



## Preparation of Supported Palladium Catalyst for Selective Hydrogenation of Phenylacetylene by Double Impregnation Method

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In this paper, Pd-Pb/CaCO<sub>3</sub> catalysts for selective hydrogenation of phenylacetylene were prepared by double impregnation method, which was compared with those prepared by conventional impregnation method, and the results showed that the addition of a certain amount of EDTA could improve the catalytic selectivity significantly. When impregnation ratio was 10 g CaCO<sub>3</sub>/10 mL EDTA, absorption rate of hydrogen was moderate and selectivity was highest (95.9 %). This was possible due to the fact that the addition of EDTA leads to a balanced increase of terrace type surface.

**Key Words:** Pd-Pb/CaCO<sub>3</sub> catalyst, Selective hydrogenation, Double impregnation method, Loading mechanism.

### INTRODUCTION

Semi-hydrogenation of acetylenic link is a valuable synthesis operation and a large number of catalysts based on palladium, platinum, rhodium and nickel are now widely used. Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/CaCO<sub>3</sub> are common selective hydrogenation catalysts and compared with activated carbon and alumina, calcium carbonate (CaCO<sub>3</sub>) can provide effective surface structure which is more suitable to contact with the substrate of catalyst. In the meantime, even dispersion can prevent aggregate sintering and improve stability. Nazimek *et al.*<sup>3</sup> proposed that double impregnation method was used to prepare metallic catalyst with high dispersion. Nazimek *et al.*<sup>1</sup>, Ryczkowski<sup>2</sup> and Cheng *et al.*<sup>3</sup> found that catalyst with high dispersion can be obtained even under high loading capacity based on experimental results of Ni-catalyst, furthermore, deposited metal is mostly located on the surface of carrier. As a special catalyst that can promote semi-hydrogenation of acetylenic link in hydrocarbon and other compound, composition and preparation method of Pd-Pb/CaCO<sub>3</sub> catalyst are reported<sup>4</sup>. Meanwhile, much research and modification of the catalyst are conducted and the prominent is concerned about the role of the second component Pb in the binary metallic catalyst<sup>5</sup>, poison effect of quinoline additives<sup>6</sup> and modification for improving hydrogenation selectivity<sup>7</sup>. However, many problems have not been solved. For example, the ageing process is conducive to improve hydrogenation selectivity, but what is reaction condition? Is double impregnation method better than conventional impregnation method?

In this paper, conventional impregnation method and double impregnation method will be used to prepare a series of palladium catalysts and ageing process will be conducted within a certain range of temperature. Also, the effect of EDTA amount on the catalytic activity and semi-hydrogenation selectivity will be investigated.

### EXPERIMENTAL

Calcium carbonate (AR), palladium chloride (AR), hydrochloride (AR, 36-38 %), EDTA (AR), lead acetate (AR), phenylacetylene (AR, 98 %), petroleum ether (AR), quinoline (AR), hydrogen gas (purity ≥ 99.99 %).

#### Catalyst preparation

**Conventional impregnation method (CI):** The catalyst preparation consists of three steps: (1) 0.74 g PdCl<sub>2</sub> is dissolved in 37 % HCl solution and the solution is diluted to 50 mL with deionized water. Then, 9 g calcium carbonate is put into the solution. Finally, the solution is stirred for 15 min at 75-85 °C. (2) 3 mL and 2.3 mL HCOONa solution are put into the above solution successively and stirring time is *ca.* 40 min. After the reaction end, the catalyst is washed with deionized water 8 times and placed into three neck flask. (3) 30 mL deionized water and 9 mL of 7.7 % lead acetate solution are firstly dipped into three neck flask successively and stirring time is *ca.* 45 min, then the catalyst is dried using busher funnel after being washed 4 times with 25 mL water. Finally, it is dried at 60-70 °C under vacuum condition for 2 h.

**Double impregnation method (DI):** A certain dry  $\text{CaCO}_3$  was first immersed into 0.01M EDTA disodium salt solution for 20 min, then dried at 150 °C for 3 h, and the following preparation steps were the same with the conventional impregnation method.

