Vinyl Acetate Formation in the Reaction of Acetylene with Acetic Acid Catalyzed by Zinc Acetate Supported on Porous Carbon Spheres[1]

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Abstract—A kind of porous carbon spheres (PCS) was prepared by the carbonization of poly(vinylidene chloride) synthesized by suspension polymerization. Structure analyses revealed the existence of bumps and holes on the surface of PCS. The PCS, with the pore size between 0.8–1.2 nm, could be used as the support of zinc acetate because of the regular shape, high specific surface area, and good mechanical strength. Vinyl acetate was produced from acetylene and acetic acid using the PCS-supported zinc acetate (PCS-Zn) under mild conditions. In a single-pass operation performed at 220°C, the conversions of acetic acid and acetylene reached 22.6 and 5.3% respectively while the activity of vinyl acetate formation was above 1000 g mol^{-1} h^{-1}.

Key words: porous carbon sphere; zinc acetate; vinyl acetate; acetylene.

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INTRODUCTION

Vinyl acetate (VAc) is one of the 50 chemical feedstock produced in large quantity worldwide. VAc, after a series of syntheses of its derivatives, has found increasing that wide applications in the production of polymers such as, polyvinyl acetate and vinyl acetate copolymers [1]. Currently, VAc is commercially produced using either ethylene and acetic acid (ca. 70%) or acetylene and acetic acid (ca. 30%) as starting materials. Although the acetylene-based method is economically less profitable compared with the case of utilizing ethylene, the daily exhausted petroleum resource and ever increasing oil price make the former route rather competitive in regions where calcium carbide and natural gas are more inexpensive and easily obtained [2].

Since the first synthesis of VAc from acetylene and acetic acid with zinc acetate adsorbed on charcoal [3], great efforts have been made in search of more industrially applicable supports and catalytically active components or their combination [4–6]. Up to now, considering the properties such as surface area, mechanical strength, reactant conversion, catalytic activity, and catalyst lifetime, active carbon has become almost the only commercial support and zinc compounds, zinc acetate in particular, have proved to be the predominant active species because they are less

toxic, inexpensive, and conveniently available [4–6]. In addition to zinc species, other metal compounds used as additives to improve the catalyst performance have also been attempted [7, 8].

In the present study, a kind of porous carbon spheres (PCS) was synthesized and used for the first time to support zinc acetate (PCS-Zn). Encouraging results in the formation of vinyl acetate from acetylene and acetic acid are expected after employing such a support that possesses high BET surface area, uniform pore size distribution, high mechanical strength, and good stability.

EXPERIMENTAL

Preparation of the PCS

The PCS were prepared by the carbonization of poly(vinylidene chloride) that was synthesized by suspension polymerization. Distilled vinylidene chloride was polymerized in suspending agent (saturated Na$_2$SO$_4$ aqueous solution). The initiator was azobisisobutylvaleronitrile (ABVN) [1% (mole ratio) of monomers]. Bentonite powder was used as the template of polymeric beads and dispersion phase. Suspension polymerization was performed at 40°C for 12 h under stirring (350–400 rpm). Poly(vinylidene chloride) beads of 40–60 mesh were obtained. The polymeric beads were then washed with hot water to remove excess bentonite powder and purified in an

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Intensity, a.u.
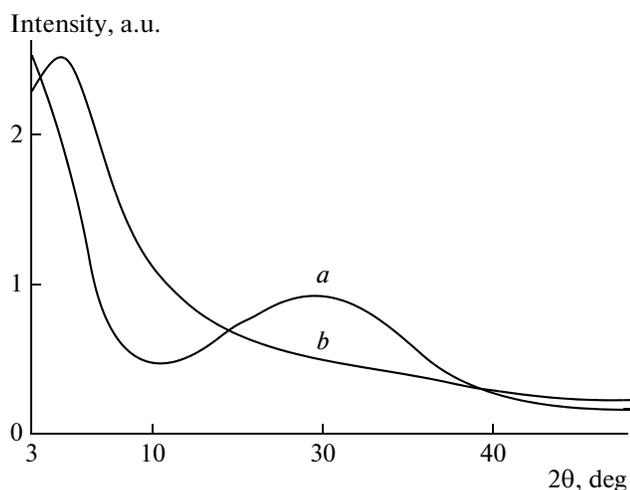
Fig. 1. XRD patterns of PCS treated at different carbonization temperatures.

