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# Mechanical and chemical breaking of multiwalled carbon nanotubes

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## Abstract

Catalytically prepared multiwall carbon nanotubes (MWNTs) were cut and functionalised by mechanical and/or chemical methods. Products were characterised by transmission electron microscopy, infrared spectroscopy and BET method. It can be concluded that physical and chemical breaking procedures complete each other very well. With certain MWNT samples containing surface oxides preliminary investigations were done for testing them as catalyst support.

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*Keywords:* Carbon nanotubes; Mechanical and chemical breaking; Surface functional groups; Pt/carbon catalyst

## 1. Introduction

In heterogeneous catalytic processes special effort was made to prevent coke formation in the reaction of hydrocarbons [1,2]. As concerns the morphology of these deposits, many interesting results have been published [3,4]. From the 1970s, carbon fibers have careened to various applications and were investigated expansively [5,6]. The discovery of carbon tubules of nanometer size induced wide-ranging research activity on their synthesis, characterisation and possible applications [7–9]. Increasing effort is also being spent on their modification. The first modification of nanotubes occurs right after their production during their purification. When oxidative treatment is applied for the removal of amorphous carbon several structural vacancies may form [10]. Decapping the tubes makes the interior accessible for various molecules. This time partial destruction of the nanotube structure takes place at the end of the tubes [11]. In both cases mentioned, the structural imperfections are closed by functional groups such as COOH, OH or C=O. However, their concentration, which is hardly measurable even by spectroscopic methods, is not sufficient for immediate practical utilisations, e.g., using them as polymer fillers [12]. In order to increase the number of active sites (open ends) one has to cut the tubes into pieces. This can be achieved both by chemical and physical methods. Single-wall fullerene nanotube ropes were cut into 100–300 nm lengths which formed a stable colloidal suspension in water with the help of surfactants [13]. Also single-walled carbon nanotubes (SWNTs) were dissolved in organic solutions by derivatisation with thionychloride and octadecylamine and were characterised by near-infrared spectroscopy [14].

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Carbon supported catalysts have important role in heterogeneous catalytic reactions and processes. In addition to graphite, recently, carbon materials of new type such as carbon fibers of various structure and carbon nanotubes proved to be promising candidates for catalyst supports. Baker et al. [15] found the platinum/“platelet-type” graphite nanofiber catalyst active in skeletal reactions of normal hexane at relatively low temperature. Compared to a commercial high surface area charcoal supported palladium catalyst, carbon nanofiber of about 50 nm diameter turned out to be advantageous as support for a palladium catalyst in the liquid phase selective hydrogenation of the C=C bond in an α,β-unsaturated molecule [16]. In a following paper Ledoux and co-workers [17] concluded that the absence of microporosity in that novel Pd/carbon nanofiber catalyst favours both the activity and selectivity in the hydrogenation of cinnamaldehyde. Ruthenium clusters with sizes in the range 4–7 nm were deposited on the surface of carbon nanotube samples and then characterised and successfully tested as catalyst in selective hydrogenation in an unsaturated aldehyde [18]. Special surface treatment of single-wall carbon nanotube support, followed by loading of well-dispersed Pt particles onto it, and preliminary kinetic investigations were discussed by Lordi et al. [19].

The aim of this paper is to report on the results obtained in the field of functionalisation of carbon nanotubes by mechanical and/or chemical methods. To prove the existence of functional groups on the surface of nanotubes, the functionalised materials were reacted with ethylenediamine. We will show here that the physical and the chemical breaking procedures complement each other. For possible application of the above-mentioned materials comprising functional groups of oxygen content as catalyst support, various Pt/carbon samples were prepared and tested in the catalytic dehydrogenation of isopropanol to acetone.

