# Relationship between surface microstructure and properties of supported catalyst Rh/Ys*

LIU Zhongyang (柳忠阳), PAN Pinglai (潘平来), ZHU Changcheng (朱长城),

WANG Xiaojun (王晓筠) and YUAN Guoqing (袁国卿)**

(Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China)

**Abstract**      The inner structure of Rh/Ys, a novel high efficiency supported catalyst, and the spreading of Rh on the Ys surface were analyzed through electron transmission microscopy and scanning tunnel microscopy. The relationship between the distribution of Rh over the support and the preparation temperature of th catalyst was determined. The formation of Rh←C bond was confirmed by XPS and far-IR spectra. The loss of Rh from the surface of the support and the catalytic activity under different preparation conditions have been compared. The internal factors for the high activity and high stability of the novel Rh/Ys catalyst have been discussed.

**Keywords: Rh/Ys catalyst, carbonylation, acetic acid, microstructure, methanol.**

The present authors have reported a series of novel carbon sieve Ys supported transition metal catalysts[1,2]. The special catalyst Rh/Ys for the carbonylation of methanol to acetic acid has superior properties to the similar homogeneous Rh catalysts. Its general properties also surpass those of Rh catalysts supported by active carbons and $SiO_2$[3].

Experimental evidence has shown that choosing proper supports and making Rh atoms finely spread over the surface are the essential methods for enhancing the activities of the catalysts. Through improving the preparation methods of the catalysts, Rh atoms can bond with the supports under proper conditions, which reduces the loss of Rh and makes the catalysts practically useful in industry. As to the dispersion of Rh atoms over the support surface, most reported methods are to add disperse agents or take special techniques, such as oxido-reduction method[4], to make Rh atoms spread more transparently over the surface of the supports. However, no effective methods have been reported to decrease the loss of Rh.

In the present work, the preparation of catalyst Rh/Ys was discussed. The microstructure of the catalyst and the dispersion of Rh atoms were analyzed by electron transmission microscopoy (TEM). The bonds between the metal and the support were characterized by X-ray photoelectron spectroscopy. A distribution mechainsm was proposed, which explained why this novel catalyst is superior to other supported catalysts. The relationship between the preparation temperature and the loss of Rh was analyzed.

## 1 Experimental

### 1.1 Preparation of the catalyst

The catalyst was prepared according to ref. [5]. After hydrogenation, it was pyrolyzed at 400, 500, 700, 900 and 1 000℃ under the pretection of inert gas for 2 h.

### 1.2 Characterization of the catalyst

The X-ray photoelectron spectroscopic measurement was carried out on a Kratos ES 300 XPS spectrometer using Mg $K\alpha_{1,2}$ X-radiation at 1 254 eV. The far-IR spectrum was recorded on a Brucker FT-IR IFS-113V spectrometer over KBr pellets. The dispersion and graininess of the catalyst were detected by a Hitachi H-800 transmission electron microscope. The loss of Rh from the support surface was detected by a Hitachi-18070 atomic absorption spectrometer. X-ray diffraction was performed on a D/Max-3B powder diffraction spectroscopy. The STM imaging for analyzing the surface structure was conducted by a CSTM-9000 scanning tunneling microscope in a constant current mode.

## 2 Results and discussion

### 2.1 Characterization of the support

2.1.1 Topography of Ys support. Ys support is of carbon beads prepared from the pyrolyzation of poly(vinyldene chloride) at high temperature. From a topographical study by scanning electron microscopy (fig. 1), scale-like layers can be observed on the surface of spherical Ys



Fig. 1. Image of scanning electron microscopy for Ys surface.

