Scanning tunneling microscopy investigation of a spontaneous monolayer dispersion system: $HgCl_2$ on highly oriented pyrolitic graphite surface

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$HgCl_2$ can disperse onto the surface of activated carbon as a monolayer to form a catalyst for making vinyl chloride from C_2H_2 and HCl. A monolayer dispersion capacity of 0.020 g. $HgCl_2$/100 m^2 activated carbon was determined by x-ray diffraction. In order to understand further the catalytic mechanism of this kind of catalyst, the dispersed structure of $HgCl_2$ supported on highly oriented pyrolitic graphite (HOPG) has been studied by scanning tunneling microscopy (STM). The $HgCl_2$–HOPG sample is obtained by putting a drop of dilute $HgCl_2$ solution on the surface of HOPG and drying in air. The $HgCl_2$–HOPG surface is imaged by computer controlled STM under ambient conditions and at room temperature. In constant-current mode, bright spots with regular structure over the periodic structure of HOPG has been observed in the image. The size of bright spot is about (4×9) Å which corresponds to a single $HgCl_2$ molecule. It suggests that $HgCl_2$ molecules form a monolayer on the surface of HOPG with a (3.6×3.6) R14.3° surface superlattice in contrast to the lattice of HOPG. The experimental result is consistent with the estimation derived from the monolayer dispersion theory.

I. INTRODUCTION

It has been reported that a great many oxides and salts can disperse spontaneously onto the surface of supports to form a monolayer or submonlayer, because the monolayer or submonolayer phase is a more thermodynamically stable form. This point has been confirmed by various techniques such as x-ray diffraction (XRD), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), secondary ion mass spectroscopy (SIMS), and ultraviolet (UV) spectra, Mössbauer spectra, adsorption, and catalytic reactions, etc.[1–3] However, the detailed structures of the monolayer or submonolayer dispersion phase on an atomic scale are still unknown due to the limitation of these techniques.

The direct imaging of surface structure with atomic resolution has emerged since the invention of scanning tunneling microscopy (STM) by Binnig, Rohrer, and co-workers in 1982.[4] By the use of STM, surface atomic arrangements of many conductors or semiconductors, as well as their absorbate overlayers, have been imaged,[5–7] but no work has been done for the spontaneous monolayer dispersion system of salts or oxides on supports of catalyst. In our previous work,[1] we reported that even at ambient temperature $HgCl_2$ can disperse spontaneously onto the surface of activated carbon to form a high activity catalyst for the synthesis of vinyl chloride from acetylene and HCl. As a simulation of the $HgCl_2$-activated carbon catalyst for STM investigation, we use single crystal graphite to replace activated carbon, because HOPG is the most popular substrate for imaging with STM and it can be easily cleaved to provide a flat plane that can be imaged in air with atomic resolution. In this paper we report the surface atomic image of $HgCl_2$–HOPG system obtained by STM together with the results from XRD measurements for $HgCl_2$-activated carbon system.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. XRD study on $HgCl_2$-activated carbon system

A series of $HgCl_2$-activated carbon samples with different components are studied by XRD. The XRD patterns were taken on BD-86 x-ray diffractomer using nickel-filtered CuK_α radiation. The catalysts were made by just mixing $HgCl_2$ with activated carbon powder and then by simply leaving the mixture at ambient temperature for 24 h. A fresh mixture of 0.10 g $HgCl_2$ and 1.0 g activated carbon powder gives an XRD pattern with sharp peaks of crystalline $HgCl_2$ as shown in Fig. 1, pattern (b). After the mixture stays at ambient temperature for 24 h, the peaks of crystalline $HgCl_2$ disappear and the pattern (b) changes into (b′), a pattern resembling the pattern (a) of activated carbon. It indicates that $HgCl_2$ has dispersed onto the surface of the activated carbon to form a monolayer or submonolayer. However, for a mixture of 0.25 g $HgCl_2$ and 1.0 g activated carbon, the peaks of crystalline $HgCl_2$ do not disappear but are markedly reduced after the mixture stays at ambient temperature for 24 h, as shown in Fig. 1, patterns (c) and (c′). This indicates that some residual crystalline $HgCl_2$ remains. There is a critical dispersion capacity of $HgCl_2$ on the surface of activated carbon between 0.10 and 0.25 g $HgCl_2$/g activated carbon. When the $HgCl_2$ content in the mixture exceeds the critical dispersion capacity, there will be residual crystalline phase of $HgCl_2$. The amount of residual crystalline $HgCl_2$ can be determined from XRD quantitative phase analysis. By using an inner standard method,[8] namely, adding a cer-

