fe/Fe₂O₃ loading on the catalytic activity of sulfonated single-walled carbon nanohorns for the esterification of palmitic acid

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The effect of dispersion of Fe/Fe₂O₃ nanoparticles in sulfonated single-walled carbon nanohorns (SO₃H/ SWCNHs) on their catalytic activity for the esterification of palmitic acid was investigated. A gas-injected arc-in-water (GI-AIW) method was employed to initially synthesize SWCNHs dispersed with iron nanoparticles (Fe-SWCNHs). The Fe-loading amount in the Fe-SWCNHs was varied by changing the number of Fe wires inserted in an anode. The results showed that Fe-loading amount proportionally increased from 6 to 13 wt% with an increase in the number of Fe wires. The surfaces of the Fe-SWCNHs were functionalized with acid functional groups by two sequential steps: impregnation of sulphuric acid and calcination in air. From the characterization results, their acid site concentrations were estimated to be 5.6–8.5 mmol g^{-1} , suggesting that the catalyst was a solid superacid catalyst. XRD analyses indicated that most of the Fe was transformed to α -Fe₂O₃. The catalytic activity of the SO₃H/Fe-SWCNHs for the esterification of palmitic acid was evaluated to investigate the influence of the Fe-loading on their catalytic activity. The results showed that the yield of methyl palmitate was significantly enhanced by an increase in the Feloading amount. It was discovered that the catalytic activity and the magnetic susceptibility of SO₃H/Fe-SWCNHs can be preserved during repeated use, if the Fe-loading amount is large enough.

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Introduction

The increasing demand for fossil fuels has given rise to environmental concerns, such as the emission of large amounts of CO₂, causing global warming. To help with this issue, several alternatives to fossil fuels have been proposed, such as solar energy, biomass, and biodiesel.^{1–3} Biodiesel is a renewable and environmental friendly alternative to petroleum-based diesel.⁴ It is a mono alkyl ester of fatty acid produced from vegetable oil or animal fat,⁵ which contains saturated hydrocarbons (triglycerides) and free fatty acid (FFA).⁶

The transesterification^{7,8} of triglycerides and the esterification of FFA are the best schemes for producing high quality biodiesel. All fatty acid sources such as animal fats or plant lipids can be used in biodiesel production. However, the production of biodiesel from human nutrition sources could lead

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to a food crisis. Therefore, the majority of researchers have focused on non-edible oil or waste cooking oil as a low cost feedstock for biodiesel production.⁹⁻¹¹

When using non-edible oil for biodiesel production, the amount of FFA in the oil is a concern, because these kinds of oils have high concentrations of FFA; for example, Jatropha seed oil consists of 48% oleic acid and 34% linoleic acid.¹² Such high amounts of FFA can cause side reactions with alkaline catalysts – so called saponification. Conversely, acid catalysts possess the advantage of insensitivity to FFA for saponification.^{13,14} They can be used with low cost oils that contain high amounts of FFA. However, the conventionally-used liquid acid catalysts, such as sulphuric acid, are corrosive, so special care is necessary to preserve the reaction systems. In addition, such liquid catalysts have drawbacks with regards to their recovery.

Solid acid catalysts, including sulfonated carbon-based materials,^{14–16} are considered to be potential candidates to replace liquid acid catalysts due to their characteristics, such as high corrosion resistance and the ability to be recovered and reused.¹⁷ Ideally, a solid acid catalyst should have the characteristics of interconnected pores with a large surface area,¹⁸ a high concentration of strong acid sites, and a hydrophobic surface to prevent deactivation by water.¹⁹

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Various types of solid acid catalysts such as ion exchange resins,²⁰ sulphate oxide,²¹ mixed oxides and derivatives²² and carbon-based acid solid catalysts^{15,16,23} have been studied. Recently, novel sulfamic-acid-functionalized iron (iron/ironoxide core shell) nanoparticles have been reported.²³ The presence of the iron/iron-oxide core shell nanoparticles enhanced the catalytic activity on ring opening of epoxidized soybean oils and the recovery of the catalysts by magnetic force.^{17,24,25} It has also been reported that iron-oxide nanoparticles can adsorb FFA from vegetable oil, which can promote the adsorption of FFA on the catalyst surface.²⁴ Thus, solid acid catalysts hybridized with iron oxide nanoparticles should achieve a high performance and act as ideal solid catalysts for the esterification of FFA. However, the effect of iron oxide on the catalytic activity of solid acid catalysts has not yet been studied so far.^{23,24,26}

