A New System Design for the Preparation of Copper/Activated Carbon by Metalorganic Chemical Vapor Deposition Method

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Abstract

A Metal-Organic Chemical Vapor Deposition (MOCVD) technique was used to prepare heterogeneous metallic catalyst supported on activated carbon. A new system design was built to achieve higher metal loading within shorter preparation time. In the optimization of system parameters, higher metal loading can be achieved by using longer deposition time, optimum carrier gas flow rate, higher operating temperature of evaporator or smaller amount of porous support. Several techniques were carried out to characterize the catalyst such as Physisorption, X-Ray Diffraction, Inductively Coupled Plasma – Optical Emission Spectroscopy and Scanning Electronic Microscopy assisted with the Energy Dispersive X-ray Spectroscopy (SEM-EDX). It was found that the B.E.T. specific surface area and total adsorption volume of the prepared catalysts were reduced after metal deposition, due to the formation of the deposited copper onto the porous media. The morphology of the cylindrical Cu/AC was analyzed by SEM-EDX. The results show that the metal was deposited with a reasonably uniform distribution onto the inner part of the porous support.

Keywords : MOCVD, Metallic supported activated carbon, SEM-EDX

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Introduction

Conventional heterogeneous catalyst preparation methods, such as impregnation, ion-exchange and co-precipitation, require several steps such as adsorption, drying, calcination and reduction, which would significantly alter and sinter the catalyst structure and reduce the active surface area of the catalyst. To overcome these problems, a novel preparation method, Metalorganic Chemical Vapor Deposition (MOCVD), was suggested. Various types of CVD system designs have been used in the semiconductor industry [Borgharkar and Griffin, 1998; Jain *et al.*, 1991; Jain *et al.*, 1993; Lecohier *et al.*, 1992a,b; Lee *et al.*, 1998; Rees *et al.*, 1992; Senzaki, 1998].¹⁻⁸ However, study of the system design to prepare heterogeneous catalysts was scanty [Suvanto and Pakkanen, 1997].⁹

Figure 1.

Recently, a CVD system, as shown in Fig. 1, was used to prepare heterogeneous catalysts. In this system design, two tubular quartz tubes were vertically placed inside two furnaces, respectively, as the evaporator (Tube A) and the deposition reactor (Tube B). Each quartz tube contains a supportive porous quartz sieve with a pore size of about 300 μm . Vacuum was used to increase the volatility of the precursor. Another tube (Tube C) was installed inside a water bath to remove condensable materials before the vacuum pump in order to protect the vacuum pump. All parts were connected by $\frac{1}{4}$ " stainless steel flexible tubes. The problem of this design is that significant precursor condensation was found between tubes A and B. This results in a long deposition time, low metal loading, and even worse, causes blockage in the system. To solve this problem, a new CVD system design was suggested in this study. The new CVD system can shorten the deposition time and increase the metal loading in the support. To distinguish the two designs, the system used by Chu *et al.* [1998]¹⁰ is referred to as the old system design.

Experimental

The new CVD system is illustrated in Fig. 2. It composes of several essential elements such as the evaporator (zone AB) for storing the organometallic precursor, the deposition reactor (zone BC) hosting the porous support, and the vacuum pump used to increase the volatility of the precursor and to make it easier for the transfer of the precursor vapor from the evaporation zone to the deposition zone.

Figure 2.

Highly porous activated carbon was chosen as the support [Auer *et al.*, 1998; Juntgen, 1986]¹¹⁻¹². Because copper has been proved to be a good active element on various applications [Mehandjiev *et al.*, 1995; Yang and Kikkinides, 1995]¹³⁻¹⁴, it will be used as the active metal element to be deposited onto the activated carbon. Nitrogen was chosen as the carrier gas and hydrogen was used for the reduction process. The gas flow rate was controlled by the NUPRO needle valves. Both evaporator and deposition reactor were made of 316 stainless steel and connected by the VCR Face Seal fittings, supplied by Swadgelok Company. There are three sieves located at points A, B and C. Sieve A is to equalize the incoming carrier gas flow and to evenly distribute the gas flux on gaseous precursor material. Sieve B is used to separate the precursor material and the porous support from being mixed together. Sieve C is to prevent the porous support from being carried away by the carrier gas. Tube D is a condensation zone which prevents the condensed precursor from blocking the tube in the latter part of the CVD system. Flexible heating tapes, purchased from the Thermolyne Company, were used as the heating elements. The heating rate was controlled by a temperature controller using a K-type Thermocouple to detect the actual temperature.