## 2. Experimental

### 2.1. Synthesis

Multiwalled carbon nanotubes were prepared by the catalytic decomposition of acetylene over alumina supported metal catalyst. The 5% Co,Fe/alumina catalyst was prepared by the impregnation of alumina with an ethanolic solution of the respective metal salt mixture. The following chemicals were deposited on the surface of catalyst supports: $Fe(CH_3COO)_2$, $Co(CH_3COO)_2 \cdot 4H_2O$ over alumina having surface area of $<10\,m^2/g$ (Acros). These anions were supposed to fulfil expectations for getting “clean” catalyst surfaces free of any presumably uncertain components. For carbon nanotube synthesis, catalytic decomposition of acetylene was carried out in a fixed bed flow reactor at 720 °C. Exact amount (approximately 50 mg) of catalyst sample in a quartz boat was placed into a quartz boat and flushed with nitrogen for 10 min. During reaction the gas feed was 15 ml/min acetylene and 500 ml/min nitrogen as carrier gas. After 40 min the system was rinsed with nitrogen again and the product was let cool down in the inert atmosphere. The amount of carbon deposit was determined by weighing samples before and after reaction. From these data carbon yield ($g_{MWNT}/g_{cat.}$) was calculated for quantitative characterisation. The product was purified by dissolving the alumina and the catalyst particles in NaOH and then, if it was necessary, purification was continued with concentrated HCl solution. A detailed description of carbon nanotube preparation is given elsewhere [20].

### 2.2. Characterisation

Transmission electron microscopy (TEM) images were taken on samples at each stage (as-grown, purified and ground carbon nanotubes, as well as carbon supported platinum catalysts) using a Philips CM10 and a Philips CM-300 types microscope. BET measurements were carried out at 77 K in order to calculate the surface areas. The pore size distribution was also determined. The KBr matrix technique of IR spectroscopy was applied to monitor the functional groups generated on the surface of the multiwall carbon nanotubes (MWNTs) by various treatments. Spectra were recorded on a Mattson Genesis 1 FTIR spectrometer.

### 2.3. Functionalisation

Mechanical cutting of carbon nanotubes was performed by simple ball-milling. In order to obtain carbon nanotubes of 200–300 nm average lengths grinding was carried out for 100 h. For chemical functionalisation of purified and mechanically cut nanotubes, the samples were reacted with different reagents such as acetylacetat-ethylester (AEE) and $SOCl_2$. As another way of cutting MWNTs, acidic treatment was performed in a mixture containing 3:1 concentrated sulfuric and nitric acids. This was followed by heat treatment at 800 °C. Finally, these functionalised materials were reacted with ethylenediamine.

### 2.4. Catalyst preparation

For the preparation of platinum catalysts, the following carbon-type materials were used as catalyst supports: activated carbon, graphite flakes, purified MWNTs with original length, ground purified MWNTs. Before impregnation, the surface of the support was oxidized in the following procedure: suspension of carbon material in 1 M $H_2SO_4$ solution was reacted with 0.2 equiv. $KMnO_4$ for 8 h at room temperature. Impregnation was carried out following the method published by Lordi et al. [19]. An amount of 150 mg of $K_2PtCl_4$ was dissolved in the mixture of ethylene glycol and distilled water (using ratio of 3:2) then 1.0 g of carbon support was added and refluxed at 120–130 °C for 8 h. This solvent mixture had to stand two demands simultaneously, namely, the solubility of Pt salt and the satisfactory wettability of carbon supports. After centrifugation the sample was washed with slightly acidic distilled water, centrifuged again, and then dried at 60 °C. The metal content of the catalyst was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES) method. Prior to analysis, the catalyst was first ashed in a quartz boat at 1200 °C in a furnace and then the residue was transferred to an HDPE sample container, where 4 ml of a conc. HCl/HF acid mixture was added, diluted to 100 ml with distilled water and sonicated for 30 min in an ultrasonic bath. The resulting opaque solution/suspension was then nebulised into a Jobin-Yvon 24 type sequential ICP-OES spectrometer using a Teflon V-groove nebuliser and analysed measuring at the Pt II 214.42 nm line.

### 2.5. Catalytic reaction

Exploratory catalytic investigations were carried out in a pulse reactor. For each reaction 100 mg of catalyst sample was placed in a microreactor (alloy steel with 40 mm length and 5 mm inner diameter) and was pretreated in hydrogen flow for 60 min at 400 °C. The analysis of material leaving the reactor was carried out by the GC method using 15% Carbowax 20 M column with 80 °C oven temperature and nitrogen carrier of 30 $cm^3\,min^{-1}$ flow rate (CHROM-5 equipped with FID, Laboratorny Pristroje, Praha). In each pulse 1 μl of isopropanol was injected onto the catalyst layer. Reaction temperature was varied between 200 and 300 °C. For comparison, results obtained in the second pulse were used.