In this work, we propose to use single-walled carbon nanohorns (SWCNHs). SWCNHs are a type of carbon nanomaterial, and have suitable properties to meet the requirements for an ideal solid acid catalyst. SWCNHs have high resistance against chemicals, suitable pore sizes, thermal stability and a hydrophobic surface in nature.²⁷ Moreover, it is possible to synthesize SWCNHs hybridized with metal nanoparticles by a one-step arc discharge technique.^{28,29} Here, the synthesis conditions of SWCNHs dispersed with Fe nanoparticles (Fe-SWCNHs) were investigated first, focusing on the amount of Fe-loading on the products to provide a suitable structure. Next, the catalysts were prepared using the Fe-SWCNHs by an impregnation method with a subsequent calcination step, and their catalytic activity was evaluated by testing with the esterification of palmitic acid. Furthermore, the effect of Fe-loading in catalyst preparation on the catalytic activity was studied.

Results and discussion

Effect of Fe-wire number in the synthesis process on the morphologies of Fe-SWCNHs: dispersion of Fe nanoparticles and Fe-loading weight

As explained in the Experimental section, the Fe-loading amount in Fe-SWCNHs can be varied by changing the number of Fe wires inserted in a hollow graphite anode used in the gas-injected arc-in-water (GI-AIW)³⁰ method. The transmission electron microscope (TEM) images of Fe-SWCNHs synthesized with various numbers of wires are shown in Fig. 1(a–d). These figures suggest that the Fe nanoparticles, indicated by the dark spots, can form simultaneously with the SWCNHs by this method, and that they are highly dispersed in the SWCNHs. Analysis by X-ray diffraction (XRD) confirmed that they are non-oxidized Fe, as further explained later.

The arc plasma at the anode tip can increase the plasma temperature to approximately 5000 K,³¹ and the vapors of carbon and Fe emitted from the anode can be quenched during their transfer to cold water. SWCNHs and Fe nanoparticles are then simultaneously formed from these vapors by a self-assembly mechanism. A previous article as reported that



Fig. 1 TEM images of Fe-SWCNHs synthesized with various numbers of Fe wires, and the mean diameters of Fe nanoparticles dispersed in the Fe-SWCNHs. (a) 1 wire, (b) 2 wires, (c) 3 wires, (d) 4 wires. (e) TEM image of SO_3H /Fe-SWCNHs prepared using Fe-SWCNHs synthesized with 4 Fe-wires. (f) Particle size distribution of Fe nanoparticles dispersed in the Fe-SWCNHs.

the most of the metallic nanoparticles dispersed in SWCNHs that are synthesized by this method should be migrated in SWCNHs.²⁹ Such a structure may help to avoid the merging of the metallic nanoparticles when they are calcined.

Although the particle sizes tend to be larger with an increase in the Fe-wire number in the GI-AIW method, it can be taken that this change is not significant, so that the high dispersion of Fe nanoparticles with diameters of 1-11 nm can be preserved in the present conditions (Fig. 1(f)). It should be noted that the number density of the Fe nanoparticles in the Fe-SWCNHs seemed to be higher when the Fe-wire number was increased. This tendency is understandable, because the increase in Fe wire number should lead to an increase in the concentration of Fe vapor in the arc plasma zone where Fe nanoparticles are formed. It should be noted that the particle sizes of the Fe nanoparticles did not significantly change, because the growth rate and the resident time of the Fe vapor in the reaction field in the quenching zone inside the cathode is limited.³¹ Instead, the number of Fe particles could increase with a higher Fe vapor concentration there. It is important to recognize from looking at Fig. 1(e) that the dispersion of Fe nanoparticles can be preserved during the calcination step, to prepare the sulfonated acid catalysts (SO₃H/Fe-SWCNHs).

We measured the Fe-loading amount in SWCNHs, and the results are plotted in Fig. 2 as a function of the number of Fe wires used in the synthesis process. It can be seen that the Fe-loading amount increases proportionally to the number of Fe wires.