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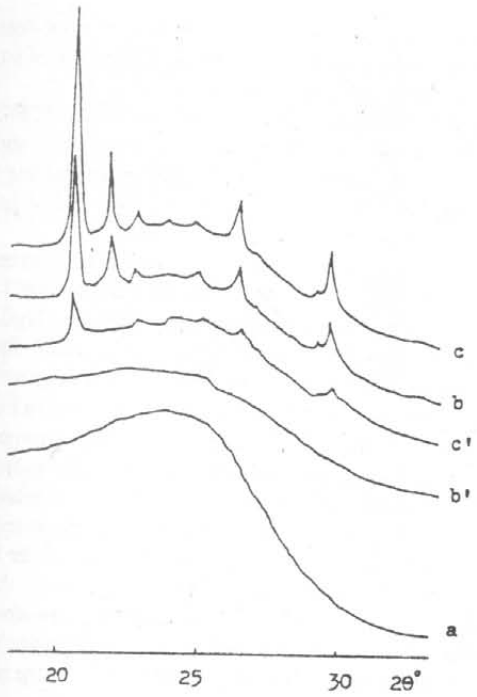

FIG. 1. XRD patterns of $HgCl_2$-activated carbon system. (a) activated carbon; (b) fresh mixture of 0.10 g $HgCl_2$/g activated carbon; (b') sample b stayed at room temperature for 24hr; (c) fresh mixture of 0.25 g $HgCl_2$/g activated carbon; (c') sample c stayed at room temperature for 24 h (activated carbon surface area about 1000 m^2/g; closed-packed capacity 0.15 g/100 m^2).

tain amount of α-Al_2O_3 to $HgCl_2$-activated carbon samples, and measuring the relative peak area $I_{HgCl_2(120)}/I_{\alpha\text{-}Al_2O_3(113)}$, the residual crystalline $HgCl_2$ can be obtained. Figure 2 gives a plot of the residual crystalline $HgCl_2$ versus the total amount of crystalline $HgCl_2$ in the samples. A threshold at 0.20 g $HgCl_2$/g activated carbon can be derived from the plot. The threshold value is the utmost dispersion capacity of $HgCl_2$ on the surface of activated carbon. It corresponds to a dispersion capacity of 0.020 g $HgCl_2$/100 m^2 activated carbon surface. As we know, $HgCl_2$ is a linear molecule with

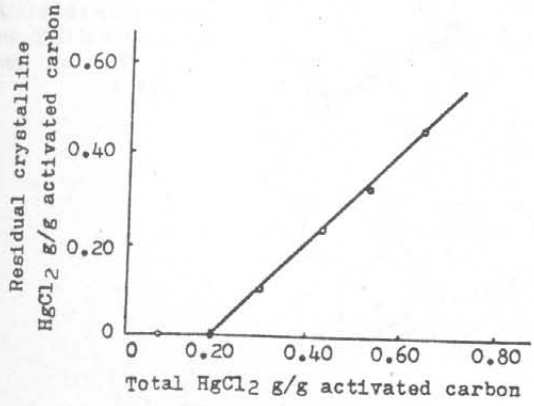

FIG. 2. Relationship between residual crystalline $HgCl_2$ and the total amount of $HgCl_2$ in $HgCl_2$-activated carbon sample. It gives the monolayer dispersion capacity of 0.20 g $HgCl_2$/g activated carbon.

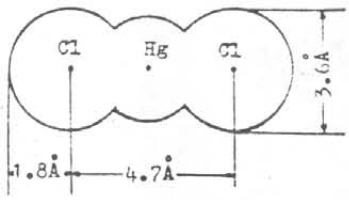

FIG. 3. Schematic diagram of $HgCl_2$ molecule. Hg–Cl bonding length is 2.34 Å. van der Waals radius: Hg, 1.50 Å; Cl, 1.8 Å.

$D_{\infty h}$ symmetry. The Hg–Cl bond length and the van der Waals radius of Cl are 2.34 Å and 1.8 Å, respectively.[9] Therefore, a $HgCl_2$ molecule (Fig. 3) occupies (8.3×3.6) Å, i.e., about 30 $Å^2$. Assumig that $HgCl_2$ forms a close-packed monolayer on the surface of activated carbon, we derived the close-packed monolayer dispersion capacity at 0.15 g $HgCl_2$/100 m^2. The activated carbon has a specific surface area of 1000 m^2/g. So the experimental dispersion capacity, 0.20 g $HgCl_2$/g activated carbon, suggests that $HgCl_2$ disperses on the surface of activated carbon as a submonolayer covering about 13% of the support surface.

