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Synthesis of open-ended MoS_2 nanotubes and the application as the catalyst of methanation

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We report the synthesis of open-ended MoS_2 nanotubes and their application as the catalyst for methanation of carbon monoxide with hydrogen. Because the catalysis of the methanation reaction occurs at relatively low temperatures, such nanotubes may provide new solutions toward harnessing the environmental load caused by CO emission.

Inorganic fullerene-like WS_2 and MoS_2 polyhedra and nanotubes, first described by Tenne and coworkers,[1,2] have aroused considerable interest because of their unique structural characteristics. These nanomaterials have been prepared through different methods such as gas–solid reaction,[1–4] chemical transport,[5] solution routes,[6] *in situ* heating,[7] and activation techniques.[8] Attention is now being focused on their potential applications in various fields of material research, such as heterogeneous catalysis,[9] ultra-low friction,[10] scanning probe microscopy,[11] and electrochemical hydrogen storage.[12] In the field of heterogeneous catalysis, polycrystalline MoS_2 particles had been used as the catalysts for methanation of carbon monoxide and hydrogen at temperatures around 350 °C (or higher) but had low activity.[13] Here we report that open-ended MoS_2 nanotubes exhibit much higher catalytic activity for methanation of CO + H_2 at relatively low temperatures (150–250 °C).

A gas–solid reaction was employed to prepare open-ended MoS_2 nanotubes. The procedure consists of three steps: (1) the preparation of needle-like tetrathiomolybdenum $(NH_4)_2MoS_4$ from ammonium molybdenum hydrate $(NH_4)_6Mo_{12}O_{39}\cdot 12H_2O$; (2) the ball milling (Kurimoto, 700 rpm for 1 h) of $(NH_4)_2MoS_4$ under a H_2 atmosphere (0.2 MPa); and (3) the sintering (400 °C for 10 h) of the as ball-milled sample in a floating hydrogen–thiophene atmosphere (50 ml min^{-1}, 95% H_2 + 5% C_4H_4S). A gas chromatograph analysis (GL Science GC353B) detected no content-decrease of C_4H_4S in the emerging gas mixture, indicating that it only acts as a growth-promoting catalyst. A notable difference is observed in the absence and in the presence of C_4H_4S. An increase of the loading amounts of C_4H_4S up to 5% was found to achieve an optimal yield of open-ended nanotubes of 3–5 grams per day. A characteristic SEM image of the products shows a large amount of nanotube filaments (Fig. 1a), homogeneously distributed over large areas. A typical TEM image at low magnification (Fig. 1b) shows that the as-synthesized product consists of many nanotubes rather than nanoparticles. The high-resolution TEM image in Fig. 1c demonstrates that the nanotube tip is completely open. The purity of MoS_2 nanotubes in our products is more than 90 wt% based on the SEM and TEM observations. The outer diameter of a typical hollow tube is ~25 nm, while the inner diameter is ~12 nm. The average distance between each of the two neighbouring fringes ($c/2$) is 0.63 nm, which corresponds to the interlayer (002) d-spacing of the 2H-MoS_2 lattice. The chemical composition of the nanotube was analyzed by energy dispersive X-ray spectroscopy (EDXS), showing an atomic Mo/S ratio of 1.0:2.0. The X-ray photoelectron spectroscopy determined by a JEOL JPS-9010MX spectrometer with Mg Kα radiation (1253.6 eV) indicates that the chemical valence of molybdenum in the nanotubes is +4 due to the fact that a binding energy of 228.9 eV, assigned to Mo $3d_{5/2}$ in MoS_2, is detected. Therefore, the reaction involved is:

$$(NH_4)_2MoS_4 + H_2 \rightarrow MoS_2 + 2NH_3 + 2H_2S \quad (1)$$

The reaction of

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

was studied in a flow microreactor (ϕ 10.0 mm × 30.0 mm), in which multi-layer MoS_2 nanotubes were sandwiched by Ni foam substrates. Mass-flow valves and pressure gauges were used to control the flow of gases into the microreactor that was mounted vertically to minimize diffusion limitation and was able to operate up to 3.0 MPa. The gas mixture emerging from the microreactor was diverted through a four-way valve to a sample loop and then analyzed by a gas chromatograph (GL Science, GC353B). The reaction temperature was varied from 100 to 300 °C.