**Catalyst evaluation and catalytic activity measurement:** The surface physical analysis of sample is investigated using X-ray powder diffractometer (Rigaku Rotaflex D/Max-C) and measuring condition is described as follows:  $\text{CuK}_\alpha$  ray,  $\lambda_\alpha = 0.15406$  nm, graphite monochromator, tube voltage 40 kV, tube current 30 mA, scanning rate 6°/min.

For evaluating catalyst capacity, phenylacetylene is used as a substrate and products are analyzed by gas chromatograph (GC-950, Shanghai Haixin, China). Column length 2 m, mobile phase 10 % 1,2,3,4-tetrakis-(cyanoethoxy)butane, stationary phase 202 pink support, flow gas hydrogen, flux 50 mL/min, column temperature 110 °C, detector temperature 110 °C, gasification chamber temperature 140 °C.

**Palladium dispersion degree of catalyst:** The Pd dispersion degree of catalyst is measured using  $\text{H}_2\text{O}_2$  titration method: 50 mg catalyst is put into reaction tube and blowed with air and nitrogen successively for 1 h at room temperature and the flux is 40 mL/min. Then, 0.5 mL hydrogen is poured into the reaction tube, and reduced volume of hydrogen can be determined using Shimadzu GC-8A. The Pd dispersion degree is calculated by  $[\text{H}_2/\text{Pd}_{\text{surface}}]$ .

**Thermogravimetric analysis of catalyst:** Thermogravimetric analysis of catalyst is investigated using Netzsch STA 449C synchronization thermal analyzer. Test conditions: air, heating rate: 10 °C/min; nitrogen, heating rate: 10 °C/min.

## RESULTS AND DISCUSSION

**Comparison of double impregnation method with conventional impregnation method:** Table-1 shows catalytic performance of catalysts prepared by double impregnation method and conventional impregnation method separately and styrene and ethylbenzene are produced. For conventional impregnation method, selectivity is 89.81 and 97.23 % before and after appropriate ageing treatment separately. Compared with conventional impregnation method, catalyst prepared by double impregnation method represents higher selectivity and catalytic activity, and conversion efficiency is 100 %. The ratio

of carrier weight to impregnation solution volume can affect selectivity remarkably. As the EDTA amount increases, selectivity increases initially and then decreases. When impregnation ratio is 10 g  $\text{CaCO}_3$ /10 mL EDTA, absorption rate of hydrogen is moderate and selectivity (95.9 %) is the best. It is noted that selectivity of catalyst prepared by double impregnation improves a little compared with conventional impregnation method, but its catalytic activity reduces and conversion efficiency is less than 50 % (1:1 of impregnation ratio).

One possible explanation is that this should be related to immobility mechanism of active component on the support: EDTA and calcium carbonate can form complexation center of metal ion. When calcium carbonate is immersed in palladium salt solution, adsorption center and complexation center can function simultaneously. When palladium ion concentration of impregnation solution is high, multi-core complexes can be formed on the surface of carrier easily, which makes Pd particles be agglomerated easily because of heat treatment. This can reduce active sites and absorption rate of hydrogen and conversion efficiency also slow down.

Therefore, for double impregnation method, multi-core complexes formed by EDTA and carrier are similar to the effect of  $\beta$ -hybrid formed during ageing treatment of catalyst prepared by conventional impregnation method. They all can lower catalytic activity by prohibiting active site of Pd catalyst, which can improve selectivity.

When citric acid is used in double impregnation method, selectivity of catalyst is only 91 %, which does not improve a lot compared with conventional impregnation method (89.8 %). To explain the results, structure of organic acid used in impregnation method is paid attention to, and it is found that the effective component is EDTA disodium salt, N atoms of amino group carry a pair of solitary electrons and EDTA disodium salt is attributed to electron donating material. In addition, as mentioned before, competitive adsorption exists in alkynes, alkanes and alkenes. Basic research<sup>8</sup> shows that thermodynamics selectivity depends on the effect of additives on adsorption coefficient for single-alkenes adsorbed species. The stronger the adsorption of catalysts, the easier the alkanes can be formed. If electron donating compounds are added, adsorption of intermediate material on the catalyst increases and selectivity reduces. As far as the reaction is concerned,