support. The distance between each layer is uniform. The layer structure is suitable for the transfer of heat and mass, and the spherical shape could reduce the dead volume of the reactor and is suitable for loading.
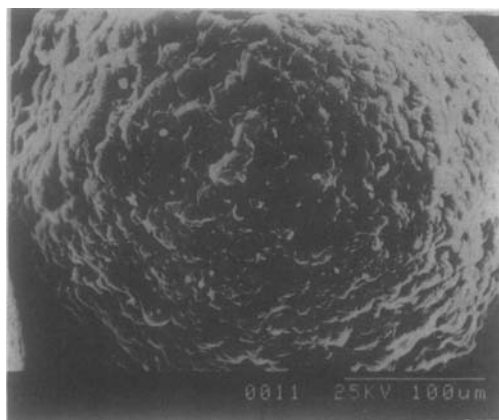
2.1.2 Inner surface and characteristic of substrate. The initial material of Ys support is poly(vinyldene chloride), which has an ordered structure. When the temperature gets its dissociation point 180℃ under an inert atmosphere, it begins to eliminate HCl to form small holes. With the elevation of the temperature, the elimination of HCl gets to completeness and the specific surface area increases. When the temperature increases from 550 to 750℃, its specific surface area increases to 200 m²/g (figure. 2).

The support Ys after carbonation at high temperature is only made up of carbon and has a non-graphitized structure, which is greatly different from the amorphous structure of active carbon. Because of the ordered structure of poly(vinyldene chloride), the structure of the obtained carbon after pyrolyzation at high temperature is more ordered than that of active carbon. With the increasing of temperature, rearrangement happens, making the structure even more ordered. This

phenomenon can be reflected in the X-ray diffraction pattern (fig. 3). The crystallinity of Ys at 1 000℃ is much higher than that at 400℃, which not only makes the surface structure more ordered, but also improves its mechanical strength and thermal stability.
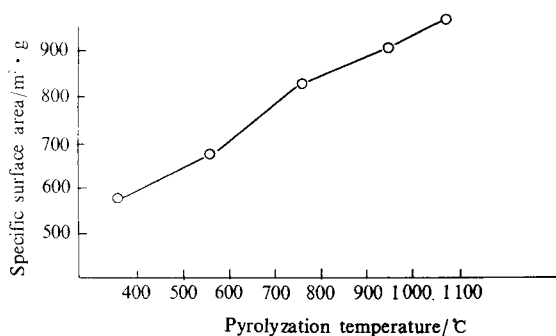


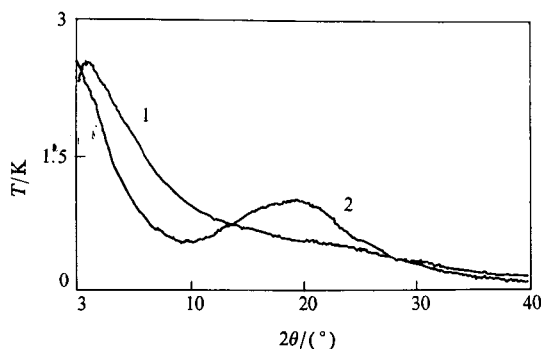Fig. 2. Relationship between specific surface area and pyrolyzation temperature.



Fig. 3. Powder X-ray diffraction patterns of Ys. 1, Pyrolyzed at 400℃; 2, pyrolyzed at 1 000℃.

2.1.3    Morphology of Ys surface.    The morphology of a support is an important factor for the activity of a catalyst. The pore sizes of the Ys support mostly concentrate in the range of 0.8—1.5 nm. Its specific surface area can get to 1 000 $m^2/g$.

Figure 4 is a TEM image of the Ys surface. Transparent black spots spread over the Ys surface, which are the bumps around the pores. To further confirm the result, we took advantage of scanning tunneling spectroscopy (STM) to investigate the morphology (fig. 5) at molecular level.

It is clearly seen from the figure that there are lots of bumps with diameters of 0.5—1.0 nm and heights of 0.5—1.0 nm on the Ys surface, which correspond to the spots in the TEM image while the gaps in STM correspond to the surface between the spots in TEM. The uneven surface provides a vast specific surface area for supporting metal atoms. It provides the essential condition for the fine spreading of metal atoms, the active centers for the catalyst. This is a typical characteristic of Ys distinguishing from other surfaces.