Norit Activated Carbon (AC) type ROW 0.8, supplied by the American Norit Company, was chosen as the porous support and was in the form of 1/32" cylindrical extrudates. This Norit AC was flushed with the de-ionized water and soaked with 5 % hydrochloric acid to wash out the unwanted biological and chemical impurities. Another essential material in the CVD system was the precursor material. An organometallic compound, copper(II) acetylacetonate or $\text{Cu}(\text{acac})_2$, purchased from the Aldrich Chemicals Company, was used as the precursor material for the deposition of copper on AC.

In each CVD process, the treated Norit AC was firstly degassed at 320°C under vacuum condition to remove the unwanted moisture and volatile organics. Then, 1 g of the fresh solid precursor and certain amount of the degassed Norit AC were placed inside the evaporator and the deposition reactor, respectively. To evenly distribute the solid precursor material and the AC inside the

system, shaking was done before the deposition experiment. After the desired operating temperature in both evaporator and the deposition reactor were attained, vacuum was slowly applied by controlling the needle valve. Until the appropriate vacuum condition was achieved, the carrier gas was allowed to flow through the CVD reactor.

Adsorption isotherm of nitrogen at 77 K was measured by an Omnisorp Coulter 100CX unit to determine the B.E.T. specific surface area, total adsorption volume and pore size distribution of the prepared catalysts.

X-Ray Diffraction (XRD) analysis was conducted to examine the metal status of the prepared catalysts and to see whether there is a crystalline form of the material present on the support. The spectroscopic results of the XRD analysis was recorded by a Philips PW1825 diffractometer using a wavelength of 1.540562 Å of the CuK α radiation. The prepared catalysts were analyzed with different angular ranges under a scanning speed of 0.01°/sec with a step of 0.01°. The equipment was operated at 40 kV and 50 mA.

In examining the metal loading of the prepared catalysts, Inductively Coupled Plasma (ICP) analysis was conducted. The prepared catalyst was firstly soaked in 65 % concentrated nitric acid at room temperature for 48 hours in order to dissolve the deposited metal into the solution. The filtrate was ready for the ICP analysis to determine the metal ion concentration by an Optima 3000XL, manufactured by Perkin Elmer Company.

Results and Discussion

Fig. 3 shows the effect of CVD system design on Cu loading of the catalyst. The examined catalysts were prepared under the conditions of a carrier gas flow rate of 1 mL/s, an evaporator temperature of 180°C and a deposition temperature of 320°C in both system designs using 1 g of fresh AC. Using the old system design, the metal loading in the cylindrical Cu/AC can reach a maximum concentration of about 2 wt % at 15.5 hours deposition time, as seen in Fig. 3(a). A decrease in metal loading after 15.5 hours was observed. This may be due to the desorption of the deposited precursor from the surface of the support after the precursor has been used up.

Figure 3.

By using the new system design in the CVD system, metal loading as high as 10 wt % could be obtained at a much shorter time of one hour, as seen in Fig. 3(b). This demonstrates the advantage of the new CVD system design.

Comparing Figs. 3(a) and (b), the metal loading using the new system design was much higher than using the old system design. This can be explained by the new design in the CVD system which greatly reduces the phenomenon of precursor condensation by using the efficient heating system design. Using larger connecting tubes of ½" rather than ¼" could also reduce the blocking effect of the condensed precursor material which happened in the outlet of the deposition reactor. The distance between the evaporation and deposition zones in the new system design was much shorter. In other words, the time needed to transfer the gaseous precursor to the support in the new system design was much shorter than in the old system design. Owing to this design modification, the metal loading in the cylindrical Cu/AC was greatly enhanced in the new system design.

The effect of carrier gas flow rate on the metal loading of catalyst was shown in Fig. 4. The metal loading of the catalyst increases as gas flow rate increases for the experimental range examined. For both system designs, the amount of porous support was 1 g, the evaporation temperature was 180°C, the deposition temperature was 320°C and the carrier gas flow rate was 1 mL/s. In the old system design, about 2 wt % of metal loading could be obtained after 15.5 hours of deposition time. While in the case of new system design, 6.5 - 8 wt % metal loading in the support was achieved with a much shorter deposition time of only 30 minutes. It is also noted that the metal loading in the new system design was less sensitive to the carrier gas flow rate. As previously mentioned, using the efficient heating system design and ½" tube could significantly reduce the precursor condensation. In conclusion, the new CVD system design greatly enhances the metal loading in the prepared catalysts, comparing to the old system design.

Figure 4.

To further study the modified design of the CVD system, several parameters were examined such as the evaporator temperature, the particle size and the amount of porous support.

Figure 5.