TABLE-1  
EFFECT OF DIFFERENT PREPARATION METHODS ON CATALYTIC PERFORMANCE OF Pd-Pb/ $\text{CaCO}_3$  CATALYST

Preparation condition	Ageing	V (mL)	t (min)	Conversion efficiency (%)	Selectivity (%)
CI	–	270	85	100	89.81
CI	370 °C, 1 h	260	100	100	97.23
10 g $\text{CaCO}_3$ /6 mL EDTA	–	285	100	100	88.39
10 g $\text{CaCO}_3$ /6 mL EDTA	370 °C, 1 h	265	180	100	97.84
10 g $\text{CaCO}_3$ /10 mL EDTA	–	265	90	100	95.91
10 g $\text{CaCO}_3$ /10 mL EDTA	370 °C, 1 h	265	210	98.1	98.20
10 g $\text{CaCO}_3$ /10 mL EDTA	360 °C, 1 h	100	160	33.29	97.66
10 g $\text{CaCO}_3$ /10 mL EDTA	355 °C, 1 h	90	120	37.01	97.36
10 g $\text{CaCO}_3$ /15 mL EDTA	–	270	100	100	93.91
10 g $\text{CaCO}_3$ /25 mL EDTA	–	290	90	100	89.25
10 g $\text{CaCO}_3$ /25 mL EDTA	370 °C, 1 h	130	110	48.52	96.74
10 g $\text{CaCO}_3$ /35 mL EDTA	–	275	80	100	91.36

\*Hydrogenation conditions:  $\Phi\text{-C}\equiv\text{CH}$  (1.2 g), catalyst (120 mg), quinoline (100 mg), solvent (petroleum ether, 20 mL), temp. 28 °C, pressure (atmospheric). \*\*Reducing agent:  $\text{HCOONa}$ .

adsorption capacity of EDTA is higher than alkene and lower than alkyne, so semi-hydrogenation selectivity is improved.

**XRD of catalyst:** XRD is used to investigate a series of samples, including calcium carbonate, catalysts prepared by conventional impregnation and double impregnation and industrial catalysts, and the results are shown in Fig. 1. It was found that calcite crystal has unique diffraction peaks (characteristic diffraction peaks  $2\theta$  value  $29.44^\circ$ ). Except that obvious characteristic peaks of calcite are shown in all diffraction peaks, there exists the second phase as shown in Fig. 1 marked with \*, which is attributed to  $\text{PbCO}_3$  (JCPDS 5-681). This shows that  $\text{PbCO}_3$  exists after loading of lead acetate onto the  $\text{Pd-CaCO}_3$ .

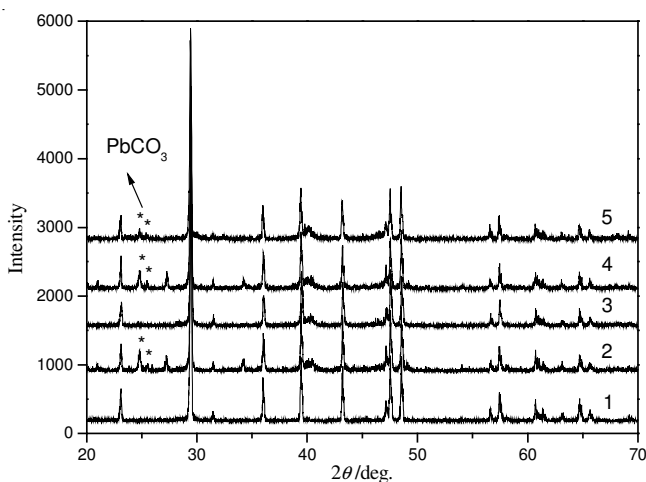


Fig. 1. XRD patterns of different catalysts. 1.  $\text{CaCO}_3$ . 2. LD-H-3 (1 was used support, conventional impregnation). 3. LD-R-7 (the same with H-3, without Pb). 4. LD-N-3 (1 was used support, double impregnation). 5. cat04 (industrial grade)

When baseline  $2\theta$  value is in the range of  $39.5$  and  $45^\circ$ , there exist two relatively broad structures, which is the only evidence of  $\text{Pd}^0$ , but can not confirm the formation of  $\text{Pd}$  [ $\text{Pd}$ ,  $\text{Pd-Pb}$  alloy,  $\text{PdO}$  or  $\text{Pd}(\text{OH})_2$ ].

