

A novel supported catalyst for the carbonylation of methanol

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Abstract

Porous carbon beads (Ys) prepared from poly(vinylidene chloride) are used as Rh supports for the carbonylation of methanol. TEM and STM images show that uniform pores spread over their surfaces. The optimum temperature for the pyrolysis is 1000°C. The special support has a specific surface area of 1000 m²/g with high mechanical strength and thermal stability. The average diameter of pore is in the range of 0.8–1.2 nm suitable for the fine spreading of Rh atoms. XPS spectra indicated that covalent bond is formed between carbon and rhodium in the catalyst, which makes the loss of rhodium become quite little. Catalytic carbonylation results show that the activity and selectivity of this catalyst very excellent. The influence of the external and internal diffusion on the methanol carbonylation was detected. The effect of varying the temperature, concentration of CH₃I, content of Rh, initial partial pressure of CO and added acetic acid was examined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Rh/Ys catalyst; Methanol carbonylation; Acetic acid

1. Introduction

The carbonylation of methanol is one of the most important reaction for the manufacture of acetic acid. Among the catalysts available for the methanol carbonylation, the homogeneous Rh catalyst from Monsanto has been put into industrial production due to its mild reaction condition, high activity and selectivity [1]. However, it is difficult to separate the products and cycle the catalyst for homogeneous catalysts. In addition, HI and water should be added to the reagents because of the properties of the catalyst. These make the erosion of equipment become a noticeable question.

Recently, the carbonylation methods of methanol in gaseous phase over supported catalyst containing Rhodium or other transition metals have been attempted [2,3]. Modified synthetic resins [4–6], active carbon [7], silicon oxide [8], zeolites [9,10], inorganic salts [11], graphite and charcoal [12] have been used as supports for Rhodium ions. Active carbon was considered to have the highest activity. Robinson group [13] and the acetic acid research group in Sichuan University [14] have systematically reported the activity of active carbon supported catalyst under pressure or normal pressure. Experiments showed that the activity and selectivity depended on the structure, the physical and chemical properties of supports.

In this paper, we systematically study a new catalyst, Rh/Ys. In this catalyst, rhodium atoms

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could finely spread over the porous carbon surface of the support Ys, which was prepared from the carbonation of poly(vinylidene chloride). It has excellent catalytic activity and selectivity under mild reaction conditions for the carbonylation of methanol to acetic acid. It also has excellent stability.

2. Experimental

The X-ray photoelectron spectroscopic measurement was carried out on Kratos Es 300 XPS spectrometer using Mg $K\alpha_{1,2}$ X-radiation at 1254 eV. All peak positions in the XPS measurement were calibrated using the binding energy of C_{1s} as reference at 285 eV. Far-IR spectrum was recorded on a Bruker FT-IR IFS-113V spectrum as KBr pellets. The detection of specific surface area and pore size for the Rh catalyst was performed over ST-03 apertometer. TEM imaging was performed using a Hitachi H-800 transmission electron microscope at operating voltage of 100 kV. The STM images were conducted by NanoIII(Digital Instruments). The loss of Rh from the support surface was detected by Hitachi-18070 atomic absorption spectrometer.

2.1. Catalyst preparation

Polyvinylidene chloride was pyrolyzed gradually from 160°C to 1000°C. Hydrogen chloride

escaped. After cooling, the resulting support Ys was immersed in Rhodium chloride solution for a period of time, then dried in vacuum. The spheretic supports was hydrogenated at 400°C for about 1 h, then pyrolyzed at 1000 m²/g for 2 h under Ar. In this way, the Rh/Ys catalyst (containing 1% Rh) was obtaining with the particle size of 40–60 mesh, specific surface area of 1000 m²/g.

2.2. Carbonylation of methanol

The carbonylation reaction was carried out in a ϕ 0.8 cm \times 30 cm stainless steel tube. About 8 g above catalyst was put in the reactor. Its dead volume was filled with glass wool. The reactor is suspended in electronic furnace controlled by a temperature-program controller. Methanol and methyl iodide were evaporated and mixed with carbon monoxide. The reaction happened under the pressure of 10 kg/cm² with the space velocities of 10 ml/h. After cooling, the liquid products were analyzed over GC-880 gas chromatograph.

