SOME ASPECTS OF CARBON NANOTUBES TECHNOLOGY

A. V. Melezhyk, A. V. Rukhov, E. N. Tugolukov, A. G. Tkachev

Tambov State Technical University, Russian Federation, 392000, Tambov, Sovetskaya str., 106.

nanocarbon@rambler.ru, artem1@inbox.ru, tugolukov.en@mail.ru, nanotam@yandex.ru

Different carbon sources (e.g. hydrocarbons, oxygen containing organic compounds) were evaluated for their use in the chemical vapor deposition (CVD) process of carbon nanotube (CNT) production with regards to their efficiency and environmental safety. The effects of both the carbon source and gas feed rates on the yield of the obtained CNT's were determined. The data obtained indicate that intermediate species formed in gas-phase thermal transformations of carbon sources play important roles in the CVD process of CNTs growth. Particularly, it is supposed that ketene, which is an intermediate species in the thermal decomposition of acetone , is the immediate source of carbon for CNTs growth in the CVD processes utilizing acetone as a carbon source.

Keywords: carbon nanotubes, CVD, source of carbon, acetone, ketene, mass yield, conversion.

1. Introduction

Carbon nanotubes (CNTs) are promising materials which have applications in various technological fields. Due to improved technology and the increased scale of CNTs production at present their cost has dropped to a level where the application of CNTs could be economically viable in many areas. The large scale production and wide application of CNTs makes the selection of raw materials important. Among the factors which should be considered when selecting a carbon source are the yield and quality of the CNTs produced, the environmental impact and the overall safety of the CVD process.

Hydrocarbons were most frequently used as carbon sources for the production of CNTs by the CVD method at ambient pressure, however, there have been few articles published concerning the analysis and relative efficiency of different hydrocarbon sources for CNTs synthesis via the CVD process [1,2].

Methane is the most readily available hydrocarbon, being the main component of "natural gas", which is widely used as an energy source. The use of methane for CNTs production has been amply documented [3–9]. The use of methane as a carbon source for CNTs synthesis has two distinct disadvantages. First, only high purity methane is acceptable for this synthesis. Ethane and propane, which usually are present in natural gas as admixtures, are much more reactive than methane and can complicate the synthetic process, yielding non-reproducible results and low quality CNTs. Methane of high purity is relatively expensive, because cryogenic temperature rectification and/or adsorption technologies are necessary for the refining of crude methane. Secondly, methane usually demands higher temperature for conversion into CNTs (850–1000 °C compared to 600–700 °C for higher alkanes and unsaturated hydrocarbons). This is of minor importance for laboratory settings, however, for industrial applications, increasing reaction temperature necessitates the use of more expensive construction materials and thermal insulation; the durability of the construction drops because of increased thermal stresses; problems arise from increased heat transfer by radiation, which is proportional to 4th power of absolute temperature; consumption of energy increases. In spite of these disadvantages, methane is still suitable for the generation of high quality single- and double-wall nanotubes

(SWNTs and DWNTs) provided that appropriate catalysts and optimal technological regimes are implemented.

Higher saturated hydrocarbons, such as propane, butane, and hexane have been used in the synthesis of CNTs via the CVD process. For these hydrocarbons, the optimal reaction temperature usually ranges from 600–700 °C. However, Ajayan et al. describe how long strands of SWNTs were grown from n-hexane with floating catalyst (ferrocene + thiophene) at much higher temperatures, 1100–1200 °C [10]. In several works, liquefied petroleum gas, consisting of propane and butane (sometimes containing an admixture of sulfur-containing organic compounds) was successfully used for the production of multiwalled CNTs [11–17].

Regarding the application of saturated hydr °Carbons in the CVD method of CNTs synthesis, it is well known that saturated hydrocarbons at ca. 700 °C or above rapidly undergo a series of non-catalytic gas phase free-radical reactions resulting in the formation of a complex mixture of hydrogen, methane, ethylene, propylene, and higher saturated and unsaturated hydrocarbons [18]. With longer reaction times, heavy hydrocarbons (condensed aromatics) appear in significant amounts.

When these facts are considered, the nature of the original saturated hydrocarbon seems to be of minor importance when compared to the optimal reaction temperature. Due to the fast thermal transformations of the starting hydrocarbons, the species which react with the catalyst of CVD process may be the products, or intermediates of hydrocarbon pyrolysis. So, if n-hexane was used by Ajayan et al [10] as the carbon source for obtaining long strands of SWNTs, undoubtedly the n-hexane molecules were not the species directly reacting with the catalyst to grow CNTs, because at 1100–1200 °C thermal transformations of n-hexane are extremely fast. In all likelihood, one could obtain similar results by supplying the reactor with a gas mixture containing methane, hydrogen, ethylene and other hydrocarbons.