To study thermal stability of loading  $\text{PbCO}_3$ , XRD is used after catalysts prepared by  $\text{CaCO}_3$  are calcined and showed in Fig. 2. Obviously,  $\text{PbCO}_3$  peak intensity remains unchanged after ageing treatment, indicating that the ageing treatment is appropriate within a certain temperature range.

**Dispersion measurement of catalyst:** As can be seen from Table-2, for conventional and double impregnation methods, the dispersion of palladium decreases after ageing treatment of catalyst and selectivity improves a little. However, the improvement in selectivity of catalyst prepared by double impregnation is not much more prominent than that in selectivity of catalyst prepared by conventional impregnation. This indicates that heat treatment can change the distribution of

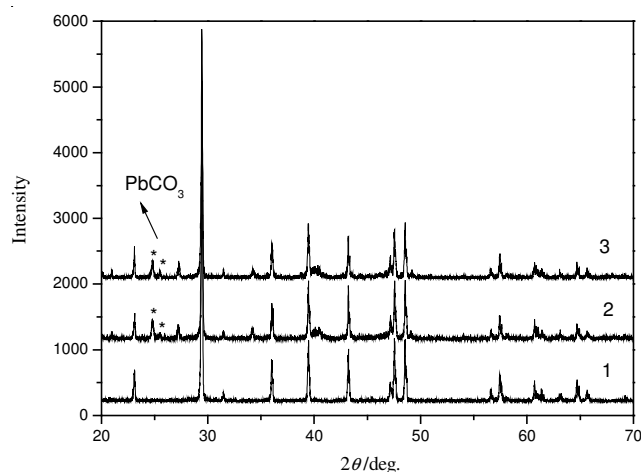


Fig. 2. XRD patterns of different catalysts after ageing treatment. 1.  $\text{CaCO}_3$ . 2. LD-H-3 (1 was used support, conventional impregnation). 3. LD-H-4 (H-3 at  $370^\circ\text{C}$ , 1 h,  $\text{H}_2$ )

palladium particles on the surface of catalyst, the reunion has deepened and the number of terrace type surface increases, which increases hydrogenation selectivity. In addition, for catalysts without ageing treatment, the palladium dispersion of catalysts prepared by double impregnation method is almost the same with that of catalysts prepared by conventional impregnation method, while the selectivity of the former is better than the latter.

**Mechanism of EDTA catalysts prepared by double impregnation method:** Thermal analysis technique is an important method to research on the  $\text{CaCO}_3$  static decomposition because of its rapidity, convenience, accuracy and easy analysis. As we all know, decomposition temperature is depend on the carbonization process. Fig. 3 shows the decomposition curves of the carriers  $\text{CaCO}_3$ , LD-H-3 (conventional impregnation), LD-H-4 (conventional impregnation, ageing treatment at  $370^\circ\text{C}$  in hydrogen atmosphere for 1 h) and LD-R-7 (the same with the LD-H-3, without Pb) in air and nitrogen, respectively, and heating rate is  $10^\circ\text{C}/\text{min}$ . It can be seen that the decomposition curves of  $\text{CaCO}_3$  in the air and nitrogen atmosphere are similar. Temperature of 50 % weight loss is defined as decomposition temperature, and decomposition temperature of  $\text{CaCO}_3$  in nitrogen atmosphere is  $702^\circ\text{C}$ . Meanwhile, decomposition of  $\text{CaCO}_3$  is actually a reversible reaction, and  $\text{CaCO}_3$  will be changed into  $\text{CaO}$  if  $\text{CO}_2$  partial pressure is lower than its equilibrium decomposition pressure at a given temperature. On the contrary, if  $\text{CO}_2$  partial pressure is higher than the equilibrium decomposition pressure, the  $\text{CaO}$  will be re-transformed into  $\text{CaCO}_3$ . Therefore, decomposition reaction can be controlled by  $\text{CO}_2$  partial pressure and reaction temperature. If reaction temperature is less than  $723^\circ\text{C}$ , even if there is no  $\text{CO}_2$  present in the atmosphere, the reaction rate