F, N per sphere

Fig. 2. Relationship between the mechanical strength (F) and carbonization temperature (T_c).

acetone stream to remove remaining monomers. The carbonization was conducted in a quartz tube at 180°C until volatile molecules, such as HCl, were removed from the polymer, and a sphere shape was kept. The temperature was then gradually elevated to 1000°C. All the above processes were conducted in an argon stream. In this way, PCS were obtained. When the spheres were cooled, they were washed in a hot solution of acetic acid and water to remove the impurity on the surface of the material. After washing, the PCS were desiccated for further use. The reagents used in the experiment were commercially obtained from Sigma Company.

Preparation of PCS-Zn

In a typical preparation, 2.0 g of zinc acetate dihydrate was dissolved in 10 ml of methanol before 10.0 g of PCS was impregnated in the solution and stirred for 0.5 h at room temperature. The mixture was put aside for 1 h before dried at 80°C in an oven. The Zn loading of PCS-Zn was found to be 5.0 wt % as measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES POEMS TJA Co.).

Formation of Vinyl Acetate with PCS-Zn

For each experiment, approximately 9 g of PCS-Zn was packed between quartz wool plugs in a quartz U-tube (i.d. = 10 mm) that was placed in an oil bath. Acetylene at atmospheric pressure was supplied to the U-tube via a flowmeter. Acetic acid was transported by a proportional pump to an evaporator before the U-tube. Products from the reaction of acetylene and acetic acid were analyzed by gas chromatography (GC) on a Shimadzu model GC-2014 gas chromatograph equipped with a flame ionization detector. A-WAX capillary column (diameter, 0.25 mm; length,

20 m) was used for separation. The products were also identified by gas chromatography-mass spectroscopy using a Shimadzu model GCMS-QP5050 instrument with a Stabilwax column.

Characterization of PCS

The detection of specific surface area and pore size distribution of PCS was performed over an ST-03 apertometer. Nitrogen sorption analyses were carried out to characterize the porosity properties. SEM was performed on a Hitachi S530 scanning electron microscope. AFM was conducted with a Nano Scope III (Digital Instruments). The samples for AFM were prepared by pressing the crushed beads to even the surface, but the size and structure of micropores were kept constant. X-ray diffraction was performed on a D/Max-3B powder diffraction spectroscope.