2.2    Spreading of rhodium on the Ys surface

The relationship between the fine spreading of rhodium on the surface of supports, the graininess and the activity and



Fig. 4. TEM image of Ys support.

stability of the catalyst is a hot topic for the heterogeneous catalysis. Generally, the finer the rhodium atoms spread, the higher the catalyst activity will be. The relationship between the size and shape of the catlayst is called "grain mechainsm". As to the rhodium catalyst, oxido-reduction methods are used to break the bigger crystal grains to form 40-nm Rh particles.
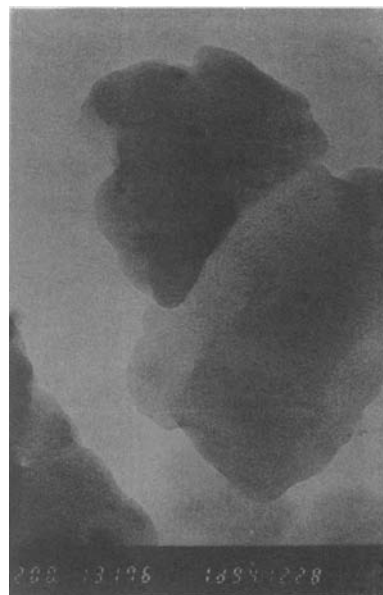
The absorbed particles on the support of the novel catalyst for the carbonylation of methanol
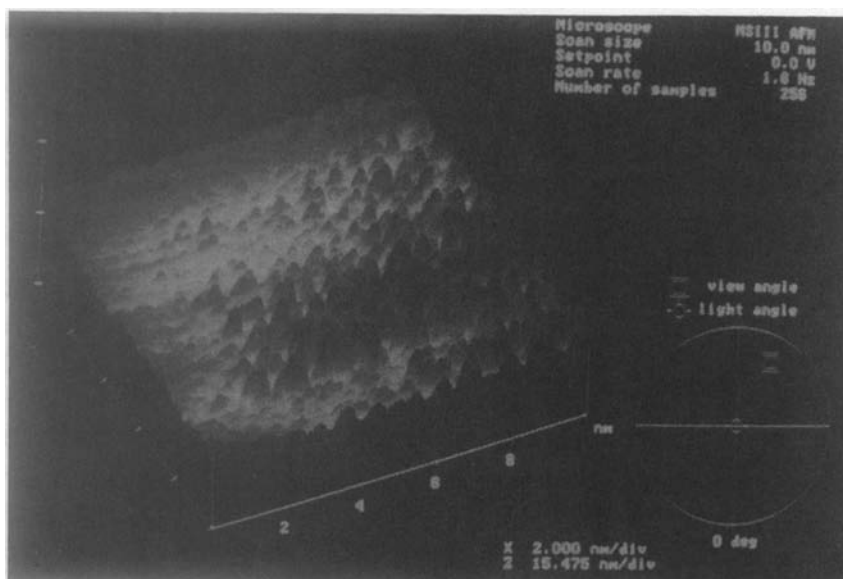
Fig. 5. STM image of Ys support.

will migrate and superfinely spread at high temperature. The big Rh crystal will immigrate from the outer surface into the inner surface. The Rh particles finish dispersion in this procedure.
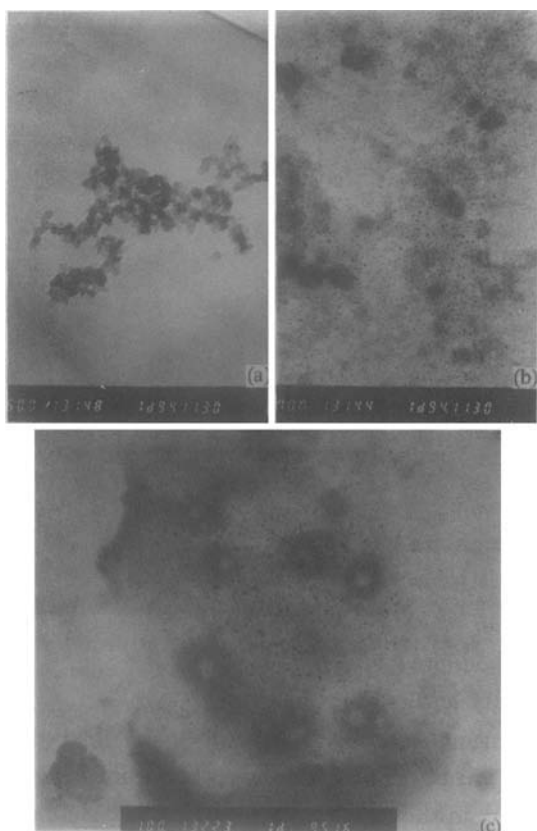