TABLE-2  
Pd DISPERSION AND CATALYTIC PERFORMANCE OF CATALYSTS WITH DIFFERENT PREPARATION METHODS BEFORE AND AFTER AGEING TREATMENT

Catalyst	Preparation condition	Pd dispersion (%)	Selectivity (%)	Conv. (%)
H-3	Conventional impregnation (CI)	30.4	89.8	100
H-4	H-3, $370^\circ\text{C}$ , $\text{H}_2$ , 1h	18.7	97.2	100
N-3	Double impregnation (DI), 10 g $\text{CaCO}_3/10$ mL EDTA	28.9	95.9	100
N-10	N-3, $360^\circ\text{C}$ , $\text{H}_2$ , 1 h	17.0	97.7	33.3

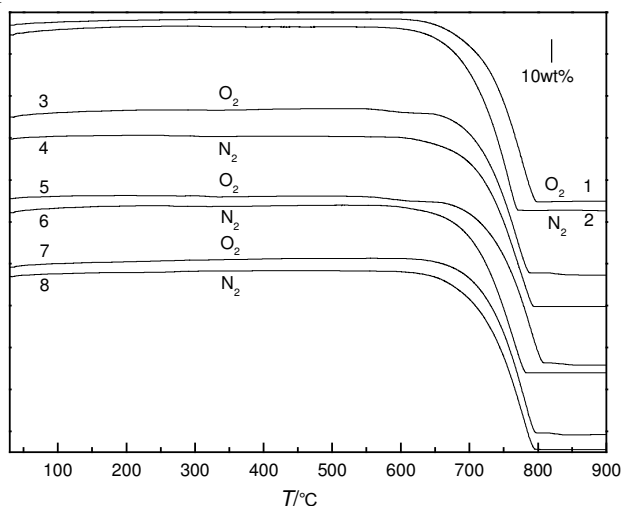


Fig. 3. TG curves of different samples in heating periods 1, 2: CaCO<sub>3</sub> 3,4: H-3 (conventional impregnation). 5,6: H-4 (H-3 ageing treatment, H<sub>2</sub>, 370 °C, 1 h) 7,8: R-7 (the same with H-3, without Pb)

becomes very slow<sup>10</sup>. Thus, with reference to thermodynamic data, decomposition temperature of CaCO<sub>3</sub> is in the range of 472-723 °C, which is the same with results reported in the literature<sup>11</sup>.

In order to explore the surface decomposition reaction clearly, high-resolution TG curves are measured and shown in Fig. 4. Among them, the TG curves of low temperature section have a slight increase, which can be considered to be due to the buoyancy effect. As can be seen from Fig. 4, the weight loss curves of pure CaCO<sub>3</sub> and R-7 in the air and nitrogen atmosphere are nearly the same, while H-3 and H-4 are different significantly. In the air, the peaks of weight loss of both H-3 and H-4 are shown at *ca.* 580 °C before maximum weight loss appears, which does not appear in nitrogen gas. Combined with the XRD characterization (Figs. 1 and 2), the weight loss was due to PbCO<sub>3</sub> endothermic decomposition.