RESULTS AND DISCUSSION

Characteristics of the PCS

The material lost about 70% of its weight after carbonization and became more carbonaceous, the particle size of which was around 40–60 mesh. As can be seen in Fig. 1, the crystallinity of the carbon was higher after treated at 1000°C than at 400°C. Correspondingly, PCS had higher thermal stability and mechanical strength when treated at higher temperatures. The relationship between the mechanical strength and the carbonization temperature is shown in Fig. 2. The influence of the mechanical strength is mainly on the stability of the carbon structure. With the elevation of carbonization temperature, there was a sharp increase in the specific surface area of the resulting carbon spheres (Fig. 3). The sorption isotherm of the resultant PCS was characteristically described as a type **I** isotherm, and the BET model was used to calculate the
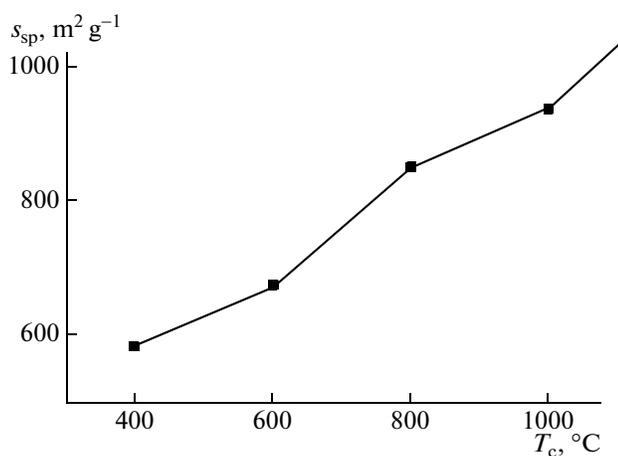
Fig. 3. Relationship between surface area (s_{sp}) and carbonization temperature (T_c).
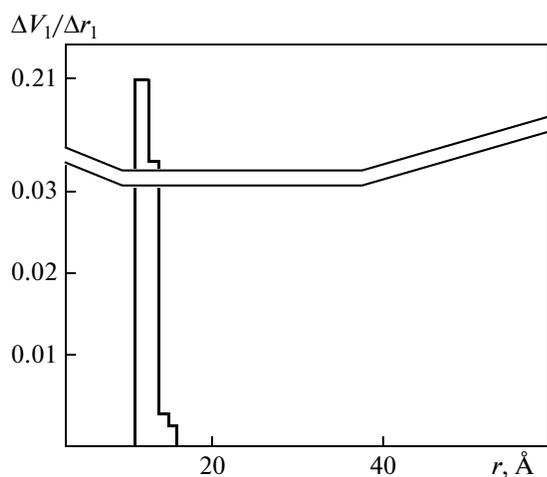
Fig. 4. Pore size distribution of PCS.
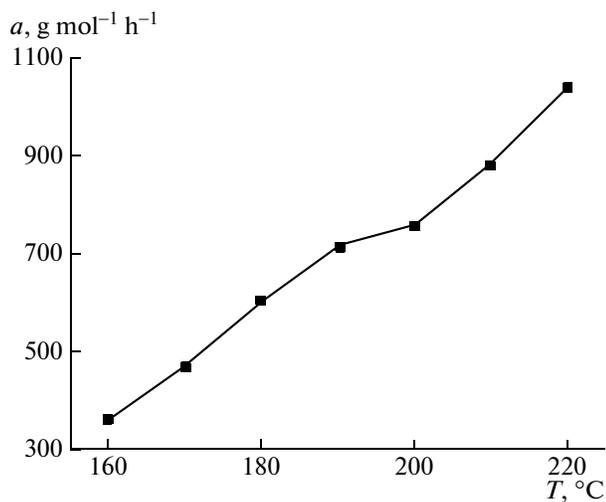
Fig. 5. Activity dependency on the reaction temperature.

porosity properties. The specific surface area of the PCS was about 930 m² g⁻¹ at the carbonization temperature of 1000°C. The pore size distribution of the PCS is demonstrated in Fig. 4, the ordinate of which denotes the differential value of pore volume and pore size. The pores in the PCS are mostly micropores and the pore size is in the narrow range of 0.8−1.2 nm.

Effect of Reaction Temperature on the Activity of VA Formation

Figure 5 shows that the activity of vinyl acetate formation increased monotonously with the increment of reaction temperatures. The reaction of acetic acid with acetylene is exothermic:

$$CH_3COOH + C_2H_2 \longrightarrow CH_3COOCH=CH_2, \quad (1)$$
$$\Delta_r G(298\ K) = 65\ kJ/mol.$$
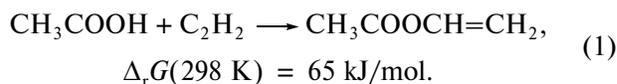
Such that it's a heat-releasing one, the reaction at 160°C produced only about 360 g of vinyl acetate per mole of Zn per hour. Further increase of the temperature resulted in more formation of vinyl acetate. Because it's a common phenomenon that, for a catalytic reaction, more severe diffusion-controlling influence arises from higher surface area of the catalyst support, suitable increment of temperature speeds up the diffusion process, thus expediting the reaction rate [9]. When the temperature was elevated to 190°C, a temperature increase of only 30°C led to the value of activity of 718 g mol⁻¹ h⁻¹, which doubles the value obtained at the reaction temperature of 160°C. Now that the present case is a single-pass operation, it's an encouraging result as expected. To increase the reaction temperature further slowed down the enhancement tendency of the activities. Additionally, a high activity value of 1040 g mol⁻¹ h⁻¹ was realized at the reaction temperature of 220°C. For all the experiments performed at different temperatures, by-products like acetaldehyde, acetone, and butenal etc. existed in the reaction mixture were generally below 1.0, 0.01, and 0.015 wt % respectively (data not listed). This indicates the PCS to be a good laboratory-scale support in the formation of vinyl acetate with high selectivity.