Figure 6(a)—(c) are the TEM images of Rh/Ys catalyst at different temperatures. When the preparation temperature was 700℃, there was a large amount of 400-nm big grains (fig. 6 (a)). These particles may be the parts that were not absorbed onto the inner surface but on the outer side of the support and formed by aggregation. The shape was spherical or about spherical. When the temperature rises, Rh atoms split into finer particles. For example, the particle size of Rh is about 5 nm at 900℃ (fig. 6(b)). When the catalyst was treated at 1 000℃ for 2.5 h, the polyhedral particles of Rh atoms immigrate into the inner surface and form loose and amorphous finer particles with the size of less than 3 nm. A large amount of them was about 1 nm in size (figure 6(c)).

Fig. 6. TEM images of Rh/Ys at (a) 700℃, (b) 900℃ and (c)1 000℃.

From the viewpoint of thermodynamics, the crystal grains will not form the shape of waterdrop but of polyhedron. Rh atoms form the shape of hexagon. The active centers focus on its side, angle and defects. Since Ys is made up of carbon and has a lot of defects on its surface,

there are lots of gaps between the crystal grains and these gaps extend to the inner surface of the support. The finer spread Rh crystal grains will provide more active centers. When the diameter of the metal grains reduce from 400 nm at 700℃ to 5 nm at 900℃, the catalytic rate increases by 3 times (fig. 7). This result indicates that the finer the Rh grains are, the more the atoms with high surface free energy and low coordinated number, and the higher the activity and selectivity.

Rh atoms take fully advantage of the Ys surface and are absorbed in a layer-like manner onto the Ys surface. Obviously, Rh/Ys provides more active centers than other supported catalysts.

During preparation, the finer the Rh grains, the better the dispersion of Rh atoms on the holes over the uneven Ys surface and the less the loss of the expensive Rh caused by the mechanic effects (table 1 and fig. 8). In addition, carbon atoms are more liable to bond with Rh atoms at high temperature. The bonds are the key factor for the migration of Rh atoms to the inner surface of Ys and the reduction of the loss of Rh. The relationship between the loss of Rh and the preparation temperature is listed in table 1.
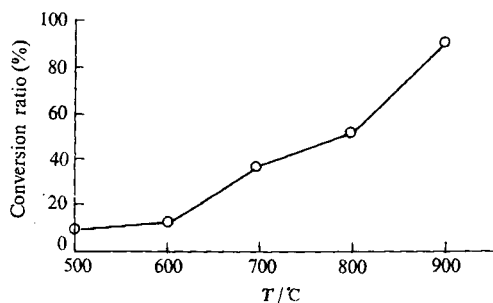


Fig. 7. Relationship between the pyrolyzation temperature and the conversion ratio. Reaction conditions: temperature, 180℃, $P_{CO}$, 1.0 MPa; Rh, 1%; liquid flow rate, 5 mL/min; catalyst, 5.0 g; $CH_3OH/CH_3I = 5:1$ (by volume).