## 3. Results and discussion

On Fe, Co/alumina catalyst excellent nanotube formation was found: the carbon yield ($g_{\mathrm{MWNT}}/g_{\mathrm{cat.}}$) was found to be 1.05. As a general characterisation of MWNT supports, Fig. 1 shows the carbon nanotubes produced are well graphitised and the sample contains just a very small amount of amorphous carbon on the outer surface. Fig. 2a shows the TEM image of the sample obtained after the mechanical treatment (100 h milling). High resolution TEM image in Fig. 2b illustrates the crystalline microstructure of the sample after the above-mentioned oxidative chemical modification procedure. It is seen that even though the tubes became substantially shorter, their shell structure did

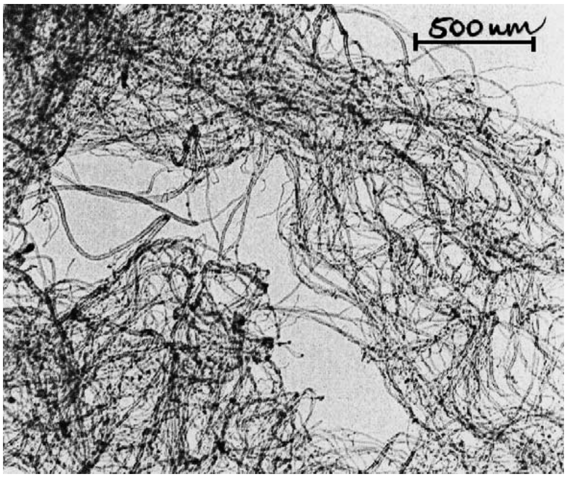

Fig. 1. Electronmicroscopy image of purified MWNTs.