Fig. 2 Effect of the number of Fe wires inserted in the anode hole in the GI-AIW method, on the Fe-loading amount, in percent, in the Fe-SWCMHs.

Transformation of Fe-SWCNHs to SO₃H/Fe-SWCNHs

The solid acid catalysts were prepared from the Fe-SWCNHs by an impregnation method as detailed in the Experimental section. Since the acid sites on these catalysts are considered to be $-SO_3H$,^{32,33} the catalysts prepared here are referred to as SO_3H /Fe-SWCNHs.

The crystal structure of the Fe nanoparticles dispersed in the Fe-SWCNHs was characterized by XRD. The diffraction patterns of the Fe-SWCNHs are shown in Fig. 3, in comparison with pure Fe powders and α -Fe₂O₃. The position of the diffraction peak of Fe-SWCNHs synthesized with four Fe wires matches well with the diffraction peak of standard Fe at 45°. The other Fe-SWCNHs synthesized with one, two and three Fe wires also exhibit similar XRD patterns, as shown in Fig. 3. These results confirm that the dark particles seen in the TEM images (Fig. 1) are Fe nanoparticles.

The XRD pattern of SO_3H /Fe-SWCNHs showed several peaks, although the intensities of the peaks should be fairly low as their crystal sizes are so small. The peak at 33° that



Fig. 3 XRD patterns of Fe powder, Fe-SWCNH, SO_3H /Fe-SWCNH synthesized with 4 wires of Fe and α -Fe₂O₃ powder.

symbolizes Fe₂O₃ can apparently be seen in the XRD pattern of SO₃H/Fe-SWCNHs. Compared with this peak, the other peaks of α -Fe₂O₃ at 35°, 40°, 54° could not be easily distinguished from the baseline noise due to the small size of the crystals. In addition to the peak of Fe₂O₃, one must pay attention to the peak at 45°, representing ferromagnetic Fe. Although the peak at 45° is less prominent here than in Fe-SWCNHs, we consider that this XRD suggests that ferromagnetic Fe still remains in the SO₃H/Fe-SWCNHs. It should be noted that SO₃H/Fe-SWCNHs can be captured by a permanent magnet, as observed by using a neodymium magnet of surface magnetic flux 150 mT. The XRD results suggesting the inclusion of ferromagnetic Fe are consistent with this magnetic experiment.

The peak around 26° should come from the carbonaceous parts of the SO₃H/Fe-SWCNHs. The slight shift of this peak to a lower angle, and the appearance of new peaks at 24° and 30° , may be caused by doping of S in structures consisting of C, Fe and O. Detailed analysis of the structures indicated by these peaks is not in the scope of this work, but it should be done in future.

Here, it should be noted that the most of the metallic nanoparticles dispersed in the SWCNHs produced by GI-AIW method are migrated to their carbonaceous part.²⁹ From this structural feature, it can be considered that the carbonaceous part of the SO₃H/Fe-SWCNHs should be partially oxidized to become porous, so that O₂ can diffuse through the carbonaceous part to reach the Fe nanoparticles in Fe-SWCNHs. According to this pore opening effect, Fe nanoparticles migrated in the SWCNHs could be transformed to α -Fe₂O₃.

It was found that this morphological change with the opening of pores on the carbonaceous part was affected by the Fe-loading amount. Table 1 shows the BET specific surface areas of SO₃H/Fe-SWCNHs, $S_{s,catal}$, synthesized with various Fe-wire numbers. Because the loading weight of the high-density Fe became larger when the Fe-wire number was larger, the specific surface area of the SO₃H/Fe-SWCNHs became lower accordingly. Here, it should be emphasized that the specific surface area of the carbonaceous parts in the SO₃H/Fe-SWCNHs, $S_{s,c}$, also decreases with the Fe-loading amount. The value of $S_{s,c}$ was calculated by eqn (1) with an assumption that

Table 1 Acid site concentrations, BET surface areas, and average micro pore diameters of SO_3H/Fe-SWCNHs synthesized by inserting various numbers of Fe wires