3. Results and discussion

3.1. The specific surface, pore size and the morphology of Ys surface

Polyvinylidene is a regular crystalline polymer. Hydrogen chloride escapes from the recur-

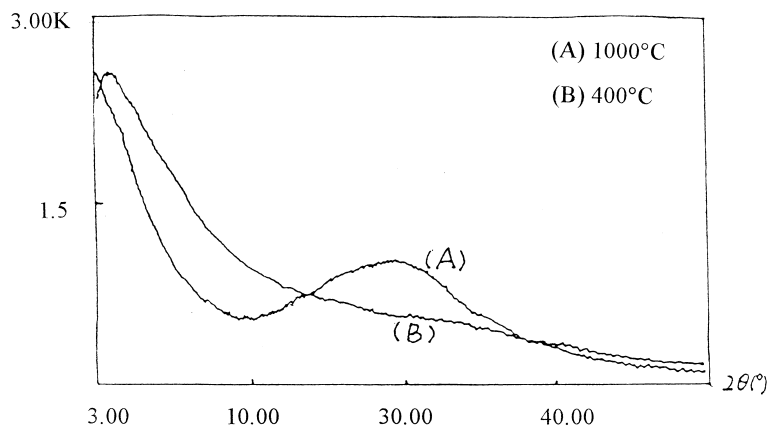


Fig. 1. XRD for Ys supports at 400°C and at 1000°C.

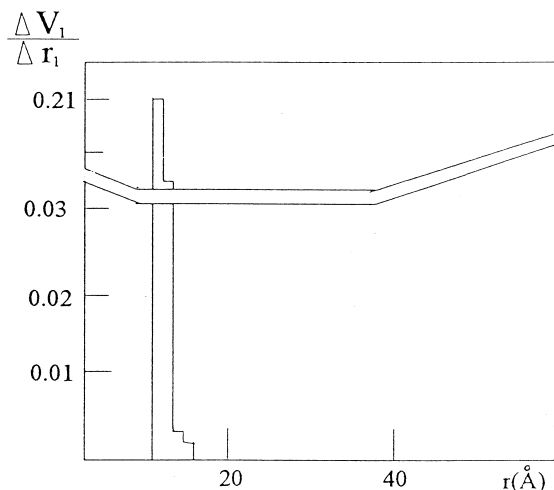


Fig. 2. The distribution of the size for Ys support.

ring units. When it undergoes controlled pyrolytic decomposition, loose porous carbon with high surface area left. Such a carbon is essentially non-graphitized. However, its inert surface is similar to that of graphite. With the elevation of pyrolytic temperature, the carbon chains rearrange into a stable low energy level. Fig. 1 confirms that the crystallinity is higher at 1000°C than at 400°C. These make Ys have higher

thermal stability and mechanical strength. Direct detection by ST-03 apertometer shows that the pore sizes of Ys support are in the range of 0.8–1.2 nm (Fig. 2) and the particle sizes are around 40–60 mesh. Specific surface area is about 1000 m²/g. Its large specific surface and uniform pore size distribution are very suitable for the methanol carbonylation of which the molecular size of the reagents, intermediate compound and products are all below 0.6 nm.

The morphology of the supports is an important factor for the activity of the catalyst. It influences the spreading of active Rhodium and the transportation of heat and determines the efficiency of the surface.

To confirm the porous structure of Ys surface, we take advantage of scanning tunneling spectroscopy (STM), which could provide nearly atomic images to investigate the morphology (Fig. 3). Bumps and holes are observed in the images. The holes with sizes of 0.8–1.2 nm correspond the pore of the supports. The uneven surface provides vast specific surface area. Rhodium atoms spread finely in the transparent holes. This is a typical characteristic of Ys from other surface.

