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Simultaneous production of hydrogen and carbon nanostructures by decomposition of propane and cyclohexane over alumina supported binary catalysts

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Abstract

Nano-scale, binary, 4.5 wt.% Fe–0.5 wt.% M (M = Pd, Mo or Ni) catalysts supported on alumina have been shown to be very effective for the decomposition of lower alkanes to produce hydrogen and carbon nanofibers or nanotubes. After pre-reduction at 700 °C, all three binary catalysts exhibited significantly lower propane decomposition temperatures and longer time-on-stream performances than either the non-metallic alumina support or 5 wt.% Fe/Al_2O_3. Catalytic decomposition of propane using all three catalysts yielded only hydrogen, methane, unreacted propane, and carbon nanotubes. Above 475 °C, hydrogen and methane were the only gaseous products. Catalytic decomposition of cyclohexane using the (4.5 wt.% Fe–0.5 wt.% Pd)/Al_2O_3 catalyst produced primarily hydrogen, benzene, and unreacted cyclohexane below 450 °C, but only hydrogen, methane, and carbon nanotubes above 500 °C. The carbon nanotubes exhibited two distinct forms depending on the reaction temperature. Above 600 °C, they were predominantly in form of multi-walled nanotubes with parallel walls in the form of concentric graphene sheets. At or below 500 °C, carbon nanofibers with capped and truncated stacked-cone structure were produced. At 625 °C, decomposition of cyclohexane produced a mixture of the two types of carbon nanostructures.

Keywords: Nanostructures; Propane and cyclohexane; Alumina supported binary catalysts

1. Introduction

The U.S. Department of Energy has recently announced its intention to develop ‘‘FreedomCar’’, a hydrogen-powered vehicle. Such vehicles would likely use polymer electrolyte membrane (PEM) fuel cells, which require hydrogen with very low CO concentration (<10 ppm). Currently, the most common method of producing high purity hydrogen is a multi-step process, involving steam reforming or partial oxidation of natural gas or gasification of hydrocarbons (including coal and biomass) to produce synthesis gas ($CO + H_2$), water–gas shift reactions to convert CO to CO_2 and H_2, and various purification steps to reduce the CO to ppm levels. Direct non-oxidative catalytic decomposition of hydrocarbons into hydrogen and carbon is an alternative, one-step process to produce hydrogen of the required purity.

In previous work, we have demonstrated that nano-scale binary, Fe-based [(4.5 wt.% Fe–0.5 wt.% M)/Al_2O_3, where M = Pd, Mo, or Ni] catalysts are very effective for catalytic dehydrogenation of light alkanes [1,2]. These catalysts decrease the decomposition temperature of the lower alkanes by several hundred degrees Celsius. They maintain good activity for several hours time-on-stream (TOS) by promoting removal of carbon, one of the decomposition reaction products, from the surfaces of the catalyst particles in the form of carbon nanotubes (CNT). Since, there is no available oxygen in the system, carbon oxides and water are absent in the product streams.

Propane is a good choice as a fuel for hydrogen production based on the following characteristics: (i) hydrogen gravimetric density (18.2 wt.%) of the fuel; (ii) ease of hydrogen extraction from the fuel; and (iii) cost and availability [3]. Traditionally, efficient catalytic dehydrogenation of propane to propene has been studied as a means of converting propane to a reactive chemical feedstock,

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propene. BASF is currently building the largest propane dehydrogenation plant capable of producing 350,000 tonne of propene/year in Tarragona, Spain. This plant will use UOP's Oleflex process [4] for propane dehydrogenation. Süd Chemie Inc. CATOFIN [5] process uses fixed bed chromia alumina catalyst to produce polymer grade propylene from propane rich stream. Grasselli et al. [6] have reviewed several dehydrogenation processes to conclude that selective oxidation of hydrogen produced is crucial for efficient production of olefins.