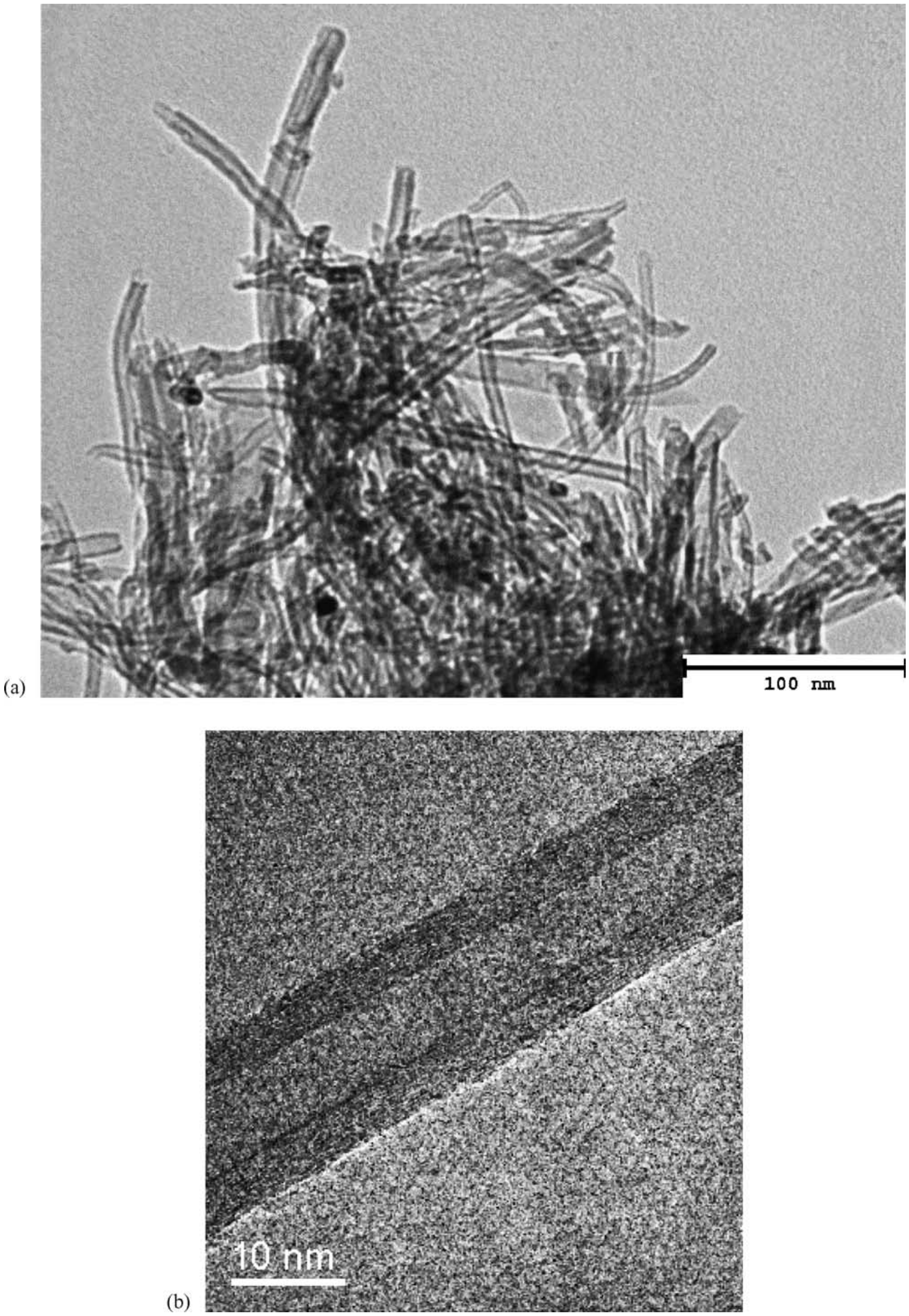

Fig. 2. (a) Electronmicroscopy image of ground MWNTs. (b) High resolution TEM image of chemically modified carbon nanotube sample.

not change much compared to that of the original material. This means that cutting the nanotubes by mechanical forces preserves their shell structure and creates new openings probably terminated by OH and COOH groups due to the atmosphere containing oxygen. Note, that this method does not generate new imperfections on the wall, therefore, the concentration of newly formed functional groups will be proportional to the change of the length/diameter ratio. We have measured the pore size distribution of the purified, chemically and physically cut nanotubes. The pore size distribution curves are presented in Fig. 3. The parent nanotubes have no significant values since most of the ends are closed. This sample has a surface area of 193 $m^2$/g. The chemically treated sample has maxima at 1.6, 2.2 and 3 nm and a surface area of 263 $m^2$/g, while the mechanically cut sample has a very sharp maximum at 2.2 nm, a more shallow one at 3 nm and a third one at 3.8 nm and a surface area of 234 $m^2$/g. These data reveal that by applying either method the surface area of nanotubes increases although the sample morphology changes substantially. It is assumed that upon breaking the tubes chemically a large quantity of functional groups was generated primarily at the ends, then, at the imperfections. To support the hypothesis, the samples were reacted with ethylenediamine. It is clearly seen in Fig. 4 that there are spectral changes both in the OH region and in fingerprint region. Characteristic bands of amine groups

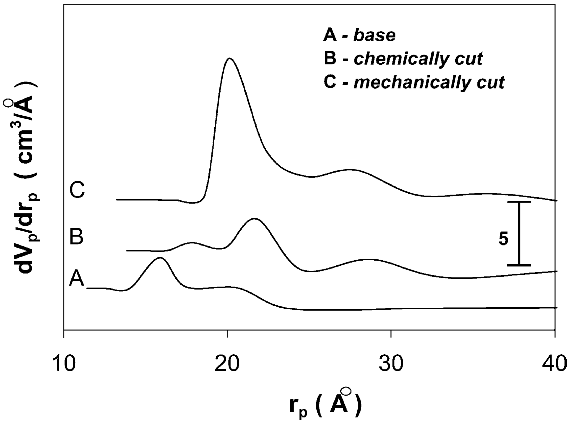

Fig. 3. Pore size distributions and surface areas of the parent, the mechanically and the chemically cut nanotubes.