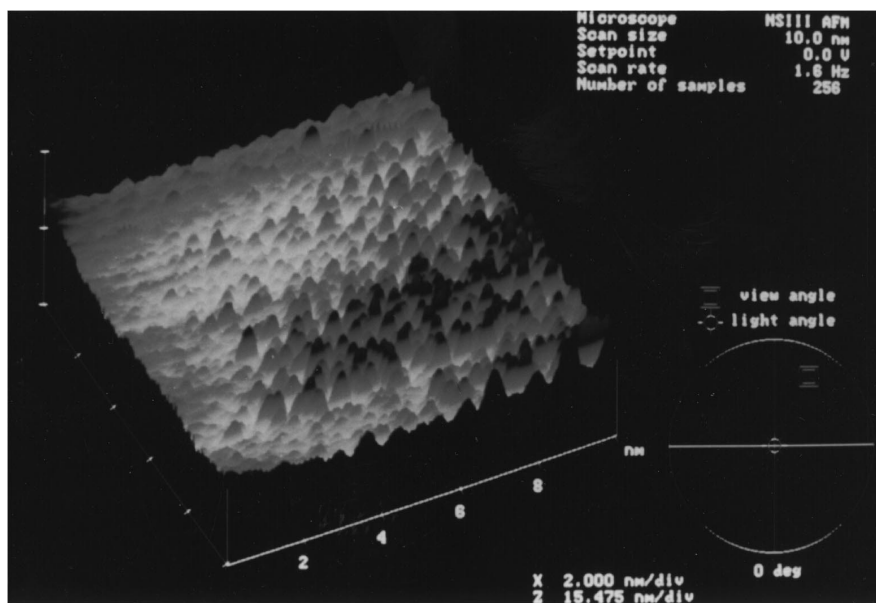


Fig. 3. STM images of the Ys surface.

3.2. The spreading of rhodium on the Ys surface and the low loss of rhodium

The spreading of Rhodium, the active center for the catalysis, on the surface of supports is an essential parameter for the catalytic activity. It

is reported that rhodium atoms are aggregated on the support surface into metallic cluster of different sizes during the preparation of catalyst [15]. The size and distribution of these rhodium clusters reflect the amount of active centers. The finer rhodium atom spreads, the higher the