Most of the 595 million gallons/year of cyclohexane, a gasoline-range liquid hydrocarbon, is made by benzene hydrogenation, with a small amount recovered in petroleum fractionation. Cyclohexane can yield 14.3 wt.% of hydrogen by complete dehydrogenation and 7.1 wt.% of hydrogen by partial dehydrogenation to benzene. Currently, about 93 percent of cyclohexane is used for the production of adipic acid and caprolactam for nylon feedstock, and the other 7% is used for solvents, insecticides and plasticizers. Catalytic dehydrogenation of saturated or partially saturated cyclic hydrocarbons to produce the corresponding aromatic compounds is of broad utility [7]. Recently, it has been widely investigated as a hydrogen source material to provide hydrogen for polymer electrolyte membrane (PEM) fuel cells [8–17]. Our group has demonstrated that partial dehydrogenation of cyclohexane and methylcyclohexane to produce pure hydrogen and benzene and toluene, respectively, can be easily achieved using catalysts consisting of 0.25 wt.% of Pt nanoparticles on stacked-cone carbon nanotubes.

In the current paper, we present the results for production of hydrogen and carbon nanostructures by catalytic decomposition of propane and cyclohexane using the same suite of catalysts developed for efficient non-oxidative dehydrogenation of lower alkanes [1,2].

2. Experimental

Supported catalysts were prepared by the incipient wetness method by adding aqueous solutions of appropriate catalyst metal (Fe + (Pd, Mo or Ni)) salts in the desired proportions to γ-alumina (150 m^2/g) and calcining the extruded pellets. The composition of the binary metal catalysts was 4.5 wt.% Fe and 0.5 wt.% M (M = Pd, Mo or Ni) with respect to the alumina support. Characterization of the catalysts [16] by XAFS and Mössbauer spectroscopy and TEM indicates that the active phase is an Fe–M–C austenitic metal alloy and that the catalyst particles are anchored to the alumina support by a Fe-aluminate, hercynite [18]. The catalysts exhibit good time-on-stream behavior for the catalytic decomposition of methane and ethane because the Fe–M–C phases are very effective in stabilizing carbon in the form of carbon nanotubes and nanofibers, which carry carbon away from the active catalytic sites.

The propane and cyclohexane decomposition experiments were carried out as described previously [1,2], in a fixed bed, plug-flow quartz reactor. Prior to reaction, the catalysts were reduced in flowing hydrogen (50 mL/min) for 2 h at 700 °C. After reduction, the reactor was flushed with an inert gas until the GC showed no residual hydrogen peak (∼15 min.). The temperature effect studies were carried out by raising the reaction temperature every 20 min to a new temperature. The gaseous decomposition products of propane were analyzed by an online GC with a TCD detector. For each run, a 10 mL/min propane or gaseous cyclohexane flow rate over 0.5 g of catalyst was used. The products from decomposition of cyclohexane were analyzed in the gas state online by two GCs connected in series with an ice water trap in between. The first GC, with a FID detector, analyzed for heavier hydrocarbons, and the second GC with a special dual-TCD analyzed for hydrogen, lower alkanes, and other gases. Chromatograms from both GCs had a well-separated methane peak, which was used to cross-calibrate them.

3. Results and discussion

3.1. Dehydrogenation of propane

The product distribution from thermal cracking of propane is shown in Fig. 1. At temperatures above 500 °C, cracking produces hydrogen, methane, ethene and ethane, but no propene is observed. The observed products total approximately 100%, with the exception of the last point at 750 °C where an abrupt drop in the propane percentage is observed and the products total to <90%. This appears to be due to an unexplained experimental error in the GC reading for propane. Above 600 °C, the breaking of C–C bonds dominates to produce highly active methyl radicals. These radicals either react with hydrogen to produce methane or undergo further dissociation to produce carbon and hydrogen. Thus, we see increases in both methane and hydrogen concentrations. We did not observe any dehydrogenation of alkanes to alkynes (or propadiene), probably