Effect of Reaction Temperature on the Conversion of Acetic Acid and Acetylene

Keeping constant of the feed flow rate of acetic acid and acetylene, the effect of reaction temperature on the conversion of acetic acid and acetylene was investigated aiming to obtain some useful hints of the role of PCS support in the formation of vinyl acetate. Figure 6 reflects the result. For all the vinyl acetate formation reaction performed in the temperature range 160−220°C, the conversion of acetic acid increased from 7.8 to 22.6% with the rise of temperature. This increment tendency is in good accord with the change
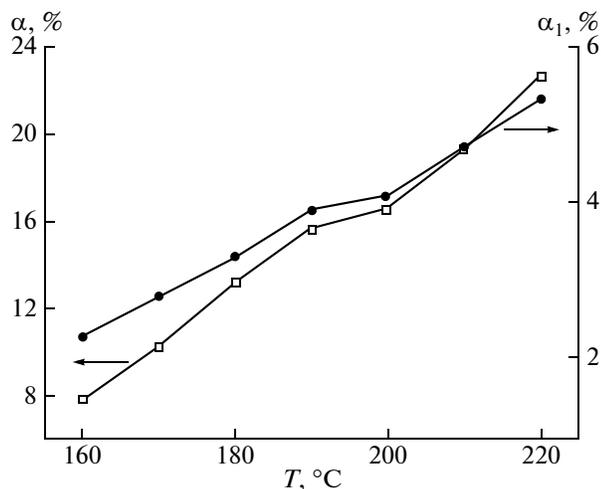
Fig. 6. Effects of reaction temperature on conversions of acetic acid (α) and acetylene (α_1).
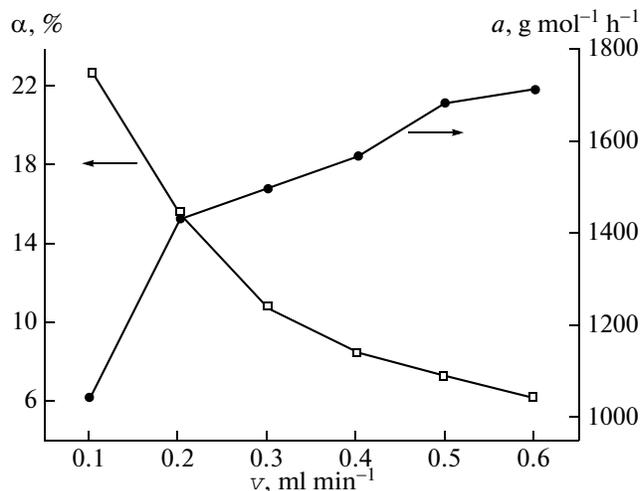
Fig. 7. Effects of acetic acid flow rate (v) on the conversion of acetic acid (α) and activity (a).

of vinyl acetate formation activities. Because the ratio of acetylene to acetic acid in the feed for these cases were maintained at 4.7/1 (mol/mol), which is well above the stoichiometric ratio of 1/1, quite a fraction of acetylene was unconverted during the single-pass vinyl acetate formation process. The highest value of acetylene conversion, 5.3%, was obtained at 220°C. For the catalyst support with much higher surface area too high reaction temperatures gave rise to marginal increase in the activities whereas more by-products were resulted. Meanwhile, high temperatures imposed adverse effect to the properties of the catalyst and more strict requirement for the equipment came forth accordingly. Considering the fact that there is always recycling system for unreacted reactants in industrial processes, both the conversion values of acetic acid and acetylene are worthy of further investigation into the potential of PCS as catalyst support for commercial applications.