## 2.3    Relationship between substrate C and Rh

The bond between the substrate porous carbon beads and Rh can be analyzed by the far-IR spectrum. Fig. 8-1 is the IR spectrum of untreated Ys-supported $RhCl_3$. An obvious Rh-Cl absorption peak appears at 388 cm$^{-1}$. After reduction at high temperature, the absorption peak of $Rh^{3+}$ disappeared (fig. 8-2), indicating that the Rh was in the state of $Rh^0$. When it was treated at 1 000℃, there appeared an obvious vibration peak at 389 cm$^{-1}$. Since only Rh and C existed in the catalyst, it seems that there appeared a new kind of bonds in the catalyst. In other words, the C atoms on Ys surface bonded with Rh to form $C_mRh_n$. After the catalyst was used for carbonylation for 4 h, the absorption peak of C-Rh bond still existed. The peak shifted from 388 cm$^{-1}$ to 386 cm$^{-1}$ due to the formation of carbonyl compound (fig. 8-4). This result is consistent with that of other transition metals. In addition, XPS results also confirmed that Rh was in the state of $Rh^0$. The bonding energy of $Rh3d_{5/2}$ was 307.2 eV. But when the preparation temperature was 700℃, there were double peaks for $Rh3d_{5/2}$ at 308.5 eV and $Rh3d_{3/2}$ at 313.5 eV in the XPS spectrum, which indicates that part charges transferred from C to Rh to form C-Rh bond during the preparation at 700℃ (fig. 9). The Rh atoms disperse from the outside to the inner surface of the support due to the formation of C-Rh bonds. The loss of Rh was controlled. The formation of C-Rh bonds is the key factor for the fine spreading of Rh over the support and the high activity, selectivity, stability and low loss of Rh.

Table 1    The loss of Rh for the Rh/Ys catalyst prepared at different temperatures

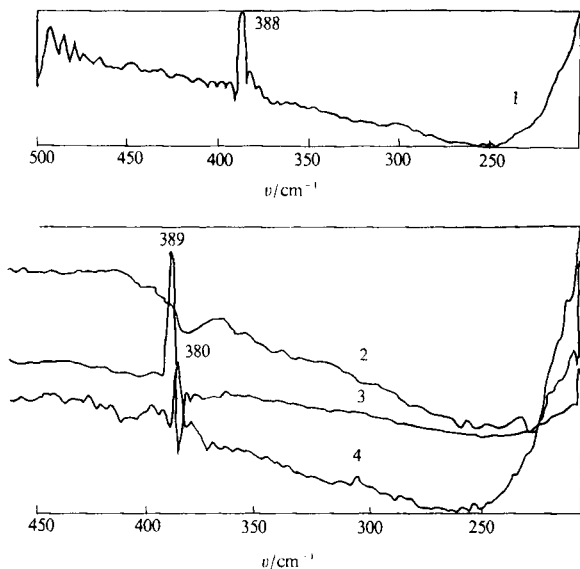| Temperature/℃ | 400 | 500 | 700 | 800 | 1 000 |
|---|---|---|---|---|---|
| Loss of Rh($\times 10^{-9}$) | 2 500 | 900 | 110 | 20 | 20 |

Fig. 8. Far IR spectra for the catalysts at different temperatures. 1, RhCl₃/Ys at ambient temperature and atmosphere. 2, Rh/Ys obtained by reduction of RhCl₃/Ys at 400℃. 3, Rh/Ys obtained by reduction of RhCl₃/Ys at 1 000℃. 4, Rh/Ys after catalyzation for the carbonylation for 4 h.
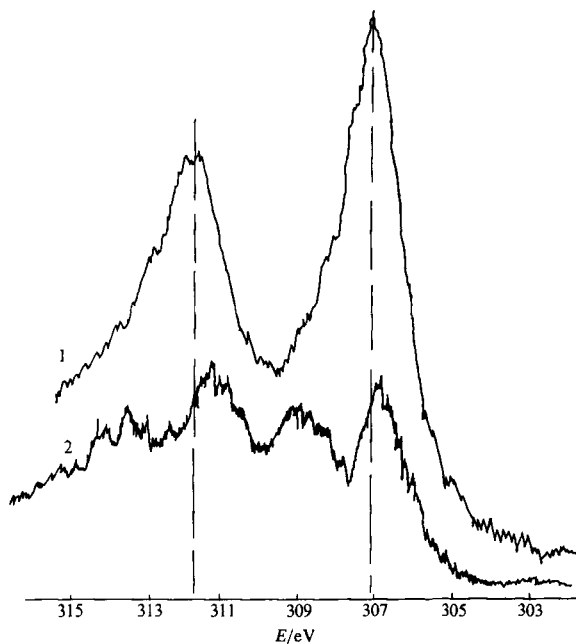
Fig. 9. XPS spectroscopy of Rh/Ys. 1, Reduction at 400℃ for 2 h; 2, pyrolyzation at 700℃ under Ar for 5 h.

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