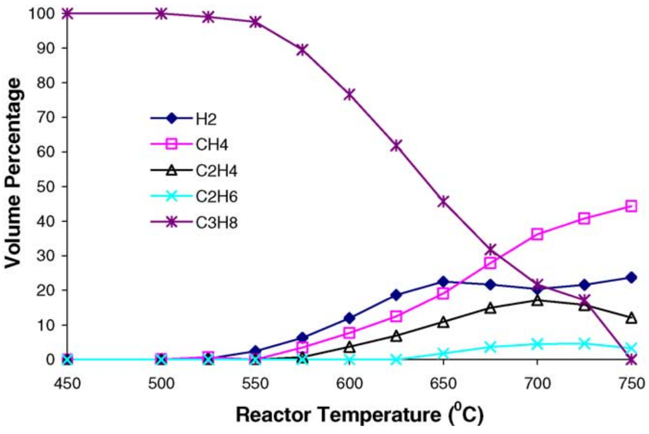

Fig. 1. Product distribution for non-catalytic thermal cracking of propane as a function of reactor temperature.

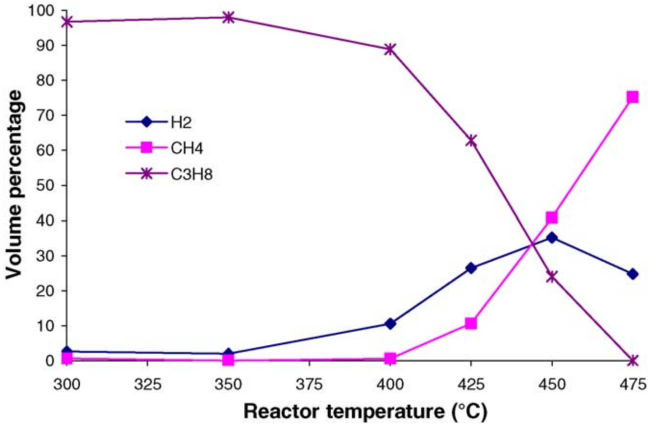

Fig. 2. Product distribution of propane decomposition over (4.5 wt.% Fe–0.5 wt.% Pd)/Al_2O_3 catalyst as a function of temperature.

because the temperature of the system was sufficiently high to instantaneously further dehydrogenate the products to carbon and hydrogen. At temperatures over 750 °C, methane produced from propane cracking is further cracked to produce more carbon and hydrogen as observed previously [1].

Fig. 2 shows the product distribution of catalytic ((Fe–Pd)/Al_2O_3) propane decomposition as a function of reactor temperature. This catalyst promotes C–C bond breaking in propane. Consequently, hydrogen as well as methane production initiates at a much lower temperature compared to thermal decomposition. Above 475 °C, complete conversion of the propane to methane and hydrogen is observed. Therefore, at higher temperatures, the methane is catalytically cracked to produce hydrogen and carbon nanotubes, as discussed in one of our earlier papers [1]. Similar trends of high methane formation at relatively low temperatures (450–500 °C) were also observed for the other bimetallic catalysts [(Fe–Ni)/Al_2O_3 and (Fe–Mo)/Al_2O_3]. No ethene or ethane production was observed in catalytic propane cracking, whereas the thermal cracking of propane produced significant amounts of ethene and ethane.

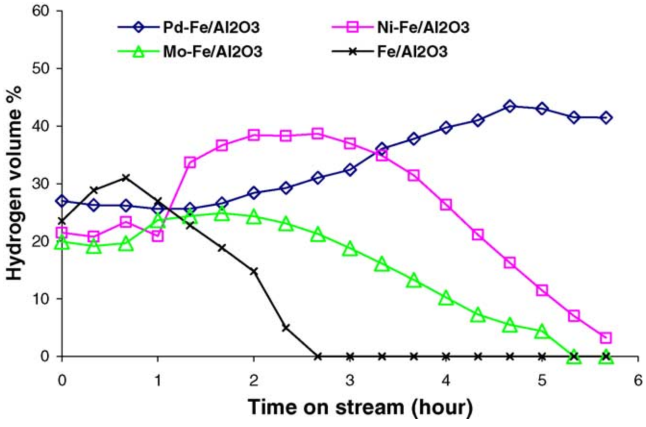

Fig. 3. Hydrogen production from propane decomposition over different catalyst at 475 °C.