B. STM study on $HgCl_2$–HOPG system

As a model catalyst for STM investigations, we use $HgCl_2$–HOPG system instead of $HgCl_2$-activated carbon. In our experiment, HOPG used for the STM study has a surface of about 2×2 mm^2. Suppose the dispersion capacity of $HgCl_2$ on the surface of HOPG is about the same as that of the activated carbon, 0.020 g/100 m^2, for an utmost dispersion of $HgCl_2$ on 2×2 mm^2 surface of HOPG, we can put only 3.0×10^{-12} mol of $HgCl_2$ or less on it. If we put a small drop (~1 μl) of $HgCl_2$ solution on the HOPG surface to make a submonolayer dispersion of $HgCl_2$ on it, the concentration of $HgCl_2$ solution should be less than 3.0×10^{-6} mol/l (8.1×10^{-7} g/ml). In our work, the $HgCl_2$/HOPG sample was prepared by putting a drop of dilute $HgCl_2$ solution (10^{-5} g $HgCl_2$/ml) onto the surface of HOPG and drying in air. STM measurements were taken by using a computer controlled STM developed at the Institute of Chemistry, Academia Sinica.[10] A tungsten tip which was prepared by electrochemical etching in 2 N NaOH solution was used for scanning. STM data were recorded using data acquisition and display system. The STM image was calibrated by using a well-known HOPG surface which exhibited a

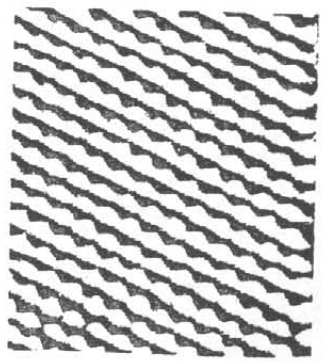

FIG. 4. STM top view of HOPG surface imaged with tunsten tip at V_{bias} -70 mV, i_t 50 nA. The image extends over a lateral area of (28×35) Å.

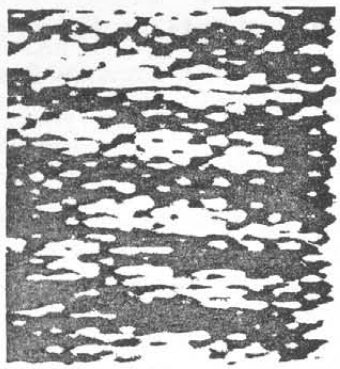

FIG. 5. STM image of a (40×48) Å region of $HgCl_2$–HOPG surface recorded in constant-current mode. The image shows bright spots with (3.6×3.6) R14.3° superlattice over the substrate of HOPG. The size of each spot is about (9.0×4.0) Å consistent with the size of an individual $HgCl_2$ molecule. It indicates that $HgCl_2$ disperse as a monolayer on the surface of HOPG.

characteristic atomic-resolution pattern of three-fold symmetric minima separated by 2.46 Å. A top view of a typical image of the HOPG is shown in Fig. 4.

Figure 5 shows a STM image of the $HgCl_2$–HOPG sample. The image was taken in constant-current mode at $V_{bias} = 70$ mV and $i_t = 50$ nA. It reveals some big bright spots arranged regularly over the background of graphite surface lattice.

Examining each big bright spot, it is measured to be about (4×9) Å which is consistent with the size of a $HgCl_2$ molecule. Thus, we assign each spot for an individual $HgCl_2$ molecule monolayer dispersed on the HOPG surface. Based on this observation, we can suggest a schematic diagram model of $HgCl_2$ molecules on HOPG surface as shown in Fig. 6. In this model, a monolayer dispersed $HgCl_2$ arranges in a (3.6×3.6) R14.3° superlattice relative to the substrate of HOPG. The unit cell is (8.9×8.9) Å. When we increase the scanning area, the resolution of STM image decreases gradually. Figure 7 is an (80×95) Å STM image of the $HgCl_2$–HOPG, which shows array of $HgCl_2$ lines with the same arranging direction as Fig. 5. The distance between lines in Fig. 7 is 8.9 Å which is consistent with the distance between rows of $HgCl_2$ molecules in Fig. 5 and supports the model of Fig. 6 also.

