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Preparation and Characterization of Nanostructured Particulate Catalytic Materials

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Laser Induced Solution Deposition (LISD) is essentially a laser chemical processing with similar mechanism of the counterpart - laser chemical vapor deposition (LCVD). It is a novel method for synthesizing nanoscale particles or thin films with the combined advantages of laser chemical vapor deposition and electroless chemical deposition in solution (electrolyte). It is simple and efficient, and it can produce high quality nanoparticles or patterned uniform thin films. In this paper the nanostructured Co/CoOx particles have been fabricated by LISD technique. We have characterized the deposited materials by using scanning electron microscope (SEM), the high-resolution transmission electron microscope (HRTEM) and X-ray diffraction technique (XRD). We have found that the sizes of the deposited particles are smaller than 5 nm uniformly suspended in the solution used in the LISD deposition, and the sizes are smaller than 500 nm on the silicon substrates inserted in the deposited solution. The results by energy dispersive X-ray analysis (EDX) have indicated that there are Co peaks and O peaks, which meant there were oxygen contamination or the deposited products were cobalt oxide rather than pure cobalt nanoparticles. The X-ray diffraction has shown that we have obtained pure Co nanoparticles in some cases but we have obtained cobalt oxides in other cases, which mainly depended on the experimental conditions such as the selection of solvents and solutes as well as the selection of the lasers including the wavelength and the power of the laser beams. The studies of the magnetic properties, catalytic properties as well as their relationship of pure cobalt nanoparticles and cobalt oxide nanoparticles are in good progress and we will publish the useful results elsewhere.

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Preparation and Characterization of Nanostructured Particulate Catalytic Materials

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ABSTRACT

Laser Induced Solution Deposition (LISD) is essentially a laser chemical processing with similar mechanism of the counterpart - laser chemical vapor deposition (LCVD). It is a novel method for synthesizing nanoscale particles or thin films with the combined advantages of laser chemical vapor deposition and electroless chemical deposition in solution (electrolyte). It is simple and efficient, and it can produce high quality nanoparticles or patterned uniform thin films. In this paper the nanostructured Co/CoO_x particles have been fabricated by LISD technique. We have characterized the deposited materials by using scanning electron microscope (SEM), the high-resolution transmission electron microscope (HRTEM) and X-ray diffraction technique (XRD). We have found that the sizes of the deposited particles are smaller than 5 nm uniformly suspended in the solution used in the LISD deposition, and the sizes are smaller than 500 nm on the silicon substrates inserted in the deposited solution. The results by energy dispersive X-ray analysis (EDX) have indicated that there are Co peaks and O peaks, which meant there were oxygen contamination or the deposited products were cobalt oxide rather than pure cobalt nanoparticles. The X-ray diffraction has shown that we have obtained pure Co nanoparticles in some cases but we have obtained cobalt oxides in other cases, which mainly depended on the experimental conditions such as the selection of solvents and solutes as well as the selection of the lasers including the wavelength and the power of the laser beams. The studies of the magnetic properties, catalytic properties as well as their relationship of pure cobalt nanoparticles and cobalt oxide nanoparticles are in good progress and we will publish the useful results elsewhere.

INTRODUCTION

Nanoscale and well-dispersed fine particle catalysts offer many advantages such as least diffusion resistance, easy accessibility to reactants, and large number of active sites. Since the efficient conversion of CO/CO₂ gases to useful fuels is a major challenge facing scientific community, novel nano-particle catalysts seem to provide a promising alternative to conventional catalysts.