Unsaturated hydrocarbons, such as acetylene, ethylene, and propylene have been frequently used for CNTs production. It follows from analysis of published data that all these hydrocarbons permit the generation of high quality carbon nanotubes, provided that optimal catalysts and conditions were used. For instance, Hao et al utilized propylene (diluted with nitrogen) as the carbon source for large-scale fluidized-bed CVD process of CNTs production [19].

The published results from numerous studies and our data would seem to indicate that the dilution of unsaturated hydrocarbons with an inert gas is necessary to retard their cycloaromatization with the unwanted formation of heavy hydrocarbons. When these gas phase reactions are not diluted, they tend to form tar-like products which condense on cold walls at the reactor outlet. The longer the reactants are in the hot zone of the reactor, the more dilute these hydrocarbons must be to avoid tar formation. Through experimentation, it was shown that the unsaturated hydrocarbons listed above can be arranged in following order by their tendency to give tar: acetylene > ethylene > propylene. Hence, from these findings, propylene appears to be most suitable as a carbon source for the CVD process. Additionally, propylene can be easily transported in a liquefied state at relatively low pressure (nearly 1 MPa), while ethylene is transported in high pressure balloons.

Aromatic hydrocarbons (benzene, toluene, and xylene) were also studied as carbon sources for CNTs production however, they do not seem to offer substantial advantages over alkanes and alkenes and thus, were not widely used.

The principal disadvantage of using hydrocarbons for CNTs production (with exception of methane) is the formation of harmful by-products such as condensed poly-nuclear aromatics. Conversion of a carbon source to CNTs in any case does not reach 100%. Practically, conversion to CNTs usually amounts 30–80% in CVD processes of multi-walled nanotube synthesis

(MWNTs) and is much less (1–10%) in cases of SWNTs and DWNTs production. Thus, the formation of harmful by-products is unavoidable even if optimal conditions are used.

Oxygen-containing organic compounds may be used as an alternative to hydrocarbons for CNTs production. Among these, ethanol was the most widely studied [20–44]. Ethanol is most suitable for obtaining SWNTs and DWNTs and less acceptable for MWNTs synthesis. In SWNTs or DWNTs synthesis via CVD, the starting material (carbon source) is usually diluted with inert gas (argon, nitrogen) to a volume content of ethanol vapor not more than several %. Dilution of the carbon source, together with the application of a catalyst with low mass content of catalytically active metals, favors the formation of thin nanotubes (SWNTs and DWNTs). One of the pyrolysis products of ethanol is water. Water vapor in low concentrations favors the formation of and increases the yield of both SWNTs and MWNTs [45–47]. Evidently, any oxygen-containing compound, even CO_2 [48] for instance, in low concentration should exhibit the same effect because of the reversible nature of reactions of oxygen-containing organic compounds in a hydrocarbon-containing atmosphere at high temperatures. However, if there is too much water in the reacting gas mixture, the growth of nanotubes is suppressed, because at high temperatures water reacts with carbon. Hence, ethanol is less suitable as a carbon source for the generation of multi-walled carbon nanotubes because usually a more concentrated carbon source is needed for efficient growth of MWNTs, and, if so, too much water is generated from the decomposition of ethanol.

Other oxygen-containing organics, such as camphor [49] and phenol [50] have been used as carbon source for CVD synthesis of carbon nanotubes, however, the advantages of these compounds as carbon sources are uncertain.

Different alcohols and ketones were studied as carbon sources for CNTs CVD synthesis and the highest quality nanotubes were obtained from acetone [51]. In view of this, acetone appears to be a promising raw material for CNTs production.

The present work evaluated different organic compounds as carbon sources for the CVD process of CNTs production.

2. Experimental

CNTs were obtained by the CVD method using a fixed bed laboratory reactor. A horizontal quartz tube reactor (inner diameter 37 mm, length 1150 mm, volume of hot zone nearly 0.5 L) was used in our experiments. Samples of catalysts were placed into the reactor on a semi-cylindrical Graflex (flexible graphite foil) support. The feed rates of gases were measured and regulated with a "MassFlow" (Bronkhorst HIGH TECH) and are given below at standard conditions. A tubular ceramic furnace PT-1.2-70 was used for precision temperature control. Mass yields of CNTs were calculated as ratio of mass of the crude product minus mass of starting catalyst divided by mass of catalyst. It was found from SEM and TEM images that in all cases the products were nanotubes without visible admixture of other particles. Conversion of carbon compounds into CNTs was calculated in % from theoretical assuming that theoretical yield corresponds to conversion of all carbon atoms of a starting compound into CNTs.