In studying the effect of evaporator temperature, 0.2 g of the fresh AC was used. The deposition time, carrier gas flow rate and deposition temperature were fixed at 30 minutes, 1.15 mL/s and 320°C, respectively. The effect of the evaporator temperature on the metal loading of the catalysts was shown in Fig. 5. The evaporator temperature examined ranges from 160°C to 200°C. It is observed that the metal loading on the catalysts was directly proportional to the evaporator temperature. As the evaporator temperature increases, it speeds up the rate of sublimation and increases the vapor pressure of the precursor material. As a result, relatively concentrated gaseous precursor can be generated in the evaporator and then deposited onto the porous support. Hence, an increasing trend of metal loading on the catalysts with evaporation temperature was observed.

Figure 6.

The amount of porous support used per experiment was varied from 0.2 g to 1.5 g to study its effect on the copper loading of the product. The prepared conditions of the catalyst were: deposition time of 30 minutes, carrier gas flow rate of 1.15 mL/s, evaporator temperature of 180°C and deposition temperature of 320°C. The effect of the amount of support on the copper loading of the catalyst is shown in Fig. 6. The copper concentration in the catalyst decreases as the amount of support used increases. This is so because the gaseous precursor requires longer time to diffuse onto each support particle when a larger amount of support was used.

Figure 7.

The effect of particle size on the metal loading of the catalysts was illustrated in Fig. 7. The examined catalysts were prepared at a carrier gas flow rate of 0.5 mL/s, an evaporator temperature of 180°C, a deposition temperature of 180°C and a deposition time of 30 minutes using 1 g of fresh AC. The metal loading was shown to gradually decrease with increasing the particle size of the support. It could be explained that an increase in particle size would have a longer diffusion path for the precursor to enter the interior of the particle. With smaller particle size, diffusion path was relatively shorter and higher metal loading was resulted.

XRD Analysis

Fig. 8 shows the XRD spectroscopy of the porous support and the developed catalysts of Cat-1 (8.42 wt %) and Cat-2 (11.36 wt %), corresponding to the catalysts prepared using a deposition time of 30 and 60 minutes, respectively. Both catalysts were prepared using the new system design, a carrier gas flow rate of 1.15 mL/s, an evaporator temperature of 180°C and a deposition temperature of 320°C. Sharp intensive peaks were observed in the characteristic positions of Cu at 43.295° and 50.431°, Cu₂O at 36.417° and 42.295°. Catalyst Cat-1 (dashed line) shows that there is a crystalline copper structure with indicative sharp peaks located at 43.295° and 50.431°. On the other hand, catalyst Cat-2 (dotted line) has both crystalline structures of elemental copper (peaks at 43.295° and 50.431°) and Cu₂O (peaks at 36.417° and 42.295°). Unlike the prepared catalysts, the blank AC (solid line) shows no crystalline structure related to copper or copper oxide. This indicates that the crystalline structure of copper or copper (I) oxide presented in the prepared catalysts is due to the deposition from the metallic precursor material, Cu(acac)₂. Although the prepared Cu/AC has been reduced under hydrogen condition at 320°C for 1 hour, the presence of oxide form of copper in the catalyst was still found, especially for catalyst Cat-2. This may be due to the instability of the elemental copper to the unavoidable air exposure during the XRD analysis or insufficient processing time in the reduction step.

Figure 8.

Physiosorption Analysis

From the measurement of nitrogen adsorption at 77K, it was found that the B.E.T. specific surface area was 1052 m²/g (blank AC), 857 m²/g (Cat-1) and 743 m²/g (Cat-2). The reduction in surface area can be explained by the deposition onto the porous surface of the support from the gaseous

precursor after the deposition process. The gradual growth of the deposited precursor forms a layer with a certain thickness and consequently reduces the specific surface area of the support.

The total adsorbed volumes of nitrogen of blank AC, Cat-1 and Cat-2 catalysts were 489 mL/g, 365 mL/g and 319 mL/g, respectively. This is so because the deposited precursor, which was subsequently reduced to copper/copper oxide, occupies some porous volume of the support. The continuous deposition of metallic precursor would accumulate and grow layer by layer on the porous surface. As a result, the total pore volume of the support is reduced as the deposition time increases.

SEM Analysis

SEM-EDAX analysis was conducted to study the morphology of the prepared Cu/AC catalyst. The copper loading on this examined catalyst is 19.1 wt % which was prepared using the conditions of 180 °C evaporation temperature, 320 °C deposition temperature, 90 minutes deposition time, and 1.15 mL/s carrier gas flow rate. The particle was cut and polished to reveal its internal cross-sectional area and longitudinal areas. Fig. 9 shows the overview of the long flat longitudinal polished surface (upper left), the cross-sectional area (near the center), and the original external cylindrical surface (bottom right). The general compositions of the longitudinal polished surface and the external surface were later examined by the EDX analysis and the results were shown in Table 1.

Figure 9.

Table 1.