Laser pyrolysis and photolysis are popular methods that have been used to prepare catalytic materials[1-5]. LISD offers several advantages over other methods because the deposition takes place in solution. All deposition experiments are carried out in the solutions of ammonia dissolved in distilled water or containing various mixtures of methanol, cyclohexane,

tetrahydrofuran (THF) and dielether. The selection of solvents is crucial for successful deposition. The principle of solvent selection is that the selected solvents can dissolve solutes completely and the solvent/solute mixture is transparent in the laser wavelength used in the experiment. Our previous results have demonstrated clearly the feasibility using LISD technique making the deposits of nano/micro particles and thin films of gadolinium borides and other rare earth hexboride compounds [6-8]. We have also succeeded in producing well-dispersed uniform nanoparticle magnetic oxides such as CrO_2 and Cr_2O_3 [9]. Selective area deposition of metallic nanoparticles and thin films from solution has been investigated and has also been applied to the deposition of copper and other materials including complex compound materials. Compared with other techniques LISD is a unique method to fabricate nanoscale complex materials. We believe in that LISD is also a unique method to produce nanoscale and well dispersed catalyst particles because it can meet the needs of high yield, high selectivity and size controllability.

In the present work we have used laser induced solution deposition (LISD) technique to prepare nano-particle syngas conversion catalysts containing ferromagnetic metals (Fe, Co) in order to control the particle size in a narrow size range since the nanometer scale metal clusters exhibit size dependent physical properties. The state of the partially filled d-shells and unpaired electrons, morphology and metallic charge distribution of these catalysts are known to govern both their catalytic and magnetic behavior.

EXPERIMENTAL DETAILS

Figure 1 shows the diagram of one of the laser-induced solution deposition systems (LISD) we have established in IfM. The system included an argon ion laser, the necessary focusing lenses elements, mask and chemical reactor as indicated. Coherent INNOVA90C-6 laser was used as energy source. Two wavelengths had been applied: (a) the multiple line visible spectrometers (MLVS, 469 to 515 nm), and (b) the multiple line ultra violet (MLUV, 333.1 to 361.4 nm). The maximum power output was 9.0 watts (W) for (a) and the maximum power output was 1.5 W for (b).

Cobalt nitrate and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as precursors. The distilled water was used to dilute the precursors to form complex $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions. The laser energy activated the decomposition of the complex ions, which transferred the Co ions into Co with the transferring electrons from the ammonia dissolved in the solution. Various concentrations of solutions and laser conditions have been tried. Here shown is the solution with 0.1 M $\text{Co}(\text{NO}_3)_2 + \text{NH}_3 \cdot \text{H}_2\text{O}$ under the exposure of focused laser beam (power = 1.7 W) in the region of UV for the deposition time of 40 min.

RESULTS AND DISCUSSION

We have tried many ways to optimize LISD deposition techniques. We have observed the deposited samples by using scanning electron microscope (SEM), the high-resolution transmission electron microscope (HRTEM) and X-ray diffraction technique (XRD). SEM is the simplest and cheapest method so we usually used SEM to check the samples for the first time. The SEM results clearly indicate that the nanoparticles have been deposited.

From the images of SEM, we can estimate that the diameters of the deposited particles are about 100 to 500 nm. Figure 2 shows the scanning electron microscope image of central

deposition area on silicon substrates. It can be compared with the Co (or cobalt oxide) nanoparticles deposited on the silicon substrates away from the central area and also can compare with the Co (or cobalt oxide) nanoparticles directly taken from the solution (not shown here due to the limitation of pages). It is obvious that the particles (average diameter \sim 100 to 200 nm) directly from the solution is much smaller than those deposited on the silicon substrates (average diameter \sim 300 to 500 nm). We postulated that the growth rate of the nucleated particles on the substrates is faster than that in the solutions.

Figure 3 shows the high-resolution TEM image of the Co/CoO_x nanoparticles directly taken from the solution after the deposition. The diameters of the deposited particles we measured are less than 5 nm with very narrow regime. Figure 4 shows the selected – area electron diffraction pattern of the CoO_x nanoparticles directly taken from the solution after the deposition. They have shown very promising and encouraging results. However, there appears the oxygen peaks in the EDX spectroscopy, which indicates oxygen contamination or the formation of cobalt oxides as shown in Fig. 5. The exact structures of the deposits need to be investigated by high resolution X-ray diffraction and nano-diffraction pattern analysis technique of high-resolution transmission electron microscopy, which we have scheduled to do in the near future. Therefore in word the preliminary experiments have shown very promising and encouraging results but much more work need to be done for the fabrication of nanostructured bimetal catalysts (Fe, Co) and (Fe, Cu) which we have proposed.