The DSC curves of CaCO<sub>3</sub> with different EDTA amount prepared by double impregnation method are measured and shown in Fig. 5. As can be seen from the figure, there is an

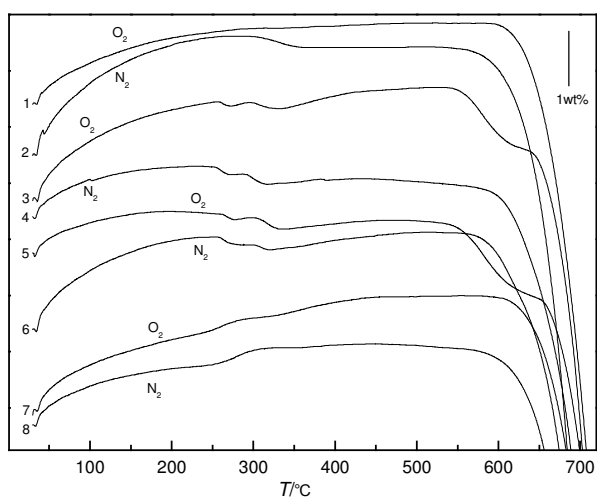


Fig. 4. High-resolution TG curves of the low-temperature plateaus in Fig. 3. 1,2: CaCO<sub>3</sub> 3,4: H-3 (conventional impregnation) 5,6: H-4 (H-3 ageing treatment, H<sub>2</sub>, 370 °C, 1 h) 7,8: R-7 (the same with H-3, without Pb)

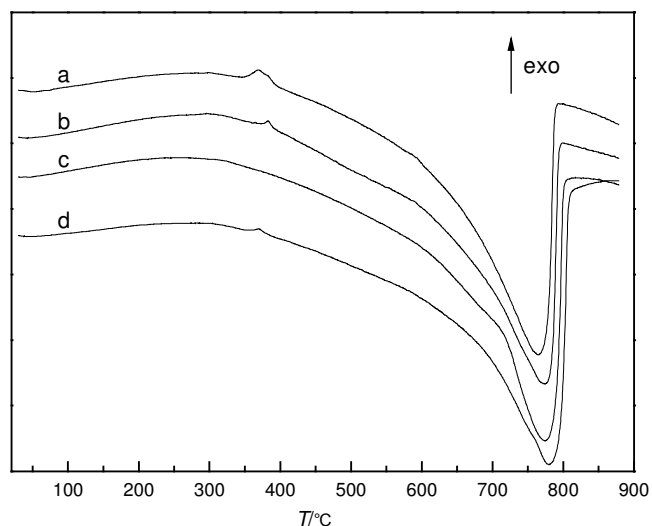


Fig. 5. DSC curves of different samples in heating periods a. 10 g CaCO<sub>3</sub>/15 mL EDTA b. 10 g CaCO<sub>3</sub>/6 mL EDTA c. CaCO<sub>3</sub> d. 10 g CaCO<sub>3</sub>/10 mL EDTA

exothermic peak at 380 °C and the exothermic effect increases with the increase of EDTA amount. This is due to the excessive amount of EDTA during the double impregnation process and some EDTA are alienated from the body after combination of EDTA with CaCO<sub>3</sub>. Furthermore, the excessive EDTA decomposes with the increase of temperature and some heat is released.

In addition, the position of maximum endothermic peaks of the carriers for different impregnation ratio are different. When the impregnation ratio is 1:1 (10 g CaCO<sub>3</sub>/10 mL EDTA), the maximum endothermic peaks of the carriers transfer to high temperature zone compared with those of CaCO<sub>3</sub> without EDTA, indicating that combination of CaCO<sub>3</sub> with EDTA (1:1) makes CaCO<sub>3</sub> stable. This is possibly related to the interaction effect, while other impregnation ratio can reduce the thermal stability of CaCO<sub>3</sub>. This can be found on the DTG curve (Fig. 6) of high temperature zone. In contrast, carrier is the unstablest in a series of catalysts when  $M_{\text{CaCO}_3}/V_{\text{EDTA}}$  is 1:1. Compared with temperature (780 °C) of the maximum weight loss (curve

