CATALYSIS OVER NANOCARBON: STYRENE SYNTHESIS AND NH₃ DECOMPOSITION

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Abstract

Nanocarbons (graphite, tube, diamond) were used as highly efficient catalyst for styrene synthesis from oxidative dehydrogenation of ethylbenzene. Long-time stability and outstanding performance suggested a much more promising future for industrialization of nanocarbon. Metal-free nanocarbons are not highly active for NH₃ decomposition while residual metal nanoparticles in commercial CNTs could efficiently catalyze this reaction. Its catalytic performance is comparably high to those of typical industrial catalysts.

Background

The \( sp^2\)-hybridized nanographite ribbon and \( sp^3\)-hybridized nanodiamond as two novel nanocarbons have attracted a great deal of scientific interests. Nevertheless, their applications have still been limited in theoretical research fields. Here we report their performance as catalysts for two important reactions. Our study will open a new window for application of all nanocarbons.

Styrene as one of the vital monomers is traditionally produced over iron-based catalysts, which has still been essentially hindered by catalyst deactivation. Therefore excessive amount of steam is always required to maintain a long-time stability, which caused high consumption of heat (Cavani et al.). We used metal-free carbon nanotube and nanodiamond as catalyst and observed a comparable or even higher activity than the existing metal-based catalysts. Compared with conventional direction dehydrogenation process, the oxidative dehydrogenation over nanocarbons could be conducted at the temperature around 200~300°C lower than that of direction dehydrogenation, by which we achieved extremely high overall energy efficiency.

Applications of H₂ in fuel cell vehicles (FCVs) and distributed power stations require an advanced and "green" technology for on-site H₂ storage and production (T–Rassi, A.). However, the H₂ storage is the most serious technical challenge enabling the fuel cell based systems to be practical. Efficient storage of H₂ would greatly minimize the complexity and cost. NH₃ is a promising H₂ carrier due to its many outstanding properties. NH₃ can be easily liquefied at a mild condition (i.e. 30°C and 8 atm) and the infrastructure for its production and distribution is well established. Liquid NH₃ also possesses a much higher gravimetric capacity for H₂ storage (17.6%) than the conventional liquid carriers, e.g. methanol (12.5%), ethanol (13%), and gasoline (~12%). Most importantly, NH₃ decomposition is a convenient and environmentally benign route to produce CO₂–free H₂ (Choudhary et al., Zhang et al.). Here we report the novel use of commercial carbon materials as superiorly active catalyst for this reaction. The performance of commercial CNTs with residual metal nanoparticles was found to be similarly active to the reported commercial metal catalysts (Zhang et al.).

Methods

For oxidative dehydrogenation reaction, the commercial carbon nanotubes and nanodiamonds were provided by Nanocyl Inc. (Belgium) and Beijing Institute of Technology, respectively. Acid-washed activated carbon (ROX 0.8, 950 m² g⁻¹) was produced by Norit Deutschland GmbH. Kinetic selectivity and rate measurements were carried out in a fixed-bed quartz reactor using 5 mg of catalyst without mass transfer artifact. 500 mg of SiC pellets was added in order to prevent temperature gradients. The reactant consisted of ethylbenzene and O₂ at 2.8 and 1.4 kPa, respectively. He was used as the diluent to maintain the reaction at an atmospheric pressure. Conventional reactions were carried in the same reactor with using 50 mg of catalyst. On-line analysis of reactants and products was performed on a Varian CP-3800 gas chromatograph equipped with TCD and FID detectors.

For NH₃ decomposition reaction, one typical commercial CNTs from Bayer MaterialScience AG (Baytubes C150P) were tested. Elemental analysis revealed that the content of residual ashes in Co-containing CNTs is 4.1wt%. To increase the intensity of surface functional groups, the fresh CNTs was refluxed in boiling HNO₃ solution. 500 mg of SiC pellets was added in order to prevent temperature gradients. The reactant consisted of ethylbenzene and O₂ at 2.8 and 1.4 kPa, respectively. He was used as the diluent to maintain the reaction at an atmospheric pressure. Conventional reactions were carried in the same reactor with using 5 mg of catalyst. On-line analysis of reactants and products was performed on a Varian CP-3800 gas chromatograph equipped with TCD and FID detectors.
Scanning electron microscopy (SEM) was performed in a Hitachi S4800 electron microscope with an EDAX Energy Dispersive X-ray (EDX) detector. The microstructure of both CNTs and metal particles were examined ex-situ in a Philips CM200 FEG transmission electron microscope (TEM) equipped with electron energy loss spectroscopy (EELS) and EDX detectors. Thermal gravimetry analysis was performed by using a Netzsch STA-449C microbalance with a heating rate of 5 K/min in a flow of 20%O2/He.