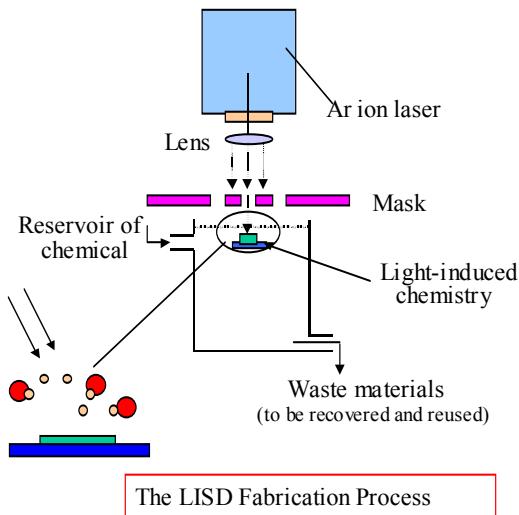


Figure 1. The diagram of laser-induced deposition from solution (LISD)

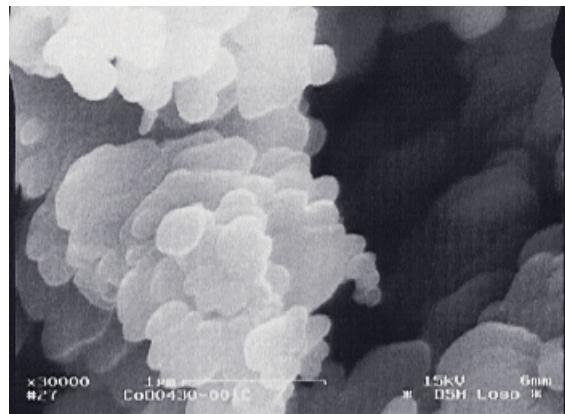


Figure 2. The SEM image of Co/CoO_x nanoparticles on Si substrate taken from the laser beam center area. The particle size is about 200 – 500 nm in diameter (magnification 30,000 ×)

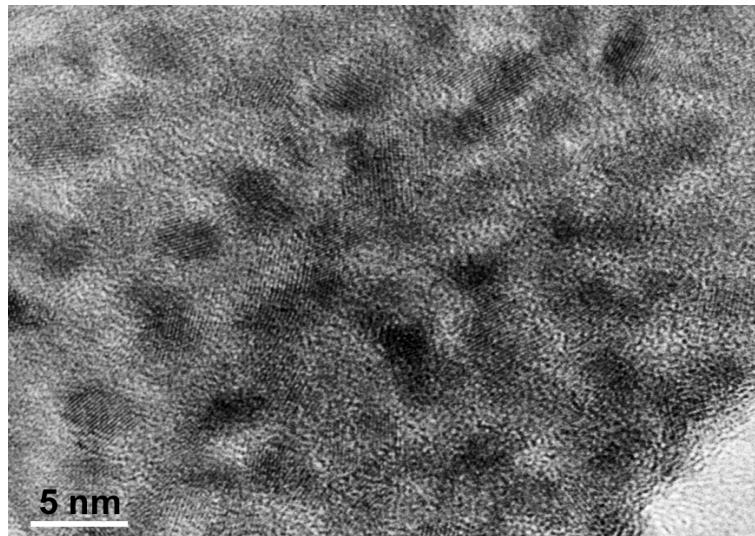


Figure 3. The high-resolution TEM image of the Co/CoO_x nanoparticles directly taken from the solution after the deposition (the diameter of the deposited particles are less than 5 nm).