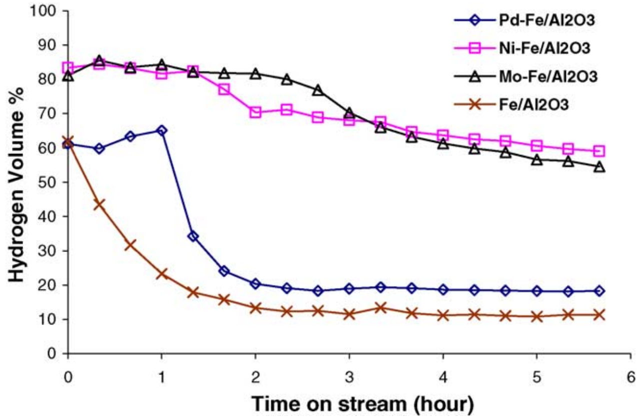

Fig. 4. Hydrogen production from propane decomposition over different catalysts at 625 °C.

Fig. 3 shows time-on-stream (TOS) hydrogen production from propane by the three binary catalysts at 475 °C reactor temperature. The (Fe–Mo)/Al_2O_3 catalyst is weakly active for hydrogen production and was the only catalyst to show almost no methane production at this temperature. Initially, very high propane conversion to methane and to a lesser extent to hydrogen was observed for the (4.5 wt.% Fe–0.5 wt.% Ni)/Al_2O_3 and (4.5 wt.% Fe–0.5 wt.% Pd)/Al_2O_3 catalysts. Hydrogen production further increased for the Fe–Pd catalyst, but declined to nearly zero for the Fe–Ni catalyst after 6 h TOS.

Catalytic production of hydrogen by decomposition of propane is much higher at 625 °C (Fig. 4) than at 475 °C (Fig. 3), which is in agreement with our previous experiments [1] on undiluted methane, in which all three catalysts showed high activity for methane decomposition at 700 °C. The activities of the bimetallic catalysts Fe–Ni/Al_2O_3 and Fe–Mo/Al_2O_3 at 625 °C showed only modest decay in TOS experiments. The monometallic 5%Fe/Al_2O_3 catalyst also has high activity for hydrogen production initially, but deactivates within about 1.5 h to the level of thermal decomposition alone. In a separate set of TOS experiments [3], we noted that

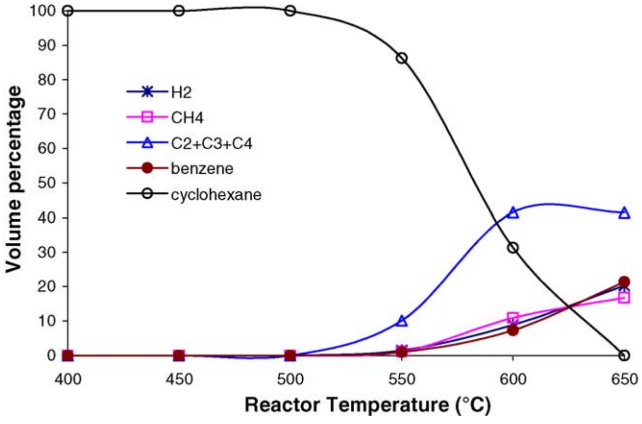

Fig. 5. Product distribution from thermal cracking of cyclohexane over the Al_2O_3 support vs. temperature.

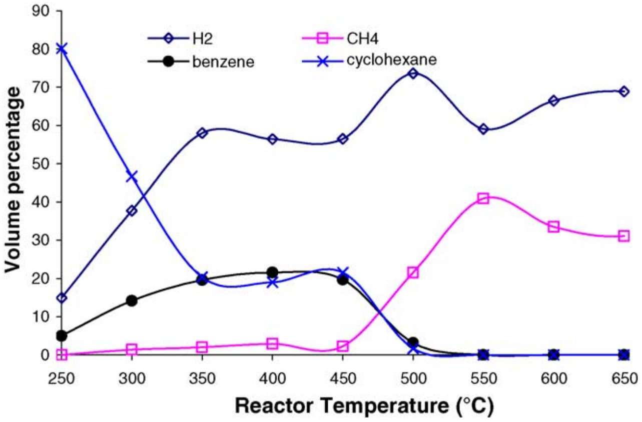

Fig. 6. Product distribution of cyclohexane decomposition over (4.5 wt.% Fe–0.5 wt.% Pd)/Al_2O_3 catalyst vs. temperature.