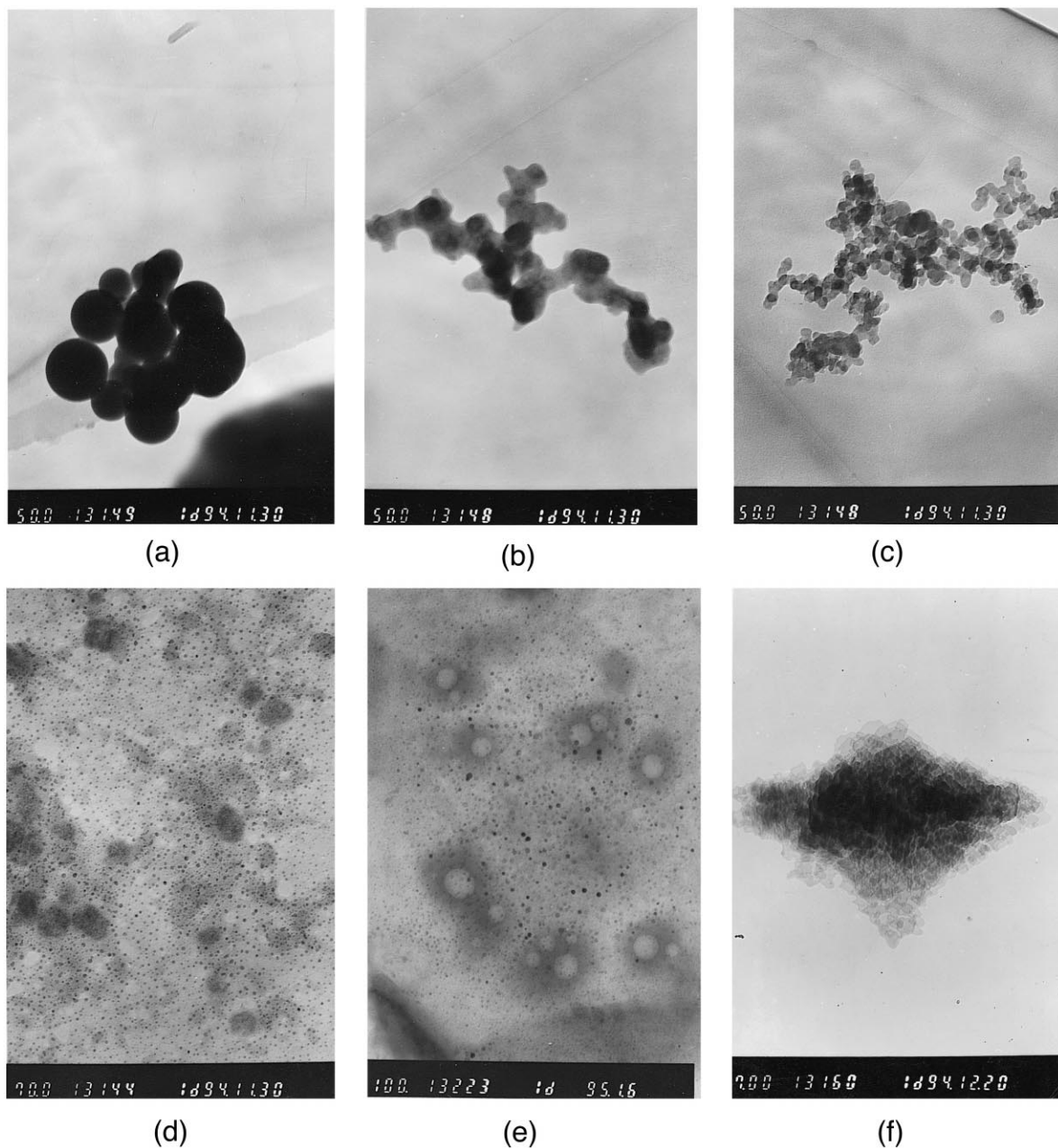


Fig. 4. TEM images of Rh/Ys catalyst at different temperatures: (a) 400°C; (b) 500°C; (c) 700°C; (d) 900°C; (e) 1000°C; (f) 1300°C.

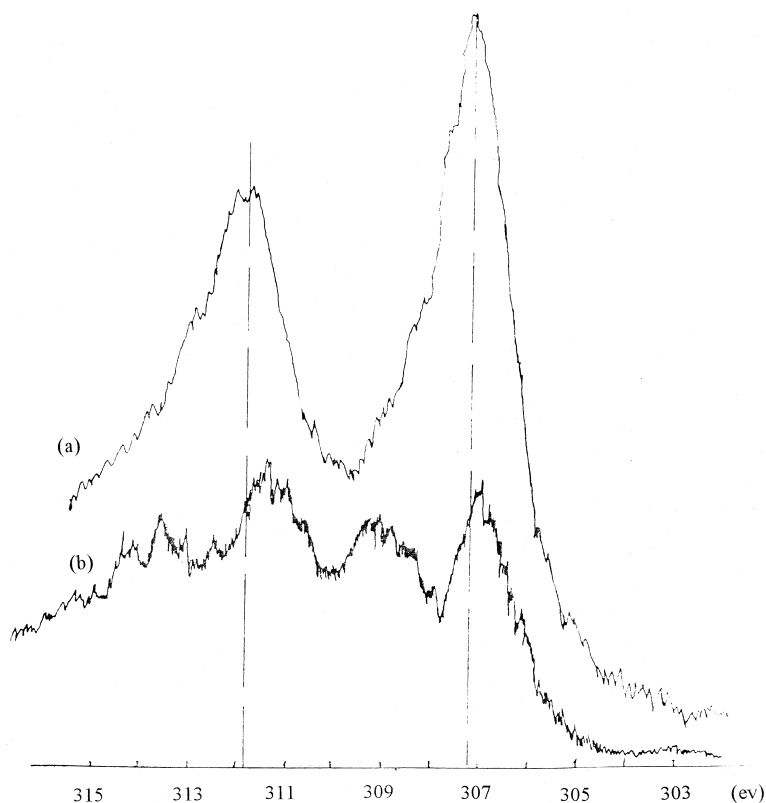


Fig. 5. XPS spectra of (a) RhCl_3/Ys after reduction by hydrogen at 400°C ; (b) Rh/Ys catalyst after sintering under Ar at 700°C .

catalyst activity. The excess aggregation will influence the formation of carbonyl compounds. The catalytic centers concentrate on the outside surface and lead to the reduction of the catalytic activity. In addition, it will induce the loss of rhodium. The common method to enhance the spreading of rhodium is to break the crystallite by oxidation–reduction reactions [16]. In our experiments, similar phenomena have been found for Rh/Ys catalyst. However, due to the special morphological structure, the rhodium

atoms on the surface spread into finer and finer particles spontaneously with the elevation of temperature. The absorbed particles on the Ys support will migrate to form superfine distribution 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. Fig. 4 is the TEM images of Rh/Ys catalyst at different temperature. At 400°C , spherical Rh atoms form a hexagon structure with the tendencies to split. The diameters of the particles are about 400 nm. When the temperature rises, Rh atoms split into finer particles. For examples, the particle sizes of Rh

Table 1
Comparison of catalytic activity among Rh/Ys and other catalysts

Catalysts	Content of Rh (%)	Catalytic rate (gAcOH/g Rh · h)
$\text{RhCl}_3\text{--NaX}$	0.25	50
$\text{RhCl}(\text{CO})(\text{PPh}_3)\text{--Al}_2\text{O}_3$	1.39	40
$\text{Rh}(\text{NO}_3)_3/\text{C}$	3.00	25
Rh/Ys	1.00	900

Table 2
Content of Rh in product in different reaction time

Reaction time/h	1	10	20	30	40
Content of Rh in product/ $\times 10^{-9}$	50	20	16	12	12