Catalyst	Acid site concentration ^{<i>a</i>} (H ⁺ -mmol g ⁻¹)	$S_{ m s,catal}^{b}$ $(m^2 g^{-1})$	$\frac{S_{\rm s,c}}{({\rm m}^2{ m g}^{-1})}$	d _m ^c (nm)
SO₃H-SWCNH (without Fe)	0.15	_	749	0.41
SO ₃ H/Fe-CNH (1 wire)	5.6	68	79	0.68
SO ₃ H/Fe-CNH (2 wire)	8.5	49	60	0.70
SO ₃ H/Fe-CNH (3 wire)	7.5	18	23	0.75
SO ₃ H/Fe-CNH (4 wire)	8.1	9	11	0.79

 a Calculated by titration experiments. b Determined based on the unit mass of the SO_3H/Fe-CNH. c Determined based on the unit mass of the carbon part.

the exposed surface area of Fe_2O_3 would be negligible in comparison with the carbonaceous part.

$$S_{\rm s,c} = S_{\rm catal} W_{\rm catal} / (W_{\rm catal} - W_{\rm Fe_2O_3})$$
(1)

where W_{catal} , and $W_{\text{Fe}_2\text{O}_3}$ are the masses of SO₃H/Fe-SWCNHs and Fe₂O₃, respectively, in SO₃H/Fe-SWCNHs. $W_{\text{Fe}_2\text{O}_3}$ was measured by the removal of the carbonaceous part *via* thorough oxidation. SO₃H-SWCNH without Fe was also prepared for comparison. Note that the acid functional group cannot be impregnated well on the SWCNH surface without Fe dispersion, as shown in Table 1.

It is reported that pores can be opened on pure-carbon SWCNHs by calcination in air.³⁴ In the case of the SO₃H/Fe-SWCNHs, Fe could catalyze the oxidation of the carbonaceous parts, so the inclusion of a larger Fe-loading amount could lead to a widening of the pores. The average micropore diameter as determined by the *t*-plot method, $d_{\rm m}$, is also shown in Table 1. It can be seen that $d_{\rm m}$ increases with the Fe-loading amount. The relatively wide pores generated with large Fe-loading amounts could contribute to the stable re-usability of the SO₃H/Fe-SWCNHs, as explained in the subsequent section.

As shown in Table 1, the resulting SO_3H /Fe-SWCNHs can possess high acid site concentrations of 5.6–8.5 mmol g⁻¹, which are comparable with those of the sulfonated solid superacid catalysts previously reported.³⁵ Therefore, the SO_3H /Fe-SWCNHs prepared in this work can be counted as superacid catalysts. It should be noted that no acid sites were detected on Fe-SWCNHs without the impregnation process. The average acid site concentration obtained from all SO_3H -Fe/SWCNHs specimens is 7.4 mmol g⁻¹. The relative error in obtaining the acid site concentration, estimated by repeated analysis, was at a level of 20%. According to the possible error, the acid site density measured in the present work is considered to be independent of the wire number used in the synthesis process.

Effect of Fe-loading amount on catalytic activities for esterification

In this work, the effect of Fe-loading amount on the catalytic activity for the esterification of palmitic acid was investigated using $SO_3H/Fe-SWCNHs$ synthesized with various Fe-wire numbers. In order to ensure fair comparison, the amounts of $SO_3H/Fe-SWCNHs$ which were supplied into the reactor were adjusted, so that the amount of acid sites used in each batch was supposedly the same. The change in the methyl palmitate yield with $SO_3H/Fe-SWCNHs$ of different Fe-loading amounts is shown in Fig. 4 as a function of reaction time. It can be observed that the yield increases with an increase in the Fe-wire numbers used for the synthesis process. This means that an increase in Fe-loading amount can enhance the catalytic activities in the esterification of palmitic acid.

The reason for this enhancement effect of Fe-loading can be discussed by considering the role of the Fe/Fe₂O₃ nanoparticles dispersed in SO₃H/Fe-SWCNHs. It is known that Fe₂O₃ has a high affinity with carboxylic acids, including fatty acids like palmitic acid.²⁴ Therefore, palmitic acid can be first



Fig. 4 Methyl palmitate yields obtained by the esterification of palmitic acid with SO₃H/Fe-SWCNHs synthesized with various Fe-wire numbers. (The reaction conditions: methanol:palmitic acid mass ratio of 33:1, amount of acid sites at 1.1 mmol reaction temperature of 64 °C, total reaction time of 60 min.)

adsorbed on the Fe₂O₃ surface at the SO₃H/Fe-SWCNHs. Then, the adsorbed palmitic acid could diffuse to the acid sites (SO₃H-) anchored on the carbonaceous part. It can be considered that the enrichment of palmitic acid on Fe₂O₃ would be so great that the amount of access of the palmitic acid to the acid sites *via* the Fe₂O₃ surface could become significantly large. We consider that such access *via* the Fe₂O₃ could be comparable to direct access.