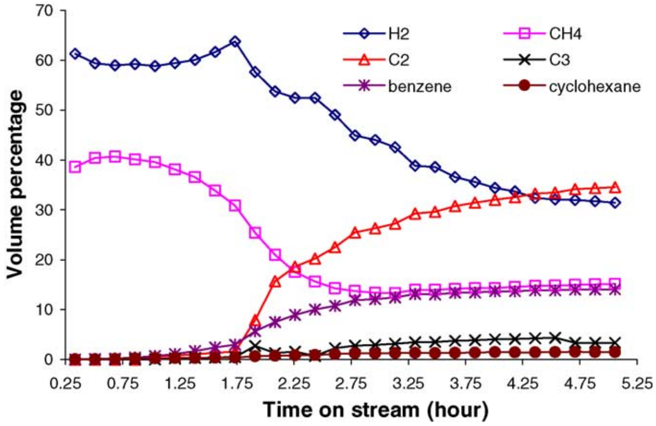

Fig. 8. Products distribution of cyclohexane decomposition over (Fe–Pd)/Al_2O_3 at 625 °C.

for a lower loading of catalysts—0.3 g instead of 0.5 g, there was no effect on the initial conversion and only the rate of deactivation was enhanced.

3.2. Dehydrogenation of cyclohexane

The product distribution from thermal cracking of cyclohexane is shown in Fig. 5. Above 500 °C, cyclohexane begins to decompose into hydrogen, methane, ethene, ethane, propane, benzene. As temperature increases, the amount of hydrogen, methane, ethylene, and ethane products increase. Above 550 °C, the conversion of cyclohexane increases rapidly as temperature increases, with 100% conversion of cyclohexane above 650 °C to 21 vol.% of benzene, 20 vol.% of hydrogen, 17 vol.% of methane and 42 vol.% of C2–C6 products in the reaction exit stream. The complexity of the products can be attributed to the acidity of the alumina and the free radical mechanism of thermal cracking reactions.

Fig. 6 shows the products distribution from catalytic decomposition of cyclohexane using the (Fe–Pd)/Al_2O_3 catalyst as a function of reactor temperature. In contrast to the complex array of products from thermal cracking, catalytic decomposition of cyclohexane produces only hydrogen, methane, and benzene. From 450 to 550 °C, the production of methane increases as cyclohexane is completely decomposed into hydrogen, methane and carbon nanotubes and nanofibers, which deposit on the catalyst bed. The amount of hydrogen and methane produced stays at about the same level from 550 to 700 °C.

Figs. 7 and 8 show time-on-stream behavior of the (Fe–Pd)/Al_2O_3 catalyst for cyclohexane decomposition at two reactor temperatures. When the catalyst deactivates, it actually increases cyclohexane conversion by producing more methane without significant reduction in hydrogen production. We expect most of the carbon nanofibers to be produced in this regime. At higher reaction temperature, there is initially a substantial amount of both methane and hydrogen production. Significant deactivation of the catalyst

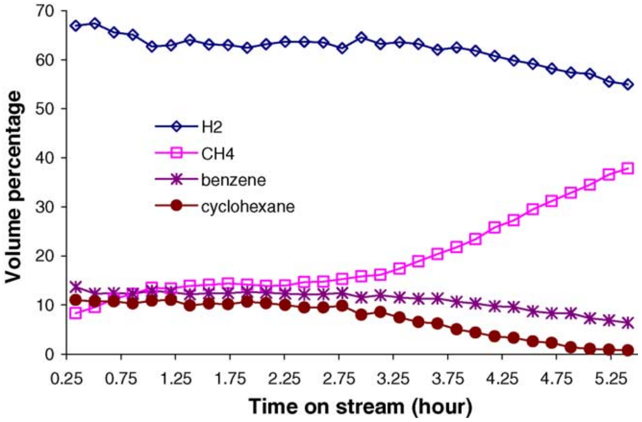

Fig. 7. Product distribution of cyclohexane decomposition over (Fe–Pd)/Al_2O_3 at 475 °C.

