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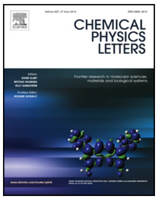

In situ measurement of activation energy for pyrolysis of ethanol as a first reaction in the synthesis of carbon nanotubes

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ABSTRACT

Using a quadrupole mass spectrometer we measured the activation energy of ethanol decomposition with various catalysts. In order to quantitatively evaluate the catalysts we subtracted their effect from that of the catalyst-free pyrolysis. As a result we derived the activation energies using iron, cobalt, nickel, and molybdenum catalysts. These metals are typical catalysts in carbon nanotube synthesis, with two of them usually mixed empirically. This empirical preparation and use of catalysts is consistent with our results. Among these catalysts, iron reduced the activation energy most. Conversely, cobalt achieved a reduction of only 0.3 eV compared to the catalyst-free reaction.

1. Introduction

Since their discovery, carbon nanotubes [1,2] have been recognized as important materials with various applications owing to their chemical stability and outstanding physical properties. Almost all of these properties originate from their unique, so-called quasi-one-dimensional, structure. Much theoretical research has predicted their outstanding value as a theoretical maximum [3–5], with many attempts made to measure this experimentally [6–8]. Because experimental results are affected by defects in each carbon nanotube, measured values have usually been poorer than the predicted values. However, when artificial defects were employed in simulations, theoretical values qualitatively showed good agreement with the experimental values, and were sometimes quantitatively comparable. Therefore, nanotube properties can be designed in terms of their purity, length, diameter, and chirality. Though it is still difficult to directly control diameter and chirality, we can control other properties by scanning experimental conditions and subsequent separation.

The growth mechanism still remains an unsolved problem. A literature search for experimental conditions was conducted, showing that some growth models [9–12] were proposed for the arc discharge and laser ablation methods. These production methods are comparably easy to predict or simulate, because isolated carbon should be supplied. Thus, molecular dynamics methods [13–17] showed reasonable results, with some researchers succeeding in growing carbon nanotubes in their simulations by applying restrictive conditions. However, chemical vapor deposition (CVD) [18–26] is, at present, the dominant method for producing carbon nanotubes. Many carbon sources have been examined with alcohol catalytic CVD [27] and super growth [28] considered to be the current superior methods. Alcohol catalytic CVD gives pure single-walled carbon nanotubes without any post-treatment, inferred from the contribution of O radicals and/or OH radicals. We also concluded that water molecules, synthesized as a byproduct, maintained catalytic activity by removing amorphous carbon. From screening the literature for carbon sources, many candidates were reported, but few were mentioned as unsuitable carbon sources. In contrast, part of authors showed the tendency in terms of the ratios of C, H, and O [29]. As mentioned above, experimental results were reported, but theoretical research of the growth mechanism was difficult owing to calculation loads. At the first stage, theoretical researchers developed a potential function among carbon atoms with catalytic metals such as iron, cobalt, and nickel. Then, they demonstrated the growth process using molecular dynamics methods. To date, observing the catalytic reaction of the growth process was difficult from both an experimental and theoretical approaches. Because first principle calculations do not require experimental results, it is suitable to predict and explore the reaction and growth processes, but the calculation load is too much to solve equations including considerable amounts of atoms. Hence, clarification of intermediate products was difficult. We experimentally observed intermediates for ethanol [30], a typical carbon source in CVD, using a quadrupole mass spectrometer and employing isotopic ethanol. This led to the clarification of some reaction schemes [31], such as the order of dissociation, reaction barrier,

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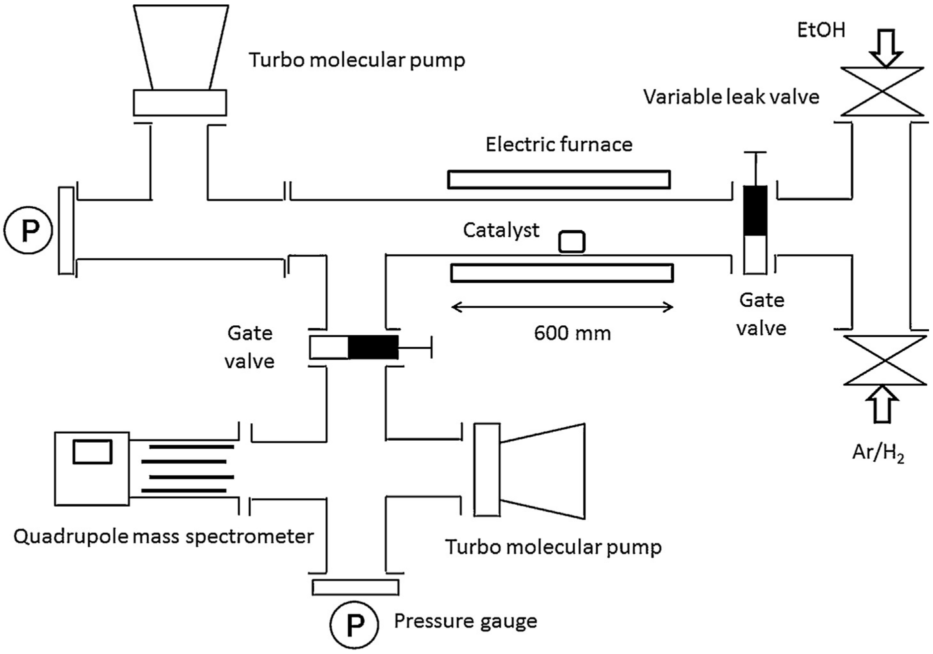