Effect of Acetic Acid Flow Rate on Its Conversion and the Activity

As indicated by Fig. 7, increasing the flow rate of acetic acid from 0.1 to 0.2 ml min^{-1} led to rapid increase in the formation of vinyl acetate, jumping from 1040 to 1430 g mol^{-1} h^{-1}. Raising further the acetic acid flow rate resulted in gradually slowing increase in the activities. A flow rate increase from 0.5 to 0.6 ml min^{-1} elevated slightly the activity from 1680 to 1710 g mol^{-1} h^{-1}, implying the limited capacity of the PCS-Zn used in the present research. Also observed from Fig. 7 is the declining conversion of acetic acid as its flow rate increased. The conversion decreased by about 50% when the flow rate of acetic acid went up from 0.1 to 0.3 ml min^{-1}. This tendency continued with further increase of the flow rate until a relatively stable value of ca. 9% was reached at the

flow rate of 0.6 ml min^{-1}. Not depicted herein for simplicity, as to a constant flow rate of acetylene of 200 ml min^{-1}, the acetylene conversion went up with increasing flow rate of acetic acid. In this case, the highest conversion of acetylene reached 9.1% at the acetic acid flow rate of 0.6 ml/min for a single-pass operation.

Because the reaction rate of acetylene and acetic acid (reaction frequency: 1.3×10^{-4}–4.2×10^{-4} s^{-1}) is far below the rates at which acetylene and acetic acid diffuse to zinc acetate in the pores of PCS, the influence of internal diffusion is negligible. So it's restricted to tremendously improve the activity by increasing the flow rate of acetic acid alone. To curb side reactions and better the performance of the catalyst at the same time, increasing of the space velocity is generally an alternative [10].

As the PCS-Zn catalyst prepared herein was from impregnation method, zinc acetate was prone to disperse in the micropores as mono-layers. There is moderate interaction between the Zn species and the carbon support, thus making it easier for the spontaneous migration and uniform dispersion of zinc acetate as mono-layers on the surface of the support at certain temperatures. It's believed that only the single-layers that contacted the carbon support behaved actively in the formation of vinyl acetate from acetic acid and acetylene [11].