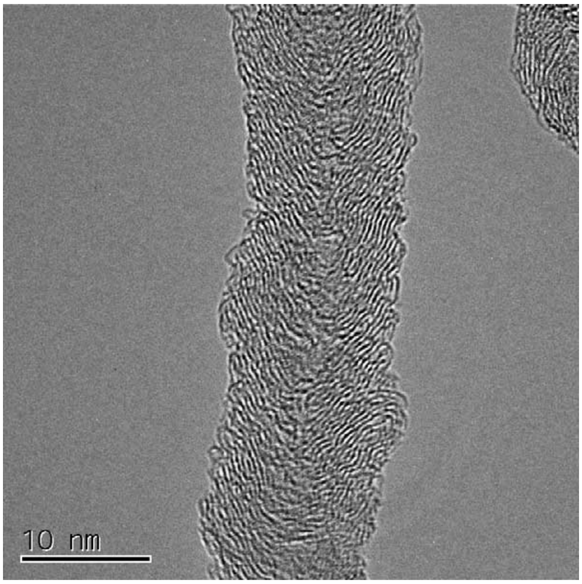

Fig. 9. HRTEM image of carbon nanofiber grown by decomposing undiluted propane over (Fe–Pd)/Al_2O_3 at 475 °C.

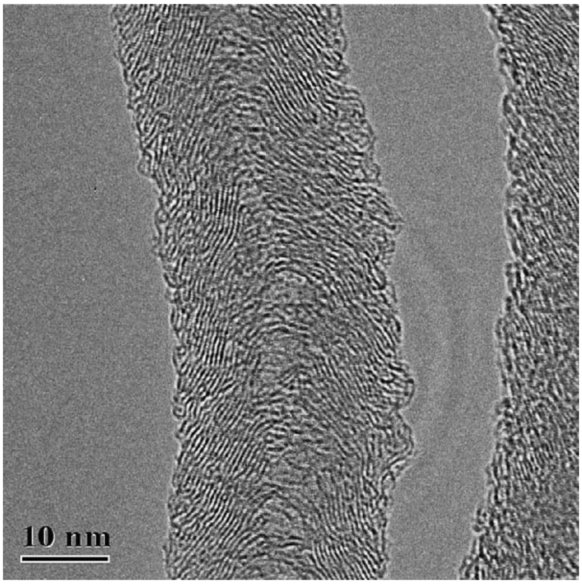

Fig. 10. HRTEM image of stacked-cones carbon nanofibers grown by decomposing cyclohexane over 4.5 wt.% Fe–0.5 wt.% Pd/Al_2O_3 catalyst at 475 °C reactor temperature.

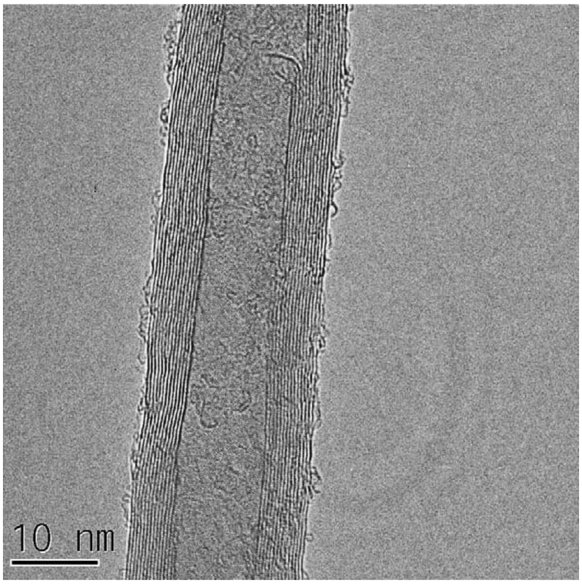

Fig. 11. HRTEM image of parallel multi-walled carbon nanotube grown by decomposing propane over (Fe–Pd)/Al_2O_3 at 625 °C.

begins after about 1.5 h TOS, where the methane is dimerized and polymerized to yield C2+ products. On the basis of these results, it was concluded that complete dehydrogenation of cyclohexane using (Fe–M)/Al_2O_3 catalysts was not as effective as partial dehydrogenation of cyclohexane using Pt supported on the stacked-cones carbon nanotubes [17].