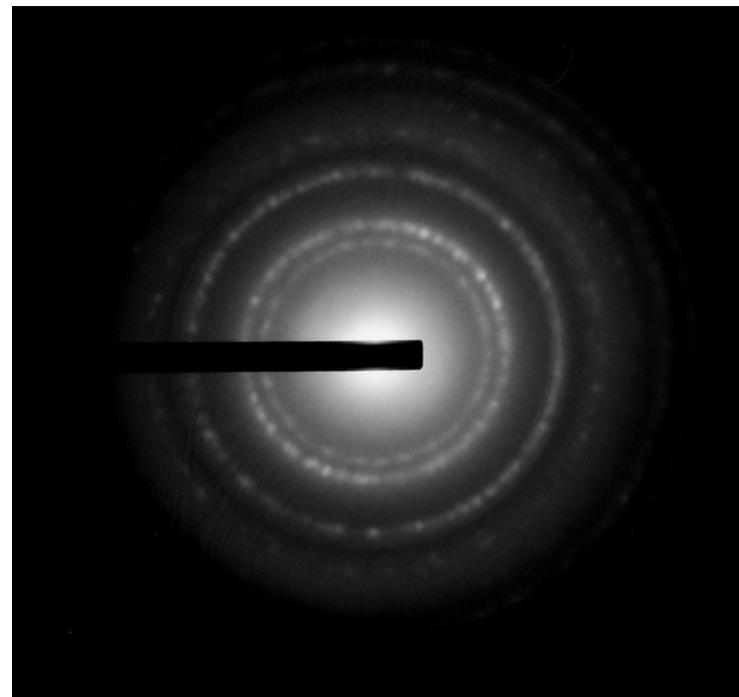


Figure 4. The selected - area electron diffraction pattern of the CoO_x nanoparticles directly taken from the solution after the deposition.

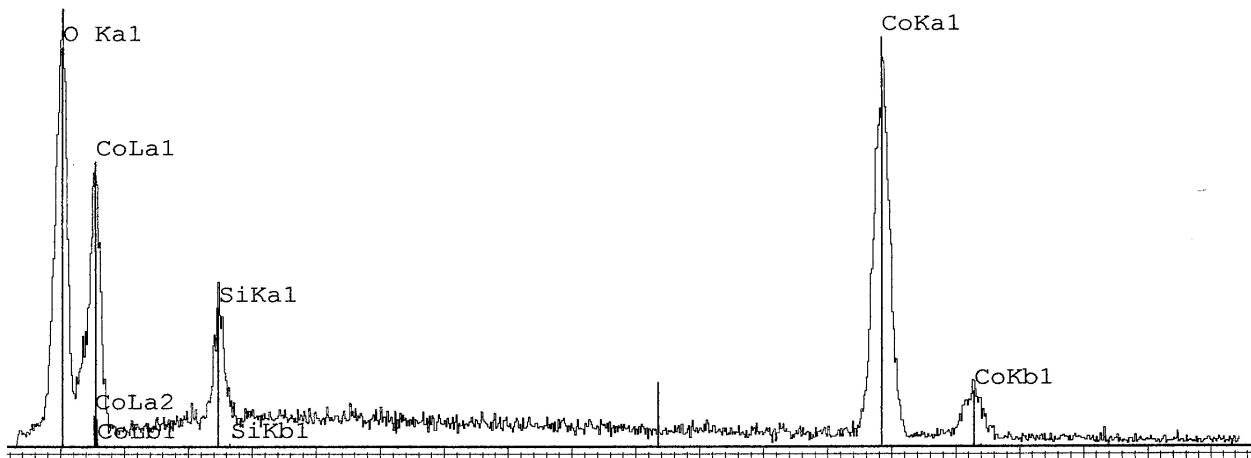


Figure 5. The EDX composition analysis shows strong Co peaks (the O peak may indicate the contamination of oxygen and the formation of cobalt oxides)

CONCLUSIONS

As a conclusion, we can say that we have shown strongly that laser-induced solution deposition (LISD) is a novel and unique method for fabricating nanoscale particulate materials such as the nano-catalysts. We have succeeded in synthesizing nanostructured pure Co or Co oxide nanoparticles. We have studied the micro-/nano-structure and the composition of the deposited nanopartilces by SEM, EDX, high-resolution TEM and XRD. The suspended nanopartilces in the solution are less than 5 nanometers and the distribution of the nanoparticles are in very narrow regime, which is unique and useful for the catalytic properties and other functional (chemical or physical) properties. The particles deposited on the silicon substrates are much larger, which is in the region of 100 to 500 nanometers in diameter.

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