Effect of Ratio of Acetylene to Acetic Acid on the Formation of Vinyl Acetate

To tap the best performance of PCS-Zn in the present study, varying flow rates of acetylene and acetic acid were tested. The result of their effects on the conversions of the two reactants and the activities is listed in table.
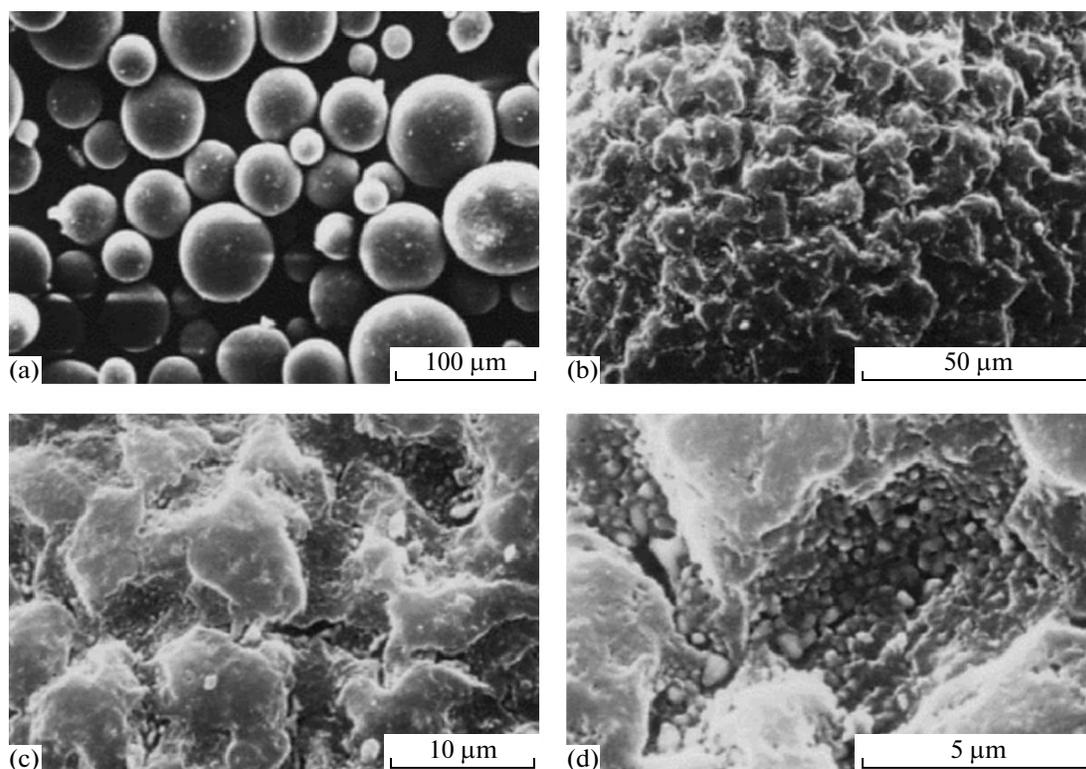
Fig. 8. SEM images of the porous carbon spheres: (a) spherical shape of the spheres, (b) scale like layers on the surface of a sphere, (c) gaps between the layers, and (d) pores between the gaps.

Known from the data is that, to obtain the acetic acid conversion above 22%, it's sufficient to employ the flow rate of acetic acid of 0.1 ml min^{-1}. Further increase in acetylene flow rate only resulted in slight increment of the conversion of acetic acid, 22.6% at 200 ml min^{-1}, 23.2% at 400 ml min^{-1}, and 23.8% at 600 ml min^{-1} when the acetic acid flow rate was fixed at 0.1 ml min^{-1}. Compared to the change of acetic acid

Data of vinyl acetate formation of at various ratio of acetylene to HAc

Entry	v_1, ml/min	v, ml/min	a, g/(mol h)	α, %	α_1, %
1	200	0.1	1039.2	22.6	5.3
2	400	0.1	1067.4	23.2	3.5
3	400	0.2	1435.5	15.6	2.3
4	600	0.1	1095.0	23.8	2.2
5	600	0.4	1586.3	8.6	1.2
6	800	0.1	1053.6	22.9	1.8
7	800	0.4	1693.2	9.2	1.1
8	800	0.6	1849.6	6.7	1.0

Note: Reaction conditions: pressure of acetylene 0.1 MPa; temperature 220°C; volume of PCS-Zn in the reactor 12 cm^3; v_1 and v are the flow rate of acetylene and acetic acid respectively, a is activity, α and α_1 are the conversion of acetic acid and acetylene respectively.

conversions, the activities in vinyl acetate formation also got steady increase with rising ratio of acetylene to acetic acid when the flow rate of acetic acid was maintained at 0.1 ml min^{-1}. Now that the acetylene introduced into the reaction system was in great excess, continuing increase of the acetylene flow rate inevitably reduced its conversions at fixed acetic acid flow of 0.1 ml min^{-1}. Simultaneous increase in the flow rates of acetylene and acetic acid improved the reaction activity to its highest value of ca. 1850 g mol^{-1} h^{-1}. However, both the conversions of acetylene and acetic acid lowered under these conditions. If the activity is expected to improve in large quantity significant increase in the total pressure of the reactants will be a choice. For the sake of operation safety it's a general rule to carry out the reaction at atmospheric pressure of acetylene [12]. It's postulated that residence time was not long enough for the reactant molecules, which were in large excess, to get access to the active Zn sites, therefore the activity was limited to some extent accordingly.