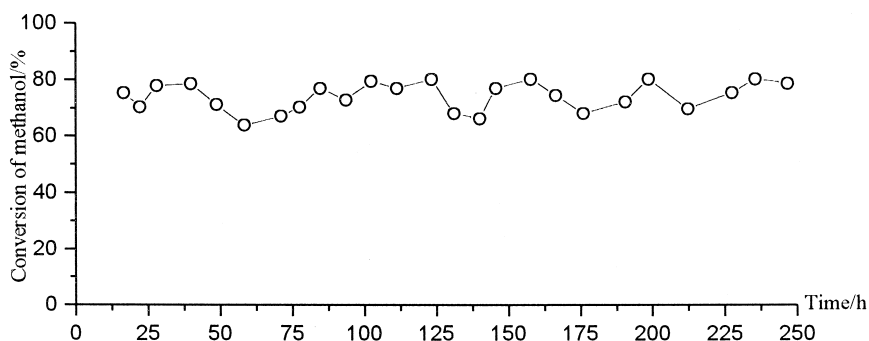


Fig. 6. The variation of Rh/Ys activity during the 250 h reaction.

are about 5 nm at 900°C. The optimum temperature is around 1000°C. The polyhedral particles of Rh atoms spread into metastable clusters of 1–1.5 nm. Even these subcrystal particles are not the standard geometrical but loose clusters with high surface free energy and relatively low coordination. If the Rh crystallites on the inert carbon surface form shapes of hexagons, the catalytic centers concentrate on the sides, angles and defects. The finer the spreading of Rh atoms, the more active centers for the catalyst.

The loss of noble metal Rhodium is another key factor for the supported Rh catalyst. In the Rh/Ys catalyst, few amounts of Rhodium were lost during the experiments. One reason is the fine spreading of Rhodium atoms. The Rhodium atoms exist in the uniform holes on the uneven Ys surface. This reduces the loss of Rhodium caused by the mechanical force.

The essential factor for the few amounts of Rhodium loss is the bonding between carbon and Rhodium. At high temperature, Rhodium atoms are liable to react with carbon substrate Ys to form covalent bands.

XPS spectra confirm formation at the C–Rh rather than Rh–Cl. Fig. 5a is the XPS spectrum after reduction by H₂ at 400°C for 2 h. The binding energy of Rh 3d_{5/2} is 307.2 eV, which is identical with that of Rh⁰. Rh ions in the catalyst were reduced to Rh⁰. When sintering temperature rise to 700°C, double peaks at 308.5, 313.5 eV (Fig. 5b) for Rh 3d_{5/2} appeared, which illustrates the charge transfer between Rhodium and carbon. In addition, a new peak at 287.1 eV appeared in the XPS spectrum of C1s. This is other evidence of bonding between Rh–C. The fine spreading of Rh atoms and C–Rh bond reduce the loss of Rh.

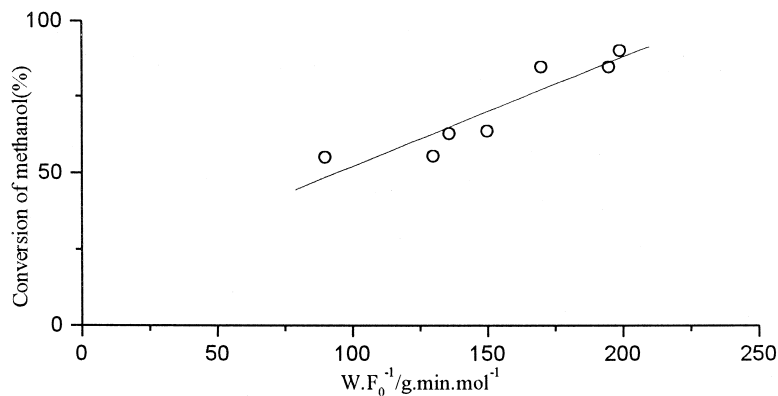


Fig. 7. Influence of external diffusion to methanol carbonylation.

Table 3
Relationship between graininess and carbonylation rates

Graininess/ mesh	Specific area/m ² g	W/F ₀	Products						Conversion of methanol/%	Selectivity/ %
			H ₂ O	CH ₃ OH	CH ₃ I	AcOCH ₃	AcOH	Me ₂ O		
30–50	996	210	1.0	15.8	21.2	41.6	21.3	< 1	86	99
60–90	990	200	1.1	17.1	19.5	40.3	19.6	≤ 1	83	99
80–120	986	200	0.9	16.0	20.8	39.1	20.4	< 1	84	99

Reaction conditions: temperature 185°C, pressure 1.2 MPa, CH₃OH/CH₃I = 4:1(V/V), Rh/Ys 9.5 g.