3.3. Transmission electron microscopy (TEM) observations

A high resolution TEM (HRTEM) image of stacked-cone carbon nanotubes grown over the (Fe–Pd)/Al_2O_3 catalyst by decomposing undiluted propane at 475 °C is shown in Fig. 9. The same type of carbon nanofibers are produced in the catalytic decomposition of cyclohexane under the same reaction conditions (Fig. 10). Similar stacked-cone carbon nanofibers were observed in our earlier experiments [2] and have also been observed by several other research groups using different reaction conditions and catalysts [19–22]. Conventional multi-walled carbon nanotubes with concentric parallel walls are produced by catalytic decomposition of either propane or cyclohexane over the Fe–Pd/Al_2O_3 catalyst at 625 °C (Figs. 11 and 12).

As noted earlier, we obtained very good results for the partial dehydrogenation of cyclohexane and methylcyclohexane using catalysts consisting of very small amounts (0.25 wt.%) of Pt nanoparticles supported on stacked-cone carbon nanofibers [18].

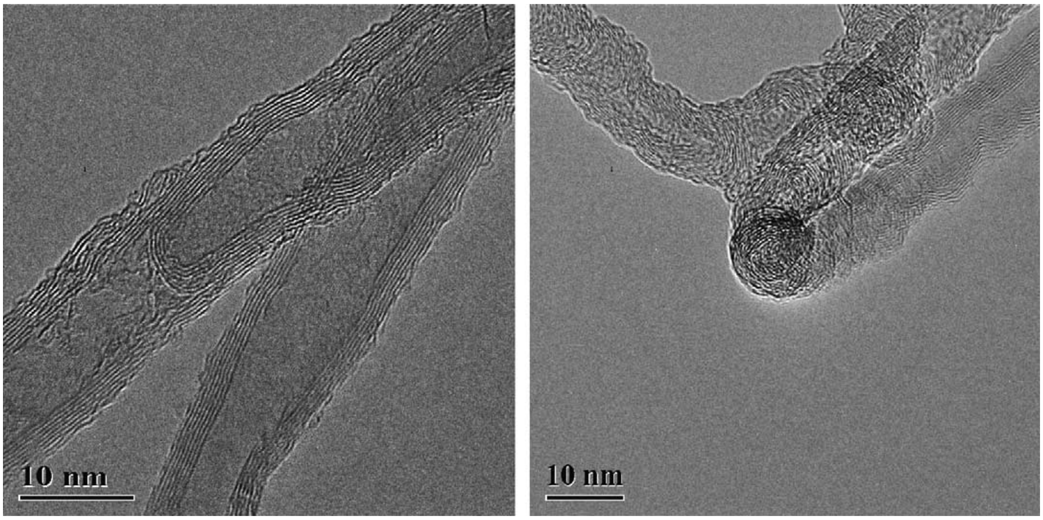

Fig. 12. HRTEM images of parallel multi-walled nanotubes as well as stacked-cones nanofibers grown by decomposing cyclohexane over (Fe–Pd)/Al_2O_3 at 625 °C.

4. Conclusions

Binary Fe–M/Al_2O_3 (4.5 wt.% Fe–0.5 wt.% M relative to Al_2O_3, where M = Ni, Mo, or Pd) catalysts are very effective for direct, non-oxidative, catalytic decomposition of propane into pure hydrogen and carbon nanotubes or nanofibers. Since, there are no carbon oxides in the product hydrogen stream, expensive separation and purification steps to produce pure hydrogen for use in PEM fuel cell applications are not required. These binary catalysts also decompose cyclohexane efficiently into hydrogen and methane at reaction temperatures of 500 °C or above.

Carbon is produced in two forms. At lower reaction temperatures (∼500 °C), binary catalysts catalyze the formation of stacked-cone carbon nanofibers. At higher reaction temperatures (∼625 °C), conventional multi-walled carbon nanotubes are produced. Cyclohexane decomposition at 625 °C produced a mixture of the two nanostructures.

Acknowledgement

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