Following compounds were used as sources of carbon:

Liquefied propane-butane — technical grade (Russian standard);
Liquefied propylene — 99.95% purity;
Ethanol — 96% (water 4%);
Acetone — "Pure for analysis" (Russian standard);
Argon was used of 99.96% purity, hydrogen — 99.98%.

Electron images of CNTs were recorded with using two-beam scanning electron microscopy complex Neon 40, Carl Zeiss. Raman spectra were obtained with using Integra Spectra spectrometer.

3. Results and Discussion

In Fig. 1 and 2 there are plots of CNTs mass yield and propane-butane to CNTs conversion on argon feed rate. Multicomponent metal oxide $(Co,Mo)/MgO-Al_2O_3$ was used as a catalyst, the process of CNTs growing was carried out over 30 min at 650 °C. One can see that at constant volume ratio of argon to propane-butane and at constant feed rate of propane-butane, CNTs yield and conversion of propane-butane to CNTs decrease with increasing gas flow speed, with a maximum in one case.
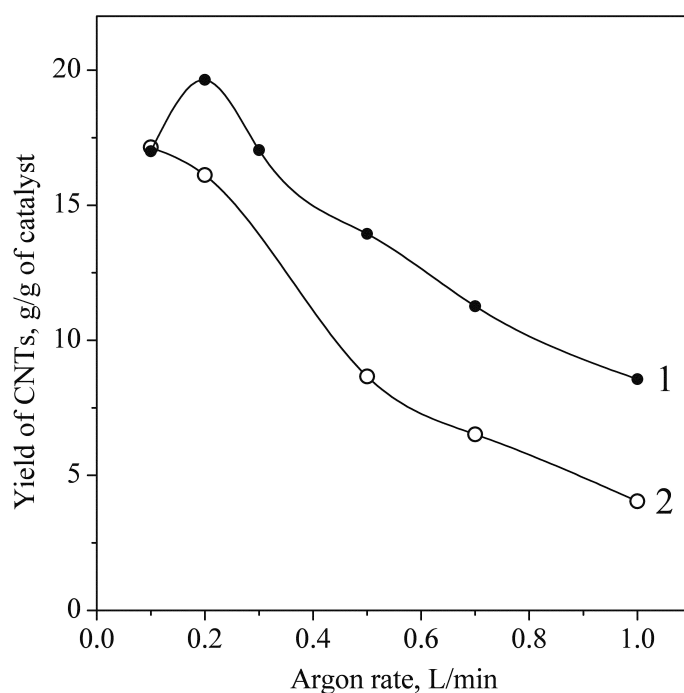

FIG. 1. Dependence of CNTs yield on argon feed rate. $(Co,Mo)/MgO-Al_2O_3$ catalyst, 30 min, 650 °C. 1 — constant volume ratio of argon to propane-butane (1:1); 2 — constant rate of propane-butane (0.2 L/min)

A much more expressed maximum was observed for the dependence of CNTs yield on propane-butane rate with $(Fe,Co,Mo)/Al_2O_3$ catalyst (Fig. 3, propane-butane not diluted with argon).

The plots Fig. 1–3 can be explained if we assume that the species which directly reacts with the catalyst is ethylene and/or propylene which is formed via free-radical thermal transformations of propane and butane prior to contact with the catalyst. If the gas flow rate is too high, the concentration of these reactive species and yield of CNTs decreases. Conversely, low gas flow rates can also result in decreased CNTs production because of, (1) deficiency of carbon source, and (2) further transformation (polymerization) of ethylene and propylene to heavier hydrocarbons.