3.3. The activity and stability of the catalyst

Rh/Ys is an effective catalyst for the carbonylation of methanol to acetic acid. Generally, the pyrolytic temperatures influence its activity quite a lot. The conversion of methanol with the catalyst treated at 900°C is almost ten times as that at 400°C. The main reasons are due to the higher spreading of Rhodium and more active centers for the carbonylation at 900°C.

The reaction happens under milder condition while the conversion and space time yield are higher. Neither HI nor H₂O was added to the reaction, which avoid the erosion of HI and H₂ produced from water gas. The activity of Rh/Ys is also higher than other supported catalyst for the carbonylation of methanol (Table 1). The preference for acetic acid is very obvious.

In addition, Rh/Ys catalyst showed excellent stability. The loss of Rh was only 12 ppb after it reacted for 40 h (Table 2). We directly used the syngas containing CO 40–89%, CO₂ 0.4–7.0%, O₂ 0.5–1.6% and H₂ 3–59% to instigate its life

for the carbonylation of methanol. The activity of Rh/Ys did not reduce very much after 250 h (Fig. 6). The conversion rate fluctuated in the range of 60–80% due to the variation of the CO content.

3.4. The influence of external and internal diffusion on the methanol carbonylation

The influence of external diffusion could be determined under the same reaction conditions by changing the amount of catalyst and then detecting the flux of the reagents and investigating the relationship between conversion of methanol and W/F₀ (W represents the weight of catalyst. F₀ represents feeding velocity). The relationship is showed in Fig. 7. Linear relationship could be observed for different amounts of catalyst (5 g and 7 g). The result showed that the external diffusion do not influence the carbonylation kinetics of the catalyst.

Table 3 is the results of carbonylation for different graininess of catalyst. The selectivity was over 99% in spite of the change of graini-

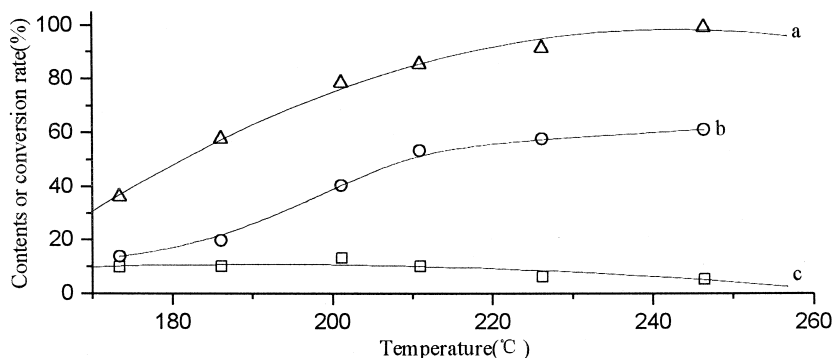
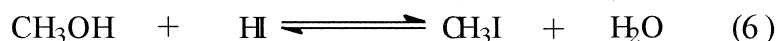
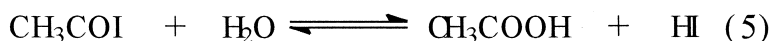
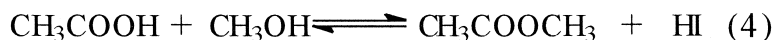
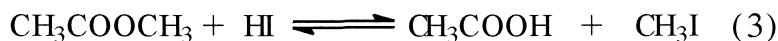
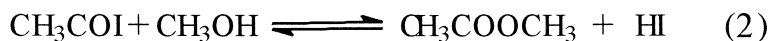
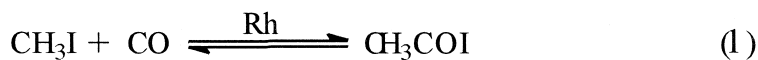


Fig. 8. Relationship between temperature and conversion or yield of methanol carbonylation.



Scheme 1.

ness, which means that the reaction is not controlled by internal pore diffusion. The small amount of Me_2O produced by the hydration of methanol could carbonylate into acetic acid with the development of the reaction. No side reactions such as water–gas reaction to produce CO_2 or H_2 had happened. The excellent reactivity of Rh/Ys lays solid foundation for its kinetic studies.