Results and Discussion

Intrinsic reaction rates are measured over four commercial nanocarbons, i.e. nanodiamond, nanotube-1 (long and thick-wall), nanotube-2 (long and thin-wall), and nanotube-3 (short and thin-wall). Major byproduct is CO2 and the concentrations of ethylbenzene, styrene and CO2 contribute a well-closed carbon balance of 100±2%. After a short induction period, each nanocarbon stably catalyzes styrene formation over 1500 minutes. The obtained steady-state styrene selectivity is as high as 95%. Both outstanding stability and selectivity to target product suggest that nanocarbons are superior catalysts for future industrial applications. One typical activated carbon that reported in literature was tested here for comparison. However, from the beginning of reaction, both ODH rate and styrene selectivity gradually decreased to a great extent. After 1800 minutes, the ODH rate was only 4% of initial one while selectivity was as low as 76%. Figure 1 shows the long-time stability of carbon nanotubes in a conventional reactor. After an initial period for around 20 hours, the reaction became to be very stable during the following 100 h. The ethylbenzene conversion and styrene selectivity stayed at around 24% and 62%, respectively. Table 1 compares the ODH activities of carbon nanotubes with the typical catalysts reported in literature. It could be clearly seen that the used CNTs is comparably or much more active than metal-based catalysts and other carbons.

Figure 1. Performance of MWCNTs in a conventional reactor (O/EB=1, 50 mg, 2.4 h⁻¹, 673 K) and TEM of fresh CNTs.

Characterization of fresh and used nanocarbons shows no significant change in morphologies and surface chemical composition. TEM images CNTs before and after ODH reaction are shown in Figure 2. Many defects could be identified over the surface of fresh CNTs, which could be attributed to corrosion of concentrated HNO3 during functionalization procedure. Even after ODH reaction for 1800 min, the surface of CNTs still remained to be clean, in good accordance with its stable catalytic performance. The ex-situ X-ray photoelectron spectroscopy (XPS) spectra only revealed a negligible variance in the relative O/C ratio over the surface before and after reaction after neglecting the contribution from adsorbed steam. No noticeable change in C1s spectra, either on peak position or composition, could be identified. It could be therefore speculated that there is no coking during the ODH reaction for 1500 min. Concerning O1s signal, there is a significant decrease in intensity, which could be mainly attributed to the elementary peaks at 536.2–536.3 eV, corresponding to adsorbed water. After removal the influence of water peak, the surface compositions of used CNTs to fresh CNTs are almost same.

Table 1. Activities of various catalysts for ODH of ethylbenzene.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (°C)</th>
<th>LHSV (h⁻¹)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Steady rate (mmolg⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6%V/CeZr/SiO₂</td>
<td>400</td>
<td>1.1</td>
<td>20</td>
<td>92</td>
<td>1.96</td>
</tr>
<tr>
<td>20%V/MgO</td>
<td>530</td>
<td>3.9</td>
<td>32</td>
<td>96</td>
<td>11.4</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>440</td>
<td>0.09</td>
<td>44</td>
<td>99</td>
<td>0.35</td>
</tr>
<tr>
<td>FePO₄</td>
<td>440</td>
<td>0.09</td>
<td>24</td>
<td>86</td>
<td>0.16</td>
</tr>
<tr>
<td>Onion-like carbon</td>
<td>517</td>
<td>0.5</td>
<td>90</td>
<td>72</td>
<td>3.06</td>
</tr>
<tr>
<td>CNFs/Graphite</td>
<td>380</td>
<td>0.6</td>
<td>30</td>
<td>85</td>
<td>1.37</td>
</tr>
<tr>
<td>CNTs (present)</td>
<td>400</td>
<td>2.4</td>
<td>24</td>
<td>62</td>
<td>3.35</td>
</tr>
</tbody>
</table>
Our recent kinetic work reveals ODH reaction over $sp^2$- and $sp^3$-hybridized nanocarbons obeyed Langmuir-Hinshelwood (LH) model. Ethylbenzene and $O_2$ molecules are adsorbed over two types of adsorption sites, respectively. Then, adsorbed ethylbenzene and $O_2$ molecules or $O$ atoms react into adsorbed styrene and water, which will desorb from the carbon surface. Kinetic isotope effects are consistent with the hypothesis that breaking of C-H bond acts as the rate-limiting step ($R_H/R_D = 1.4$ at $400^\circ$C). In-situ characterizations (i.e. IR, XPS) proved that the unit of active sites for dehydrogenation of aromatic molecule comprises two connecting carbonyl groups.

Could carbonyl-based sites catalyze other dehydrogenation reaction (e.g. N-H bond in NH$_3$)? With this aim, we tested four samples, i.e. CNTs-fresh, CNTs-so, CNTs-mo and CNTs-ho, in NH$_3$ decomposition. As seen in Figure 3, the activity decreases with the extent of functionalization. The higher the strength of oxidation, the lower the NH$_3$ conversion. As revealed by SEM images and elemental analysis of samples, the weight fraction of residual Co in CNTs decreases according to the order: CNT-fresh > CNTs-so > CNTs-mo > CNTs-ho. Here, the activity for NH$_3$ decomposition could be mainly attributed to residual Co nanoparticles in CNTs that also catalyzed the CNTs growth during CVD process. The future research on NH$_3$ decomposition will focus on CNTs as support for metal or nitride nanoparticles and metal-carbon interaction.

**Reference**