In Fig. 4 the dependence of CNTs yield on the flow rate of propylene diluted with argon at constant volume ratio of argon to propylene (6:1) was determined using the same conditions as in Fig. 3 (catalyst $(Fe,Co,Mo)/Al_2O_3$, 30 min, 650 °C). In this case, some decrease in the
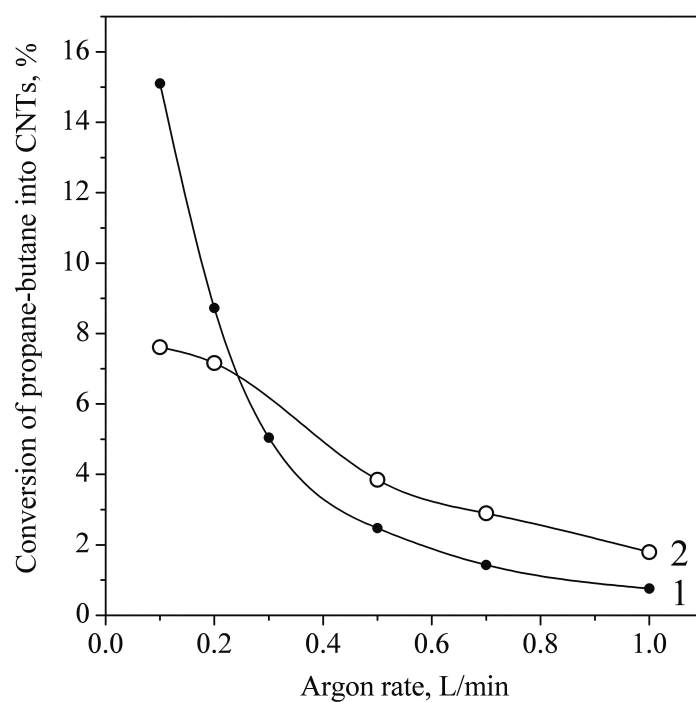
FIG. 2. Dependence of conversion of propane-butane to CNTs (% of theoretical) on argon feed rate. (Co,Mo)/MgO–Al$_2$O$_3$ catalyst, 30 min, 650 °C. 1 — constant volume ratio of argon to propane-butane (1:1); 2 — constant rate of propane-butane (0.2 L/min)
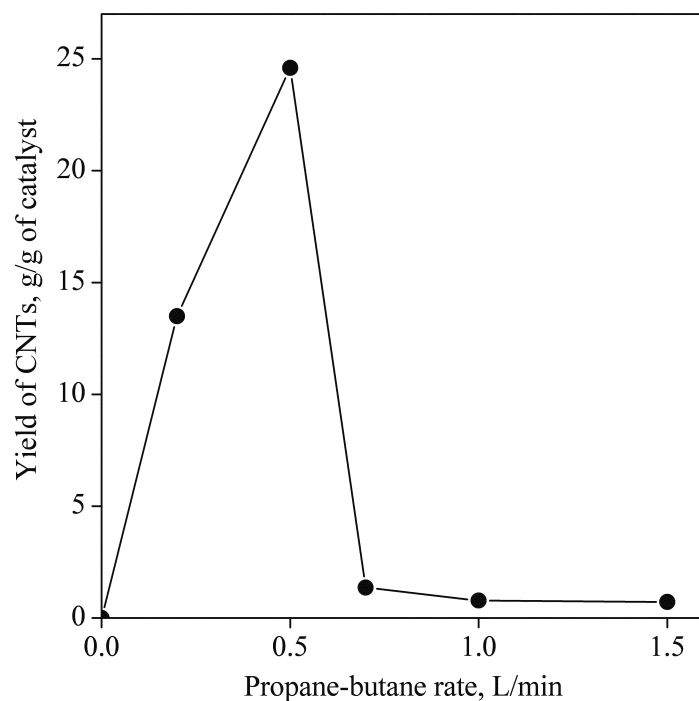

FIG. 3. Dependence of CNTs yield on the propane-butane feed rate. (Fe,Co,Mo)/Al$_2$O$_3$ catalyst, 30 min, 650 °C. Propane-butane not diluted with argon

yield with increasing argon rate was also observed, however, the decrease in the yield was not as drastic as in Fig. 3. These data indicate that in the CVD process with propylene, some gas phase reactions also be occurring, but for now, it is difficult to identify them.
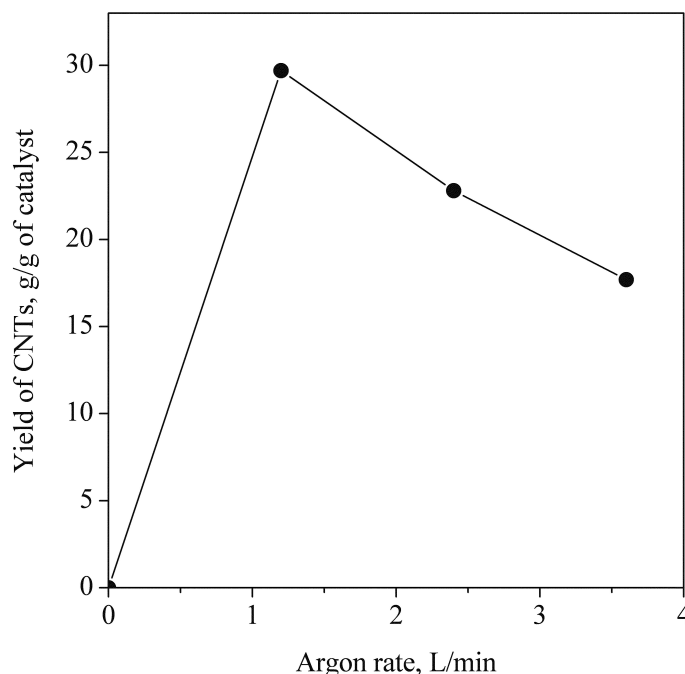