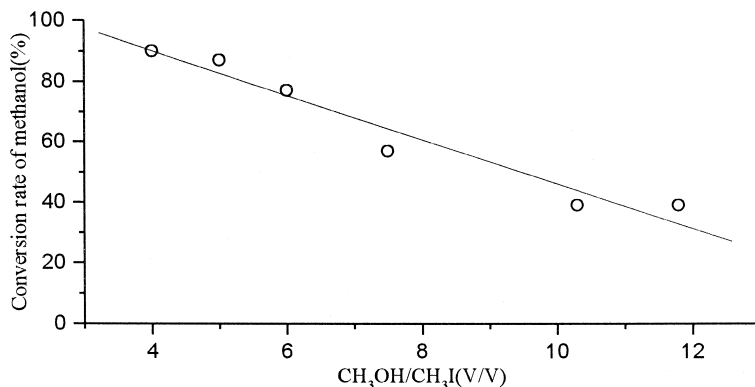
3.5. Influence of temperature on the reaction

The methanol carbonylation is very susceptible to temperature (Fig. 8). At low temperature, the main product is methyl acetate. The conversion of methanol is very low. The content of acetic acid increased when temperature rose. With the elevation of temperature, the conver-

sion of the methanol rose while the content of the CH_3I decreased. When the temperature was over 220°C , the conversion became and kept constant. This could be explained from its mechanism. (Scheme 1). The active centers are Rh atoms, which may form carbonyl compound during the reaction.

When temperature is low, the reaction stops at Scheme 1(2). Methyl acetate is the main product. With the escalation of temperature and the prolong of time, the reaction shift towards the right. The main product becomes acetic acid. The catalyst promoter, CH_3I , cycles during the reaction. The resulting water was consumed in the reaction.

Higher temperature did enhance conversion of methanol. However, it also brought about the loss of the CH_3I because of the increase of

Fig. 9. Relationship between concentration of CH_3I and conversion of methanol.

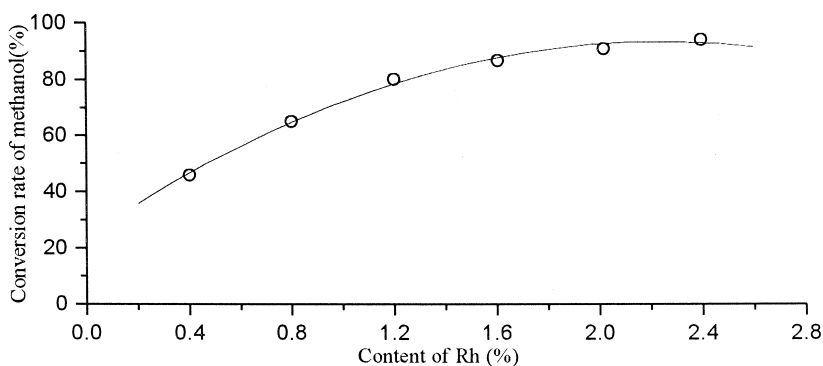


Fig. 10. Relationship between content of Rh and conversion of methanol.

CH_3COI produced from the reaction between CH_3I and CO . In addition, it produced large amount of reaction heat which would influence the internal pore diffusion and make the reaction gradually controlled by the internal pore diffusion.

3.6. Influence of concentration of reaction reagents on carbonylation rate

Iodomethane plays a key role in the methanol carbonylation. Under the catalysis of Rh, it will carbonate into acetic iodide (Shown in Scheme 1(1)), which will immediately react with either methanol or water to form iodomethane and acetic acid (Shown in Scheme 1(2), (5)).

The order of CH_3I is 1 for Rh/Ys catalyzed reaction (Fig. 9). When $\text{CH}_3\text{OH}/\text{CH}_3\text{I}(\text{V}/\text{V})$ was 1/4–1/10, the carbonylation rate had a linear relationship with the concentration of

CH_3I . However, when the volume of CH_3I was over 1/3 that of methanol, the linear relationship disappeared because of the reduction of the concentration of CH_3I and the production of HI which cannot change into CH_3I due to the lack of enough methanol.

3.7. Influence of content of rhodium

The carbonylation rate will be enhanced with the raise of Rh content. When the content got to 1.6%, the rate gradually kept constant (Fig. 10). The result is similar to that of other gas/solid, gas/liquid or gas/liquid/solid catalyst.