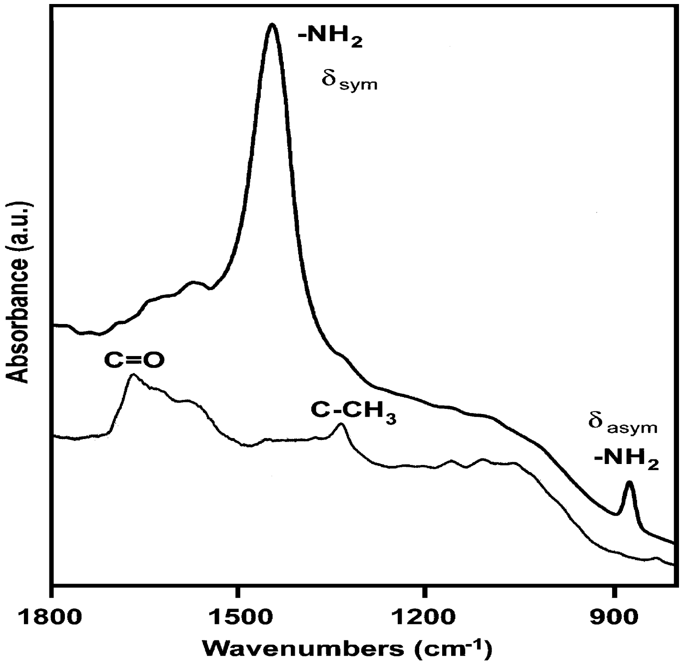

Fig. 4. IR spectras of the chemically functionalised nanotubes.

appeared upon treatment with ethylenediamine. This treatment is effective for each chemically treated sample. From this follows that the functionalised samples contain reactive functional groups indeed.

Since surface hydroxides are essential for successful loading of platinum onto MWNTs, ground sample as support was chosen for catalyst preparation. For comparison, active carbon and graphite flakes were also used as catalyst supports. In order to form oxygen containing functional groups on the surface, each support was treated by potassium permanganate before catalyst preparation. Platinum loading was followed both by analytical and electron microscopy methods. Since during the redissolution of Pt we had some difficulties of complete removal of certain carbon supports (ashing was found to be unexpectedly inefficient for catalysts with MWNT support) the results for Pt content obtained by the ICP-OES method applied here can be reckoned as a lower estimate only. For Pt/purified MWNT, Pt/ground MWNT, Pt/graphite flakes and Pt/active carbon, 0.25, 0.25, 0.05 and 0.12 m/m% platinum content was found, respectively. As it can be seen in Fig. 5, TEM image confirms the presence of platinum particles on the surface. The average diameter of platinum particles was measured to be 3 nm.

Preliminary catalytic investigations were carried out in a pulse reactor. For testing the influence of the stainless steel reactor, blank reaction was carried out at each temperature and no isopropanol conversion was found. Conversion, selectivity of acetone and turnover frequency data obtained after the second pulse are summarised in Table 1. At each reaction temperature, the only side-reaction resulted in propene formation was the dehydration of isopropanol. Turnover frequency data were calculated from the flow rate of reactant molecule and the dispersion of platinum. The latter value was estimated from TEM measurements (average particle diameter was found to be 3 nm) presuming spherical particles on the surface. These activity data reveal that carbon nanotube is much better catalyst support for platinum than either graphite flakes or active carbon. Since the difference in the amount of deposited metal is insignificant (within an order of magnitude), the platinum particle sites were quite uniform, the different behaviour of the catalyst samples can be explained by other effects (for instance, different metal–support interaction). Surprising