FIG. 4. Dependence of CNTs yield upon argon feed rate. (Fe,Co,Mo)/Al$_2$O$_3$ catalyst, 30 min, 650 °C. Constant volume ratio of argon to propylene = 6:1

The data given above prove that gas phase hydrocarbon transformations can play a valuable and even critical role in the CVD synthesis of CNTs. Particularly, the time a gas species remains in the hot zone of a reactor is of critical importance. Proper identification of these transformations is valuable for adjusting the optimal synthesis of CNTs. These parameters should be taken into consideration when designing the CVD reactor.

Inevitably carcinogenic heavy aromatics form as by-products when hydrocarbons are used as raw materials for CNTs synthesis, therefore, some oxygen-containing organic compounds, namely, ethanol and acetone, were studied as alternative sources of carbon.

Experiments with ethanol were conducted at 750 °C, which was found to be optimal (by mass yield) for the catalyst used ((Co,Mo)/MgO–Al$_2$O$_3$). As it follows from Fig. 5 and 6, it is impossible to achieve a good mass yield of MWNTs together with good conversion of ethanol into MWNTs. This is most likely due to the formation of large amounts of water via the thermal decomposition of ethanol.

The thermal decomposition of acetone is principally different from that of hydrocarbons and alcohols. The pyrolysis of acetone, which occurs at 500–700 °C, gives ketene in up to 80% yield if the ketene is quickly removed from the heating zone via the following process:

$$CH_3 - CO - CH_3 \rightarrow \dot{C}H_3 + CH_3 - \dot{C} = O \rightarrow CH_4 + CH_2 = C = O.$$
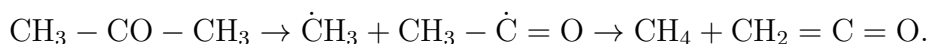
The formation of ketene can occur either via a free-radical mechanism, as written above, or as a heterogeneous reaction of acetone molecule on the Lewis acid catalysts (e.g., alumina).

Ketene is toxic, but, as an unstable gas, it quickly polymerizes with the formation of diketene first, and then predominantly 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one.
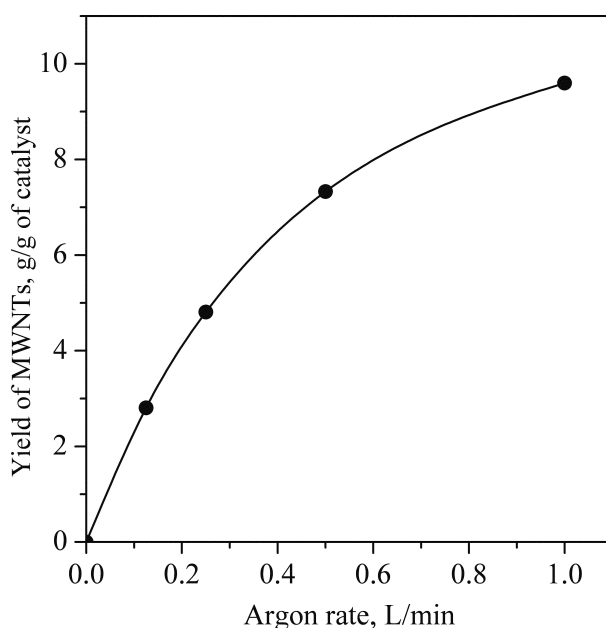
FIG. 5. Dependence of MWNTs yields upon argon flow rate. Catalyst (Co,Mo)/MgO–Al$_2$O$_3$, 750 °C, 30 min. The feed rate of argon is proportional that of ethanol, 1 L/min argon (gas) at 40 ml/h ethanol (liquid)
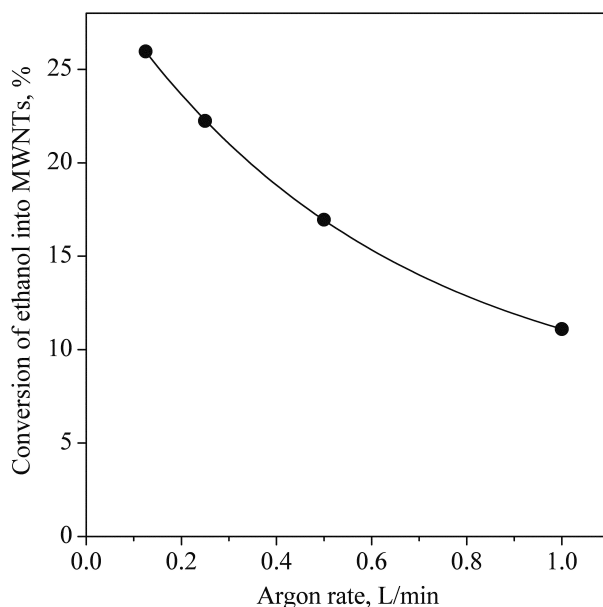