From this table, the atomic Cu concentration in the cylindrical external surface was about 80% and there was no carbon on this external surface indicating that this is a new layer due to the deposition of copper/oxide onto the external surface of carbon. In the polished internal flat area, the atomic Cu concentration was about 8.6 wt % indicating that copper was able to be deposited into the interior structure of cylindrical Cu/AC. This confirms that the cupric precursor diffused into the inner porous media and deposited on the internal porous surface of Cu/AC.

Figure 10.

Table 2.

To study the metal dispersion inside the catalyst particle, ten zones in the longitudinal polished flat surface at different distance (increases from zone 1 to zone 10) from the boundary were selected and studied by EDX analysis, which is shown in Fig. 10. The dimensions of the sampling zone were 60 μm $\times$ 60 μm . About ¼ depth of the longitudinal distance of the Cu/AC was analyzed and the results were given in Table 2. Near the edge (<170 μm) there is a high loading of copper (>49 wt %) and a very low content of carbon implying that there is a new deposited copper layer near the boundary. The copper composition drops to around 5 wt % when the depth was longer than 170 μm . The similar copper concentration inside the particle at different positions confirms that the copper was successfully and almost uniformly deposited onto the internal surface of cylindrical Cu/AC. To examine the metal dispersion along the radial direction, seven zones across the whole diameter in the polished surface were selected and studied by EDX, as shown in Fig. 11. The distribution of atomic copper concentration for each zone was shown in Table 3. Again there is a new copper layer near the particle external surface (copper content > 77 wt % in zones 11 and 17). The copper content inside the internal surface is about 3.5% confirming the successful deposition of copper onto the internal porous structure of activated carbon.

Figure 11.

Table 3.

Conclusions

By using the new CVD system design, higher metal loading in the porous support can be achieved within shorter preparation time. In general, the metal loading on the support increases as deposition time or at optimum carrier gas flow rate, within the experimental range studied. The B.E.T. specific surface area and pore volume of the developed catalysts decrease as a result of metal loading increases after the CVD process. From the SEM-EDX analysis, copper was found to be deposited onto the internal porous structure of the support. Similar copper concentration in the interior of the support was obtained. Therefore, it can be concluded that MOCVD is a promising technique for preparing heterogeneous catalysts.

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Table 1 : Composition of the polished area and the external surface in Fig 9

Composition in each examined area	Cylindrical external surface (Fig. 13)	Polished longitudinal flat surface (Fig. 14)
C (wt %)	-	45
O (wt %)	8.9	12
Cu (wt %)	80	8.6
Au (wt %)	11	35

Table 2 : Composition of ten sampling areas in the longitudinal polished surface in Fig. 10

Sample zone (Location from the edge)	C (wt %)	O (wt %)	Cu (wt %)	Au (wt %)
1 (84.85 μm)	5.7	4.0	77	13
2 (169.7 μm)	23	7.9	49	20
3 (254.6 μm)	48	11	5.2	36
4 (339.4 μm)	47	11	7.3	35
5 (424.3 μm)	50	12	4.2	34
6 (509.1 μm)	47	12	8.9	32
7 (843.5 μm)	48	11	4.5	37
8 (928.4 μm)	51	10	4.6	35
9 (1013.3 μm)	48	12	4.2	36
10 (1365.2 μm)	47	11	5.6	37

Table 3 : Composition of the sampling area along R_1R_2 as shown in Fig. 11.

Sample zone (Location from the edge)	C (wt %)	O (wt %)	Cu (wt %)	Au (wt %)
11 (85 μm from R_1)	5.0	3.6	82	9.1
12 (170 μm)	42	11	16	32
13 (255 μm)	48	11	3.5	37
14 (centre)	49	11	3.5	36
15 (255 μm)	48	11	3.7	38
16 (170 μm)	37	8.5	22	33
17 (85 μm from R_2)	5.8	4.8	77	13

List of figures:

- Figure 1 Schematic diagram of the old CVD system design [Chu *et al.*, 1998]¹⁰
Figure 2 Schematic diagram of the new CVD system design
Figure 3 Effect of the CVD system design on Cu loading of Cu/AC
Figure 4 Effect of carrier gas flow rate on Cu loading of Cu/AC
Figure 5 Effect of evaporator temperature on Cu loading of Cu/AC
Figure 6 Effect of the amount of support on Cu loading of Cu/AC
Figure 7 Effect of particle size on Cu loading of Cu/AC
Figure 8 XRD spectroscopy of blank AC and the developed catalysts
Figure 9 Overview of the cylindrical Cu/AC
Figure 10 Sampling zones on the longitudinal polished flat surface of Cu/AC
Figure 11 Sampling zones in the radial direction (along R_1R_2) on the polished surface

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.