The yield of methyl palmitate at 60 min reaction time is plotted against the Fe-loading weight percentage in Fig. 5 to clarify the relationship between the Fe-loading amount and the catalytic activity of the SO₃H/Fe-SWCNHs. It can be clearly observed that the yield at 60 min is nearly proportional to the Fe-loading weight percentage, in which the yield reaches 92% at the highest Fe-loading of 13 wt%.

The catalytic performance of a conventional sulphuric acid catalyst for the esterification of palmitic acid under the same conditions can be referred to in our previous work.³⁶ The methyl palmitate yield with the conventional catalyst was 20% in 60 min. In comparison, the yield obtained by the SO₃H/Fe-SWCNHs catalyst synthesized in the present work was almost



Fig. 5 Effect of Fe-loading amount on the maximum methyl palmitate yield in 60 min of reaction time.

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five times as high as the yield obtained with the conventional one.

Reusability of catalysts in esterification

The stability of the catalytic activity of the SO_3H/Fe -SWCNHs during reuse was investigated. The details of this procedure are explained in the Experimental section. The results are depicted in Fig. 6 and 7. As presented in Fig. 6, SO_3H/Fe -SWCNHs synthesized with an Fe-wire number of 4 exhibits excellent reusability for esterification. The yield slightly decreased by 5% in three reaction cycles. In the cases of the SO_3H/Fe -SWCNHs synthesized with Fe-wire numbers of 1, 2 and 3, the yields decreased by 10–30%. This catalyst deactivation may be due to pore plugging by the adsorbed palmitic acid molecules, which limits their access to the acid sites. As mentioned previously, Fe-loading could widen the pores. Thus, the plugging would not occur when the Fe-loading amount as large as in the case of an Fe-wire number of 4.

Magnetic properties for re-use of SO₃H/Fe-SWCNHs

The stability of the magnetic properties of the $SO_3H/Fe-SWCNHs$ during reuse for the esterification reaction was investigated, as shown in Fig. 7. In this figure, the results obtained from $SO_3H/Fe-SWCNHs$ synthesized with various Fe-wire numbers are shown, and a monotonous trend in the magnetic properties in accordance with the Fe-wire number is not seen. Fig. 7(a,b) shows the AC magnetic susceptibility of the $SO_3H/Fe-SWCNHs$ before they were used for the esterification experiment, and Fig. 7(c,d) shows the AC magnetic susceptibility after reuse 1–3 times. The influence of the reuse of $SO_3H/Fe-SWCNHs$ on their magnetic properties can be evaluated by a comparison between (a,b) and (c,d). It can be seen that the influence of reuse on the AC magnetic susceptibility of the $SO_3H/Fe-SWCNHs$ is not significantly changed for any Fe-wire numbers in any frequency range, in which the AC magnetic



Fig. 6 Reusability of $SO_3H/Fe-SWCNHs$ synthesized with various numbers of Fe wires for the esterification of palmitic acid with methanol. (The reaction conditions were the same as described in Fig. 4.)



Fig. 7 AC magnetic susceptibility (χ_{AC}) of the as-prepared Fe-SWCNHs (4 wire) and SO₃H/Fe-SWCNHs obtained from synthesis processes with different Fe wire numbers, as function of the frequency of the AC magnetic field (15 mG) applied on the specimen. Re[χ_{AC}] and Im[χ_{AC}] denote the real and imaginary parts of the complex number of χ_{AC} , respectively. (a) and (b) show the AC magnetic susceptibility of the SO₃H/Fe-SWCNHs before use for the esterification experiment, and (c) and (d) show the magnetic susceptibility after use for the esterification experiment. Rxn in (c) and (d) denotes the number of repetitions for the esterification experiment.

susceptibility is not decreased remarkably by reuse of the SO_3H/Fe -SWCNHs in catalyzing the esterification reaction. In other words, the magnetic properties of Fe/Fe_2O_3 dispersing in the SO_3H/Fe -SWCNHs did not leach out during the esterification reaction.