3.8. Influence of initial partial pressure of CO on the carbonylation rate

As shown in Fig. 11, with the elevation of the initial partial pressure of CO, the reaction

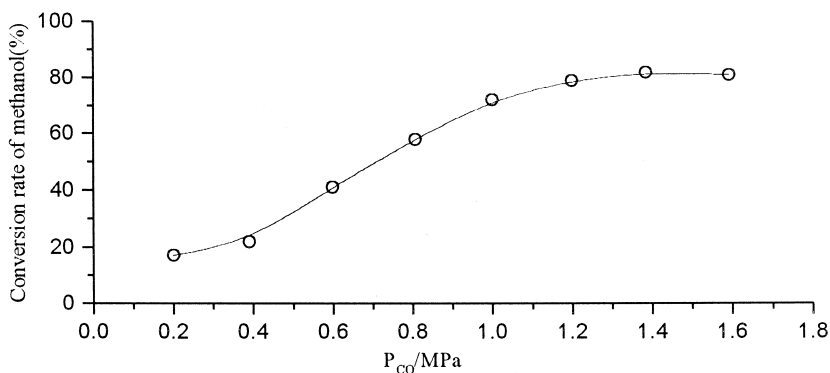


Fig. 11. Relationship between initial partial pressure of CO and conversion of methanol.

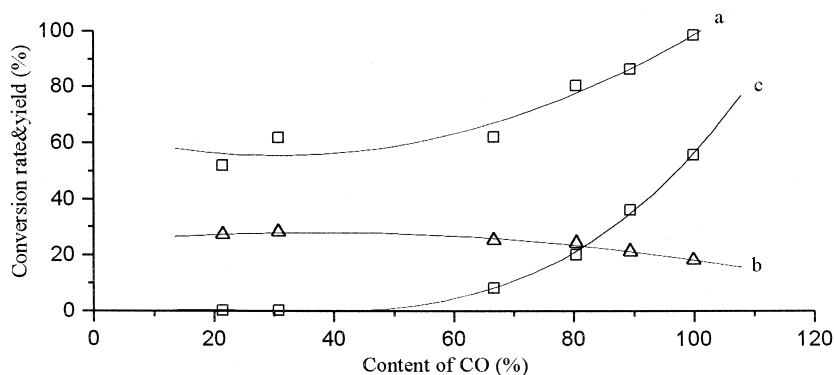


Fig. 12. Relationship between purity of CO and conversion and yield.

rate increased correspondingly. When the pressure was up to 1 MPa, it would not influence the conversion rate of methanol. We also carried the reaction of CO with some other inert gases such as H_2 , CO_2 and N_2 . The result showed that the selectivity was only determined by the partial pressure of CO rather than inert gases (Fig. 12).

3.9. Influence of added acetic acid on the carbonylation reaction

During the homogeneous carbonylation of methanol to acetic acid, extra acetic acid was usually added to the medium to increase its polarity and enhance the carbonylation rate. As to Rh/Ys catalyst, the conversion rate increased with the addition of acetic acid in a certain

scale. This is because there is a reaction equilibrium between CH_3OH and CH_3COOH (Fig. 13).

4. Conclusion

Rh/Ys is a novel, high efficiency catalyst for the carbonylation of methanol to acetic acid. Rh atoms spread finely in the uniform pore on the Ys surface. In comparison with other carbonylation catalyst, this catalyst is of high activity, thermal stability while the erosion to the equipment could be avoided and the loss of Rhodium is reduced. It could even catalyze the carbonylation of methanol and refine syngas. Thus, this catalyst is suitable for the industrial production of acetic acid.

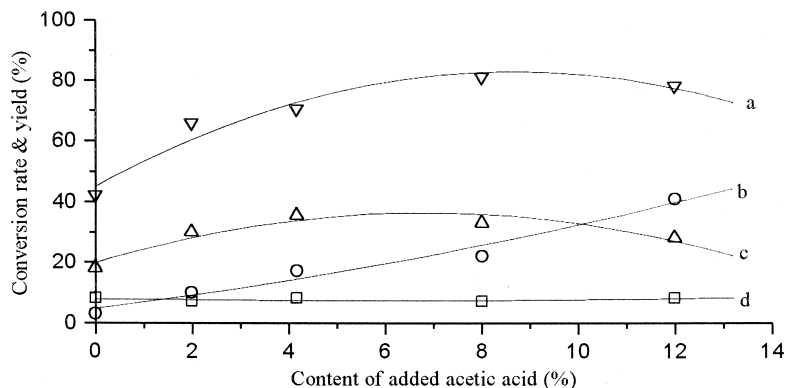


Fig. 13. Relationship between added acetic acid and conversion and yield.

Acknowledgements

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