FIG. 6. Dependence of ethanol conversion into MWNTs upon argon feed rate. Catalyst (Co,Mo)/MgO–Al$_2$O$_3$, 750 °C, 30 min. The feed rate of argon is proportional to feed rate of ethanol, 1 L/min argon (gas) at 40 ml/h ethanol (liquid)

Ketene reacts rather quickly with water to form acetic acid. Diketene is toxic liquid which is insoluble in water, and as a result, reacts slowly with that medium. The last compound is not harmful and is used for the impregnation of antibacterials onto foodstuff packing materials. Due to high reactivity of ketene and its derivatives it is unlikely that they can remain in nature for a long time and thus, are not likely to accumulate in living organisms, unlike condensed poly-nuclear aromatics which are known to acumulate in organisms.
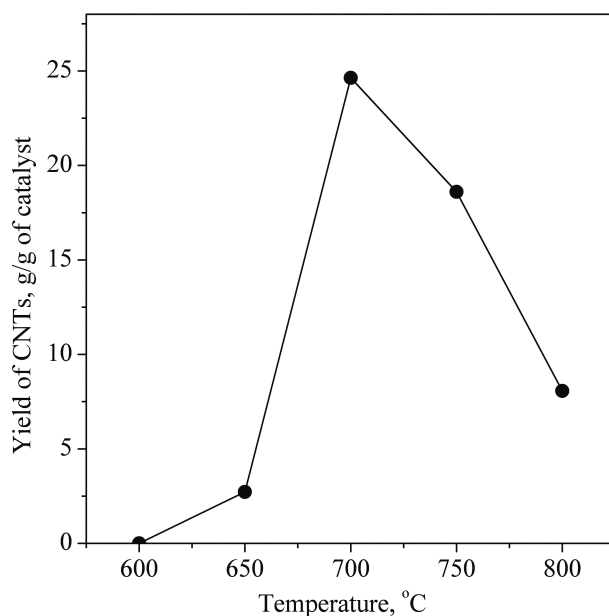
FIG. 7. Dependence of CNTs yield from acetone on temperature. The catalyst is $(Co,Mo)/MgO–Al_2O_3$. Feed rate of acetone (liquid) was 18.3 ml/h, argon (gas) 1 L/min, duration of synthesis 30 min

Thus, one can hope that the neutralization of acetone pyrolysis by-products, if it used as a raw material for CNTs production, is simpler than sequestering poly-nuclear aromatics, the by-products obtained from hydrocarbons.

A series of experiments were performed in a laboratory reactor in order to evaluate possibility of using acetone for the CVD production of CNTs. Multicomponent metal oxide $(Co,Mo)/MgO–Al_2O_3$ was used as the catalyst. The preliminary reduction of catalyst with hydrogen (10–15 min) was essential for obtaining good yields of nanotubes when using acetone. On contrary, in cases of hydrocarbons or ethanol, the prior reduction of this and other catalysts was not required. Presumably, these hydrocarbons themselves quickly reduce the catalysts in situ.

As shown in Fig. 7, the maximum yield of CNTs from acetone on this catalyst was obtained at 700 °C. Subsequent experiments were conducted at this temperature.

The yield of acetone-derived CNTs passes through a maximum with increased argon feed rate and decreases with increased substrate in the feeder gas (Fig. 8) as is the case for CNTs synthesis from propane-butane. Fig. 9 shows that a similar dependence was observed for the conversion of acetone into CNTs, but the maximum was observed only at a constant feed rate of acetone. The conversion value at low argon feed rates is sufficiently high, which proves the efficiency of acetone as a feedstock for production of carbon nanotubes. The optimal combination of mass yield and the conversion of acetone to carbon nanotubes was observed at an argon feed rate of ca. 0.3–0.5 L/min.