The consumption rate of CO observed as a function of temperature for open-ended MoS_2 nanotubes is shown in Fig. 2. The major products detected by GC were CH_4 and H_2O. Trace C_2H_6 accounted for less than 0.5 mol% of the reaction products. The conversion of CO to CH_4 is complete at temperatures higher than 200 °C. It is worth noting that in the case of polycrystalline MoS_2 particles, less than 30% conversion occurred at 300 °C and high activity was obtained only at a higher temperature of 400 °C.[13] After 50 consecutive hours of

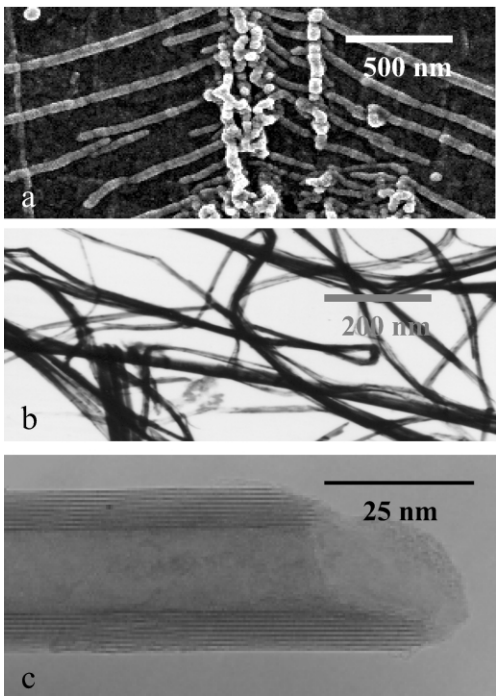

Fig. 1 Images of the as-synthesized MoS_2 nanotubes: (a) SEM image showing the entangled ropes, (b) low-magnification TEM image, and (c) HRTEM image for one open-ended tube tip.

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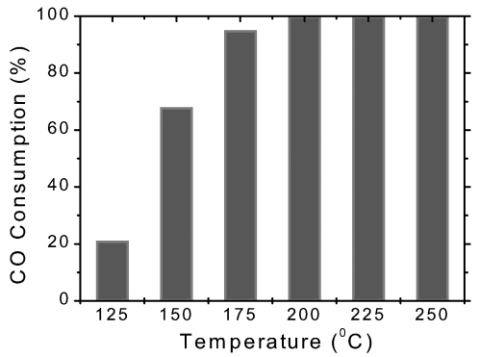

Fig. 2 Catalytic activity of open-ended MoS_2 nanotubes for methanation of carbon monoxide and hydrogen.

catalyzing, no obvious deterioration has been observed, signaling a promise catalysis life.

The accepted mechanism for methanation of CO and H_2 involves three steps: (1) the adsorption of CO and H_2; (2) the cleavage of the C–O bond to produce CH_x species; and (3) the hydrogenation of CH_x species with activated hydrogen atom.[14] An interesting point is where the catalytic action of the MoS_2 nanotubes take place. There have been many studies on the relationships between the structure and the activity of molybdenum sulfide catalysts.[15] In MoS_2 platelets (2H), most of the catalytic action occurs on the dangling bonds of the Mo atoms at the prismatic (100) faces of the platelet. However, the open-ended nanotubes only expose such prismatic edges at their open ends, which are only a small fraction of their surface. Consequently, one is led to believe that the entire surface of the nanotubes is reactive, perhaps due to its curvature, which leads to a distortion of the bond angles. The next question is which of the two faces of the nanotubes is more reactive, or perhaps the reaction occurs also on the van der Waals galleries between the two layers of the multiwall nanotubes. Since MoS_2 nanotubes exhibit smaller band gaps and unique electronic structures compared to the polycrystallites,[16] we can imagine the 'activated hydride' islands of H···S–Mo–S···H groups, which coagulate with a proper size for hydrogen spillover. These questions will have to be addressed in future studies.

In summary, open-ended MoS_2 nanotubes are highly effective for catalytic methanation of CO and H_2 at relatively low temperatures, and this provides a potential solution to the energy conversion of global carbon oxides. Its further study may also lead to a way to eliminate CO species in fuel cells and thus to solve the key 'poisoning' problem of noble-metal catalysts.

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