The ordered arrangement of $HgCl_2$ molecules shown in

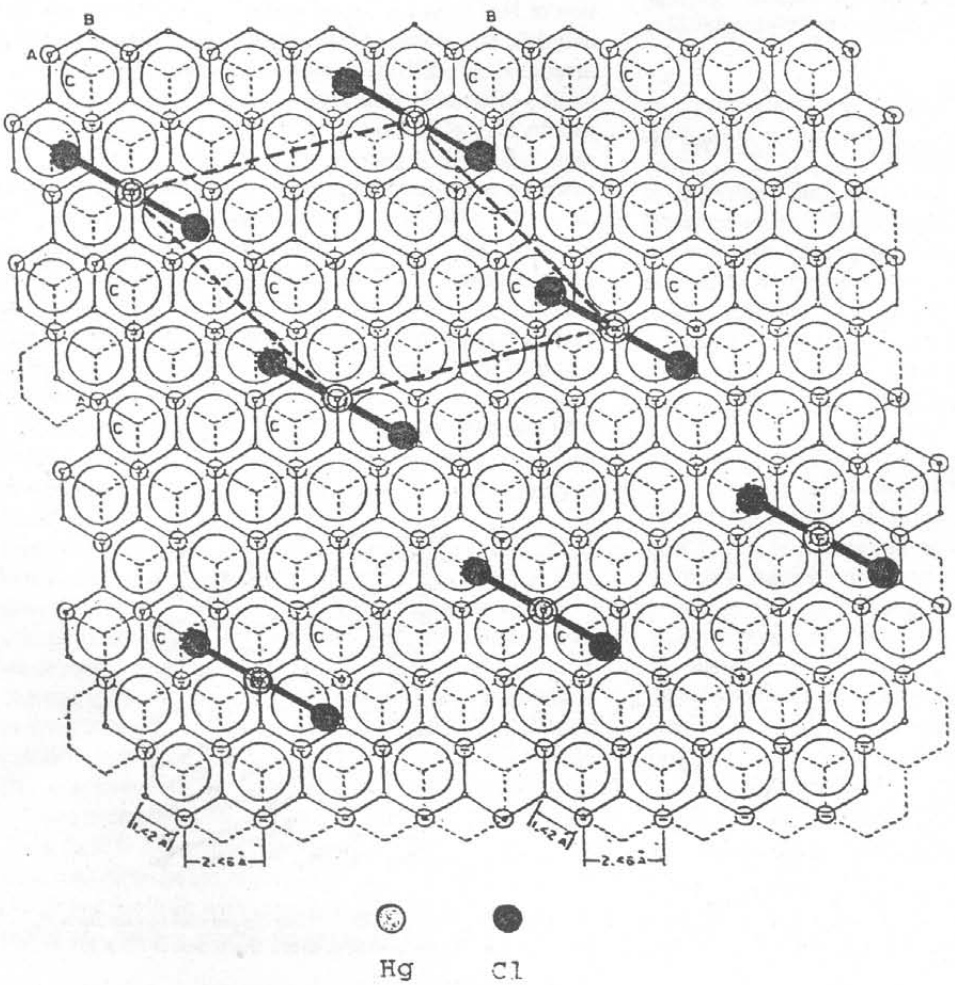

FIG. 6. Schematic diagram of the inferred (3.6×3.6) R14.3° surface structure of $HgCl_2$–HOPG system. The unit cell is (8.9×8.9) Å.

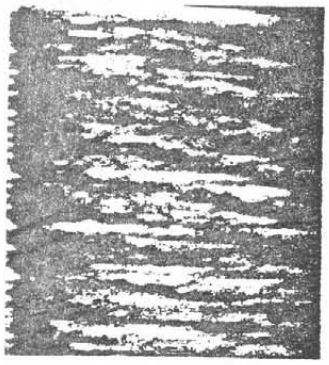

FIG. 7. STM image of a (80×95) Å region of $HgCl_2$–HOPG surface recorded in constant-current mode. The array of $HgCl_2$ lines parallel to each other and the distance between the lines is 8.9 Å.

the STM patterns of Figs. 5 and 7 is only a small part of the surface of the $HgCl_2$–HOPG sample. It is not the whole picture of the sample. On some other region of the sample we have found less or no $HgCl_2$ molecules from their STM images. Even in Figs. 5 and 7 we can also find some region without $HgCl_2$ molecules. But we did see monolayer dispersed $HgCl_2$ molecules on the surface of HOPG. It is the first time that a spontaneous monolayer dispersion on an atomic scale was observed. At this point, one may inquire into the nature of this dispersion phenomenon. First, $HgCl_2$ is a molecular crystalline and the bonding between $HgCl_2$ molecules is a weak van der Waals force. When $HgCl_2$ disperses on the surface of HOPG, the interaction force between the $HgCl_2$ molecules and the surface of HOPG will be the same order as that between the $HgCl_2$ molecules in the crystalline. Second, when the three-dimensionally ordered crystalline $HgCl_2$ phase change into a less-ordered two-dimensionally dispersed phase, it will increase entropy of the whole system as to make the free energy of the system decrease. This is why the $HgCl_2$ molecules can form a monolayer on the surface of HOPG.

The XRD result shown before indicates that $HgCl_2$ can only occupy 13% of the surface of the activated carbon. The stimulation of the $HgCl_2$/activated carbon catalyst with $HgCl_2$–HOPG is limited, because the surface of an activated carbon is not the same as that of a HOPG. There are impurities, defects and many polar groups, such as –OH, >C=O, –COOH, etc., on the surface of activated carbon. From our observation it seems that only a small part of the activated carbon surface can be similar to the surface of HOPG which can be occupied by $HgCl_2$ molecules to form an ordered monolayer.

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