One can assume that ketene is an intermediate species involved in the growth process of CNTs in this system, however, the decreases in yield and conversion with increased argon feed rate in acetone-based syntheses is less pronounced than in cases of propane-butane systems. Molecules of acetone may also be able to participate in the process of CNTs growth together with ketene. In prior work [51] it was assumed that transient methyl radicals were the source of carbon for CNTs growth in this system. However, in view of the very short lifetime of
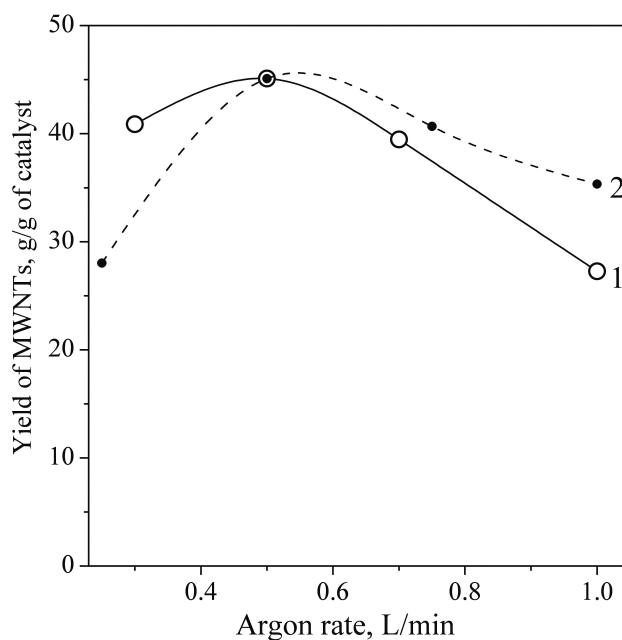
FIG. 8. Dependence of mass yield of CNTs from acetone on argon feed rate. The catalyst (Co,Mo)/MgO–Al$_2$O$_3$, 700 °C, duration of synthesis 30 min. 1 — constant feed rate of acetone, 18.3 ml/h (liquid); 2 — feed rate of acetone is proportional to feed rate of argon, 18.3 ml/h acetone (liquid) at 0.5 L/min argon (gas)

FIG. 9. Dependence of acetone conversion into CNTs on argon feed rate. The catalyst (Co,Mo)/MgO–Al$_2$O$_3$, 700 °C, duration of synthesis 30 min. 1 — constant feed rate of acetone, 18.3 ml/h (liquid); 2 — feed rate of acetone is proportional to feed rate of argon, 18.3 ml/h acetone (liquid) at 0.5 L/min argon (gas)
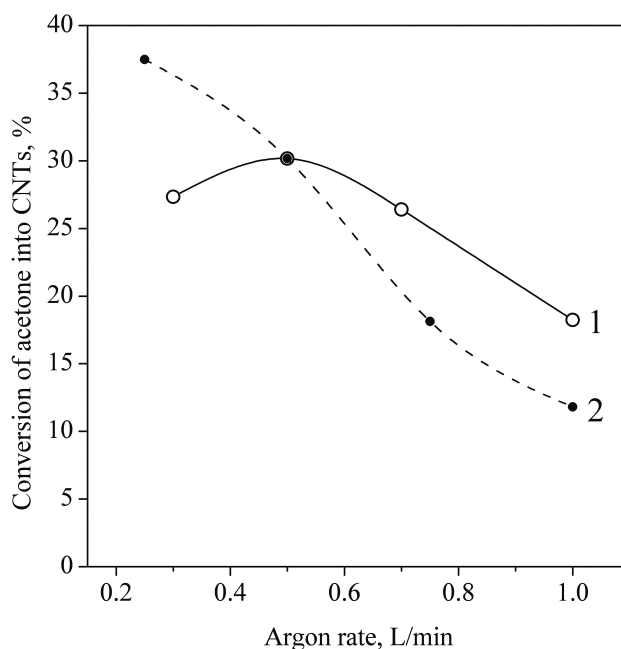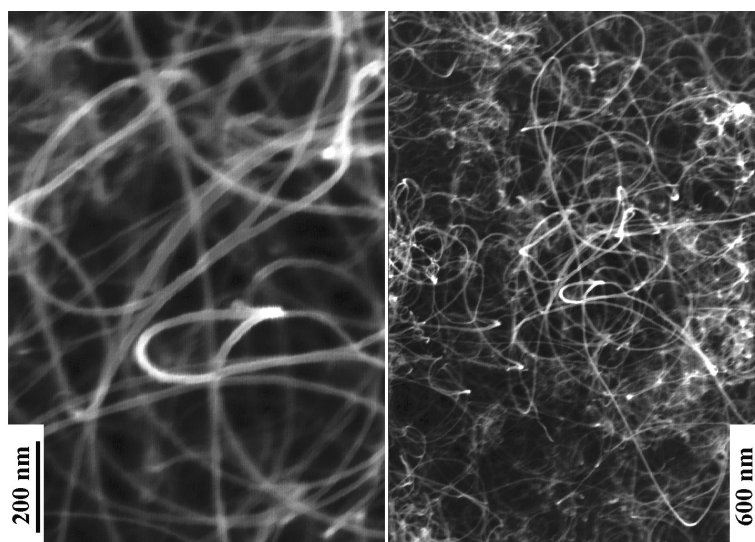
FIG. 10. SEM images of CNTs obtained from acetone. Catalyst (Co,Mo)/MgO–Al$_2$O$_3$. 700 °C, duration of synthesis 30 min. Argon feed rate 0.7 L/min (gas), acetone 18.3 ml/h (liquid). Mass yield of CNTs is 39.5 g/g of catalyst
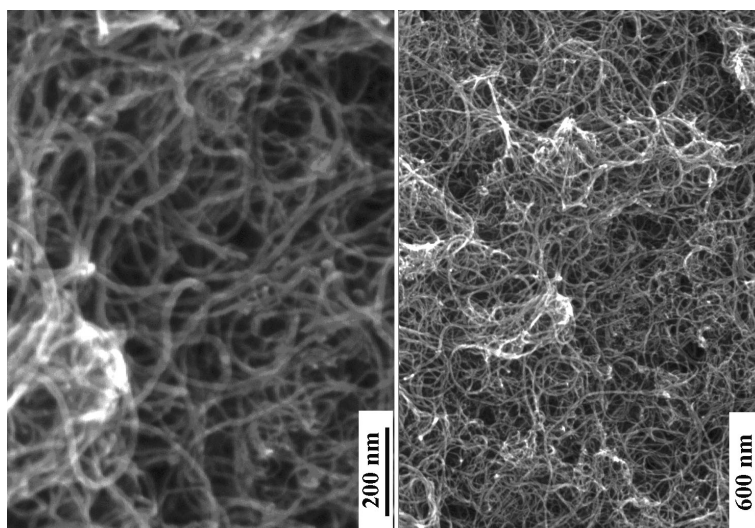