Conclusions

Fe-SWCNHs were used as starting materials for preparing sulfonated SWCNHs by an acid impregnation method. It was found that the Fe-loading amount was proportional to the number of Fe-wires in the anode used in the GI-AIW method, and the Fe-loading amounts reached 6–13 wt% in the present conditions.

It was observed that the SO₃H/Fe-SWCNHs possessed high acid site concentrations of 5.6–8.5 mmol g⁻¹, and so can be regarded as solid superacid catalysts. Most of the Fe nanoparticles dispersed in the SO₃H/Fe-SWCNHs were oxidized, causing a transformation to α -Fe₂O₃ during a calcination step. Nevertheless, traces of Fe remained, which allowed the magnetic recovery of the SO₃H/Fe-SWCNHs using a permanent magnet.

The catalytic activity of the SO_3H/Fe -SWCNHs for the esterification of palmitic acid with methanol was investigated. The results clearly show that high amounts of Fe loading provide high yields of methyl palmitate because the presence of the

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 Fe/Fe_2O_3 can enhance the adsorption of palmitic acid molecules on the surface of the Fe_2O_3 nanoparticles. The enriched palmitic acid molecules could then diffuse to the acid sites. In addition, the reusability of SO_3H/Fe -SWCNHs was tested, and it was revealed that the deactivation of the catalytic activity of the SO_3H/Fe -SWCNHs is significantly reduced when the Feloading amount is large enough. It is noteworthy that the magnetic susceptibility of the SO_3H/Fe -SWCNHs can be preserved when they are used repeatedly.

From a sustainability point of view, firstly, the catalyst prepared here does not use any rare metals which are sometimes used to prepare catalysts for biofuel synthesis,³⁷ although a high capacity for strong acid sites is realized. Moreover, our catalyst can be recovered from the solution simply by using a permanent magnet. Only a little energy is required for this recovery system. One may worry that the synthesis of the SWCNHs by the arc discharge method is energy intensive and costly. In relation to this, it is reported that the cost of producing SWCNHs can be reduced by an order of two, by optimization of the reaction conditions when an electrode of moderate purity is employed.³⁸ In addition, new routes to synthesize SWCNHs at relatively low temperatures are being explored.³⁹ Thus, we expect that the energy-base yield for preparing the catalyst proposed here may be significantly improved by further optimization.

Experimental methods

Synthesis of Fe-SWCNHs by an arc discharge method

Single-walled carbon nanohorns dispersed with Fe nanoparticles (Fe-SWCNHs) were synthesized by a N₂ gas injected arc-inwater (GI-AIW) method.³⁰ The set-up and dimensions of the reaction system of this method are illustrated in Fig. 8. The cathode and anode were high purity graphite rods (99.9995%). Various numbers (from 1 to 4) of Fe wires (0.5 mm in diameter) were inserted in the anode in a hole drilled along its axis. Both electrodes were submerged in water at room temperature. To generate arc discharge, a DC current was supplied



Fig. 8 Set-up of the apparatus for the synthesis of Fe-SWCNHs, and dimensions of the cathode, anode and Fe wires.

to the electrodes by a welding machine (Shindaiwa, STW200A) at 80 A and 40 V. For continuous arc discharge, the anode was delivered along the axis of the cathode hole with a speed of 1 mm s⁻¹. The N₂ gas was injected into the arc plasma zone inside the cathode hole at 10 L min⁻¹ when the arc discharge was generated for 1 min. Under these conditions, Fe-SWCNHs were synthesized and finally collected from the water surface.

Determination of Fe-loading amount (wt%) in Fe-SWCNHs

As-grown Fe-SWCNHs were oxidized by ambient air in an open-end quartz tube placed in an electric furnace at 900 °C for 30 min. All carbonaceous parts were oxidized, and only reddish brown powders remained there. XRD analysis was used to confirm that the reddish brown powders were Fe_2O_3 , and no carbon was detected. The weight of the remaining Fe_2O_3 was measured, and then the Fe-loading amount (wt%) in the Fe-SWCNHs was calculated.