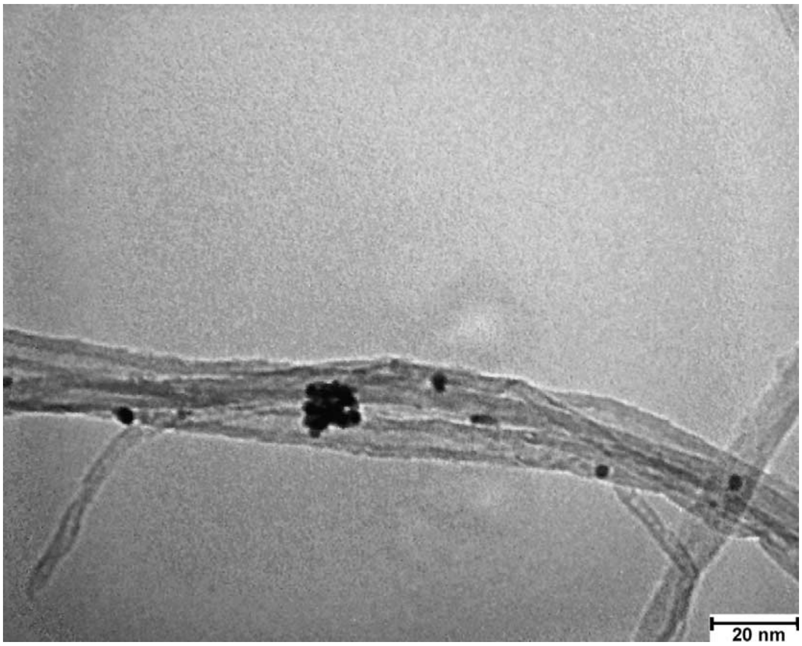

Fig. 5. Electronmicroscopy image of Pt/purified MWNT.

Table 1
Conversion, selectivity and turn over frequency (TOF) data in isopropanol dehydrogenation over carbon supported Pt catalysts

| Catalyst | Conversion (%) | | | Selectivity (%) | | | TOF (molecule/Pt s) | | |
|---|---|---|---|---|---|---|---|---|---|
| | 200 °C | 250 °C | 300 °C | 200 °C | 250 °C | 300 °C | 200 °C | 250 °C | 300 °C |
| Purified MWNT | 0 | 2.4 | 4.0 | 0 | 42.7 | 42.4 | – | – | – |
| Pt/purified MWNT | 37.5 | 79.2 | 56.6 | 86.4 | 50.8 | 40.8 | 784 | 1656 | 1183 |
| Pt/ground MWNT | 0 | 15.7 | 37.7 | 0 | 54.5 | 53.6 | 0 | 328 | 788 |
| Pt/graphite flakes | 0 | 0.8 | 2.4 | 0 | 100 | 95 | 0 | 50 | 150 |
| Pt/active carbon | 0 | 0.1 | 3.5 | 0 | 100 | 20.4 | 0 | 4 | 146 |

difference was found between the two MWNT supports, too. The activity of Pt/purified MWNT catalyst was much higher compared to Pt/ground MWNT. Comparing TEM images (Figs. 1 and 2) it can be seen that the length of ground MWNT is about 100–200 nm and that of purified MWNT is in the range of micrometer. Diffusion of either catalyst or reactant molecule is much more hampered using the latter sample as catalyst support. The probability of the formation of Pt particles inside the tubular support is much higher using ground carbon nanotubes. (Even formation of Pt wire inside the tube is known from the literature [21].) Since the platinum particle size and the inner diameter of the nanotube are about of the same value, it is presumable that part of platinum is trapped inside the tubes and not accessible for the reactant molecules any more. Albeit low magnification TEM is not suited for getting evidence of this phenomenon, explanation of difference in activity can be assumed. Concerning selectivity, it is favourable to use Pt/purified MWNT catalyst at lower reaction temperature. During catalytic investigations one more interesting feature arose. In the blank reaction, purified MWNT was also tested, and above 250 °C some activity was observed. Our previous results revealed [22] that carbon nanotubes always contain traces of metal ions, which can act as active sites in the reaction.

## 4. Conclusions

Breaking the multiwall carbon nanotubes can be performed either by chemical or by mechanical methods. The chemically cut samples can be easily used as polymer fillers or reinforcing materials since they have reactive functional groups not only at the ends but also on the outermost shell enabling them to make chemical bonds with the polymer matrix. Mechanical breaking of the nanotubes results in a material with small length/diameter ratio. This sample is recommended to use as adsorbent for various processes or as graphite-like catalyst support. The sample is probably not appropriate for use as polymer filler. Preliminary catalytic investigations showed that MWNTs are promising candidates for catalyst support.

If we apply chemical and mechanical breaking together, the concentration of the functional groups increases significantly, thus these methods complement each other very well.

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