FIG. 11. SEM images of CNTs obtained from propylene. Catalyst (Co,Mo)/MgO–Al$_2$O$_3$. 650 °C, duration of synthesis 30 min. Hydrogen feed rate 1.2 L/min, propylene 0.2 L/min (gas). Mass yield of CNTs is 24.5 g/g of catalyst

methyl radicals, their participation in this heterogeneous process of CNTs growth seems to be less probable than the participation of ketene molecules.

Participation of free radical intermediates ("polycyclic free radical condensate") is thought to occur in the CVD process of CNTs synthesis from hydrocarbons [52]. In reality, the formation of liquid, tar-like condensates or deposits on cold walls at the outlet of CVD reactor was often observed. These condensates may be adsorbed on growing nanotubes, however, it is open to question whether they are an intermediate or a by-product in the CVD synthesis of CNTs. It should be noted that the cycloaromatization of unsaturated hydrocarbons can proceed on the same catalysts at the same temperatures which are usually used for CNTs synthesis.

In our investigations to obtain carbon nanofibers from acetylene (which is especially prone to cycloaromtization reactions), condensates were predominantly formed on "bad" catalysts, when the yields of CNTs were low.

The data obtained prove that acetone can be a suitable source of carbon for the production of CNTs by the CVD method.

SEM images of MWNTs obtained using acetone and propylene on the same catalyst, (Co,Mo)/MgO–Al$_2$O$_3$, are shown in Fig. 10, 11. CNTs obtained from acetone are less deformed, which indicates higher quality. As is known, Raman spectra are often used for estimation of disorder-order ratio of CNTs structure. The D/G ratio in Raman spectra for different samples of MWNTs obtained from acetone in these experiments ranged from 0.60 to 0.76. This is close to the D/G value of 0.67 found in prior work for high-quality MWNTs obtained from acetone on a (Mn,Co)/zeolite catalyst [51].

4. Conclusions

Intermediate species, which are formed in gas-phase thermal transformations of hydrocarbons, participate in the CVD process of CNTs synthesis. The temperature, flow rate and time present in the reactor are critical factors determining yield of CNTs and conversion of a carbon source into CNTs.

Acetone is a promising source of carbon for an environmentally-benign CVD process for CNTs production. It is possible that ketene, which is an intermediate in the thermal decomposition of acetone, participates in the CVD process of CNTs growth.

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