Influence of PCS Structure on the Formation of VAc

The effective diameter of zinc acetate is 0.77 nm [13] which lies in the range of the pore diameters of 0.8–1.2 nm of the PCS support. So most of the zinc acetate was embedded into the pores of PCS especially at a low zinc loading as in the present research.
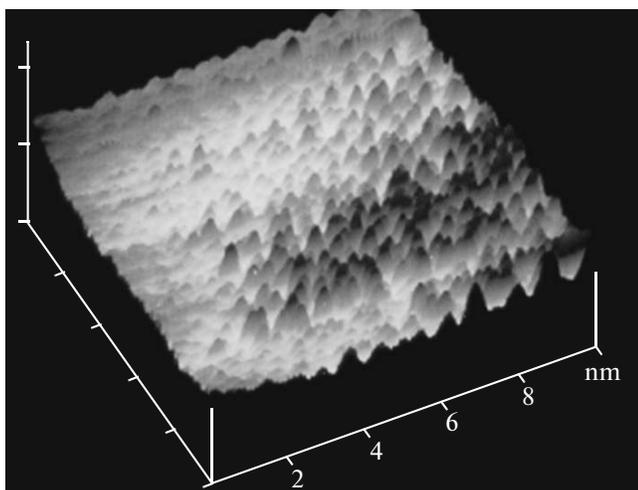
Fig. 9. AFM image of the porous carbon sphere surface. (Scan size: 10.0 nm, Setpoint: 0.0 V, Scan rate: 1.6 Hz, Number of samples: 256).

Because the PCS was synthesized via polymerization method using very pure monomer, it meets the basic demands on a support: low contents of ash and toxic elements; surface area ca. 1000 m^2 g^{-1}, and well developed microporous structure etc. In addition, micropores are advantageous in the adsorption of zinc acetate without adverse effect on the pore structure.

As already described, the PCS possessed uniform size and global morphology. Such a support is suitable for repeated use due to its excellent mechanical strength originated from the high crystallinity. Found in the SEM images (Fig. 8) is that the PCS was of regular spheres (Fig. 8a) with scale-like layers (Fig. 8b) on its surface. Such a layer structure is advantageous for heat transfer and mass transport at large scale. Meanwhile the spherical shape could effectively reduce the dead volume of the fixed-bed reactor. Figure 8c depicts explicitly the gaps between layers and the uniform distance between layers. As noticed in Fig. 8d, most pores were existed in the limited space between gaps, such that the reactant molecules easily permeated to the micropores directly via the gaps, thus greatly reducing the diffusion resistance. In contrast, the adsorption on common activated carbon had to proceed step by step, first from the bulk phase into mesopores and from mesopores into micropores subsequently.

A more detailed three-dimensional AFM image of the sphere surface is illustrated in Fig. 9 that provide nearly atomic images to probe the morphology. Bumps and holes were observed on the surface. The hole size in the range of 0.8—1.2 nm agreed well with the pore distribution value obtained from nitrogen sorption.

Compared to planar surface of other carbon supports, the rugged surface of PCS provided enormous specific surface area and offered much contact area for the reactants and zinc acetate. Moreover, the holes also helped to collect the product and possibly reduced the extent of side reactions.

CONCLUSION

The porous carbon spheres possessing high mechanical strength, narrow pore size distribution, and high surface area proved itself to be an effective support for zinc acetate. The PCS with bumps and holes on its surface facilitated both heat transfer and mass transport during the reaction process. Small in pore diameter as it is, the PCS-Zn catalyst still exhibited high activities in the formation of vinyl acetate from acetic acid and acetylene at atmospheric pressure and moderate temperatures. The single-pass conversions of acetic acid and acetylene were comparable to others' results and the catalyst was supposed to be used repeatedly due to the good physical properties of PCS support.

ACKNOWLEDGMENTS

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