Figure 1. Experimental schematic. The quartz glass tube (I.D. 50 mm) penetrated an electric furnace. The background pressure was at 1×10^{-5} Pa, the reactor section at 5×10^{-2} Pa, and the measurement section at 5×10^{-3} Pa.

and dominant intermediates. Recently, some theoretical research focused on the surface reaction and also used the deformation of chemical bonds in source gases and derived activation energy of catalysts. So far, there are qualitative reports about catalyst roles during pyrolysis, but no quantitative reports. Therefore, in this study, we explore the catalytic activity of iron, cobalt, nickel, and molybdenum, the most common catalysts for CVD synthesis of carbon nanotubes.

2. Experimental

Figure 1 shows an experimental schematic. Catalysts were prepared on quartz glass ($25 \times 25\,\mathrm{mm}^2$) and placed in the middle of the furnace. Because the preparation method of the catalyst substrate has previously been described [32], we explain it briefly here. Usually, bimetallic catalysts, such as iron–cobalt, nickel–cobalt, and cobalt–molybdenum, are used for synthesis, but in this study we employed a single metal for investigation of catalytic activity. Before catalyst deposition on the quartz glass substrate, it was cleaned by acid-alkali treatment to remove unintentional metal compounds and organic contaminants. Catalyst metal was dissolved in ethanol in the form of chemical compounds, with a solution concentration of 0.01 wt.%. The substrate was dipped into the solution and pulled up at a rate of 6 cm/s. The substrate was then calcined in air at 400 °C to remove organic compounds. Before experimentation, the substrate was reduced using 5% H_2 in Ar. Ethanol was lead into the furnace through variable leak valve and dissolved. We measured reaction products by using a quadrupole mass spectrometer. The temperature of the furnace was between 500 °C and 1100 °C with a pressure of 5×10^{-2} Pa. After the furnace, the products were introduced into a measurement section at 5×10^{-3} Pa. At this pressure, and because the mean free path was long enough, collisions between source gases or reaction products were negligible. All of the products were ionized by electron impact of 50 eV, with ratios of each product giving fragments from excess energy. We had to remove this fragmentation for the purpose of qualitative discussion.

3. Results and discussion

Figure 2 shows the fragmentation pattern of ethanol. In this figure we normalized using the mass of ethanol (46 amu). This fragmentation pattern was measured at room temperature so that pyrolysis was negligible. Throughout this study, we quantified the pyrolysis of ethanol depending on the catalyst species. We therefore had to distinguish between pyrolysis and fragmentation. For example, a mass of 28 amu was produced by both pyrolysis and fragmentation. From the fragmentation pattern, the ratio of fragment (28 amu)/parent (ethanol, 46 amu) is 1.11; we could then subtract the fragment from the total normalized intensity, leaving us with the quantity of pyrolysis product. As for the amount of

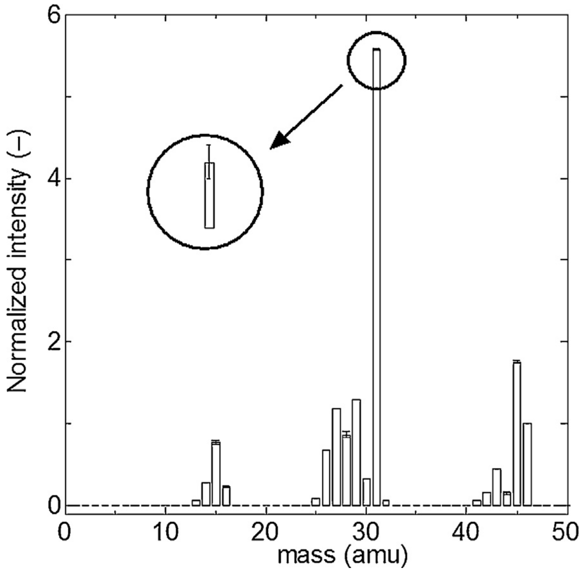

Figure 2. Fragmentation pattern of ethanol. Referring to ours and others' previous studies, we ignored some spectra. Error bars were small enough for qualitative evaluation.