Synthesis of $\mathrm{SO}_3\mathrm{H}/\mathrm{Fe}\text{-}\mathrm{SWCNHs}$ catalyst by an impregnation method

As-grown Fe-SWCNHs prepared by the GI-AIW method with various Fe-wire numbers were immersed in concentrated sulphuric acid (95%) for 24 h. After acid impregnation, the Fe-SWCNHs were washed by distilled water three times and then dried in an oven in ambient air at 110 °C for 12 h. Finally, the Fe-SWCNHs were calcined in a furnace with an air supply of 10 L min⁻¹ at 400 °C for 3 h. The resulting sulfonated Fe-SWCNHs (SO₃H/Fe-SWCNHs) were obtained and kept in a vacuum desiccator.

Morphological characterization of Fe-SWCNHs and SO₃H/Fe-SWCNHs catalyst and size distribution of Fe nanoparticles

The morphologies of the as-grown Fe-SWCNHs and SO_3H /Fe-SWCNHs were analysed by a transmission electron microscope (TEM) (JEOL, JEM-1010). The size distributions of the Fe nanoparticles dispersed in Fe-SWCNHs were determined by measuring the diameters of 500 particles of Fe nanoparticles in TEM images.

X-ray diffraction analysis

X-ray diffraction patterns were recorded on an X-ray diffractometer (Ringaku, Ultima IV 285 DX) with Cu K α radiation from 40 kV and 20 mA. Pure Fe and Fe₂O₃ powders were also analyzed to compare their peak positions with those of the catalyst.

Magnetic properties analysis

Analysis of the magnetization in the Fe-SWCNHs and SO_3H -Fe-SWCNHs was carried out by measuring the AC magnetic susceptibility at room temperature with a maximum magnetic flux of 15 mG (Magqu Co., XacQuan-II).

Acid site concentration of the SO₃H-Fe-SWCNH catalysts

The acid site concentrations of the catalysts were determined by acid base titration using standard NaCl solution as an ionexchange agent. 5.0 ml of 2.0 M NaCl ion-exchanged with 25 mg of the catalyst specimen under agitation (150 rpm) for 24 h was titrated with 0.01 M NaOH solution. Phenolphthalein was used to detect the equivalence point.

Catalytic activity analysis by esterification of palmitic acid

The catalytic activity of the SO₃H/Fe-SWCNHs were evaluated by the liquid phase esterification of palmitic acid with methanol, as follows. A 100 ml three-necked flask equipped with a water condenser was used as a reactor. This flask was submerged in an oil bath of which the temperature was controlled by a stirring heater. The solution in the flask was also stirred by a magnetic bar. Powdery palmitic acid (1.28 g) was placed into this reactor, until it melted. When the palmitic acid became a clear solution at 64 °C, 5.27 g of warm methanol (99.8%) was added into the reactor. After this, the catalysts were added into the reactor with the same amounts of acid sites at 1.1 mmol. The reaction temperature was controlled at 64 °C and the reactants were well mixed under an agitation of 600 rpm for 60 min. The methyl palmitate produced from the esterification reaction was collected periodically to measure its concentration with a gas chromatograph (Shimadzu, GC-14B). Ar was used as the carrier gas through a GC column (GL Science Ltd., Unisole 3000, 3 mm in diameter and 2 m in length) and a flame ionization detector. The methyl palmitate yield (Y, %) was determined according to eqn (1).

$$Y(\%) = \frac{\text{mole of methyl palmitate formed}}{\text{theoretically expected mole of methyl palmitate}} \times 100$$
(2)

Reusability of SO3H-Fe-SWCNH catalyst

The stability of the catalytic activity of SO_3H/Fe -SWCNHs during reuse for the esterification of palmitic acid was investigated. To reuse the SO_3H/Fe -SWCNHs remaining in the reaction solution, the SO_3H/Fe -SWCNHs were separated from the solution using a permanent magnet with a surface magnetic flux of 150 mT. The catalysts were washed by methanol three times and dried in air. The catalysts were then used for a new batch of esterification to start the next reaction cycle. The reusability was evaluated by the determination of the methyl palmitate yield at 60 min. In addition, the AC magnetic susceptibility of the reused catalysts was measured after use for every cycle.

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