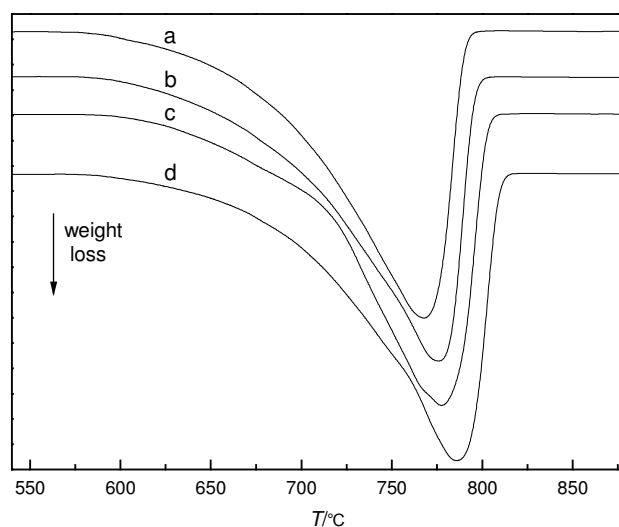


Fig. 6. DTG curves of different samples in heating periods. a. 10 g CaCO<sub>3</sub>/15 mL EDTA b. 10 g CaCO<sub>3</sub>/6 mL EDTA c. CaCO<sub>3</sub> d. 10 g CaCO<sub>3</sub>/10 mL EDTA



d in Fig. 6), it also transfers to high temperature zone and the maximum endothermic peak exists at 800 °C, as shown in Figs. 7 and 8. This is related to introductions of Pd and Pb.

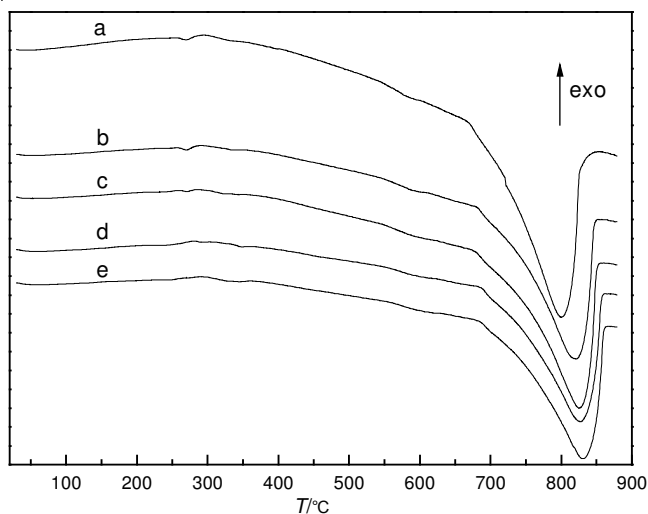


Fig. 7. DSC curves of different samples in heating periods a. 10 g CaCO<sub>3</sub>/10 mL EDTA b. 10 g CaCO<sub>3</sub>/15 mL EDTA c. 10 g CaCO<sub>3</sub>/6 mL EDTA d. 10 g CaCO<sub>3</sub>/35 mL EDTA e. 10 g CaCO<sub>3</sub>/25 mL EDTA

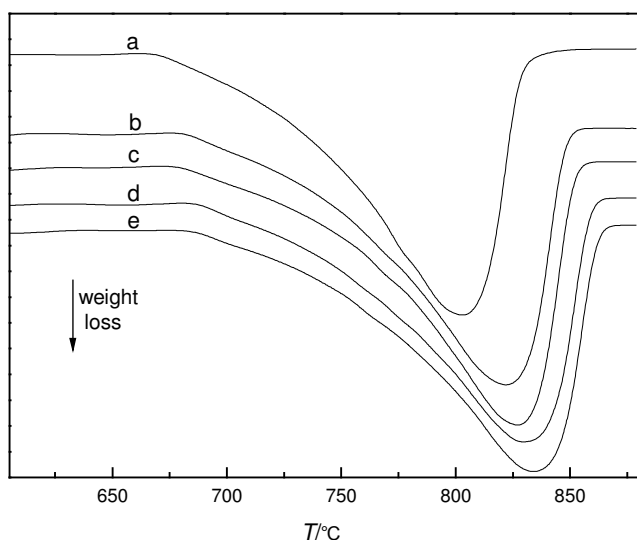


Fig. 8. DTG curves of different samples in heating periods a. 10 g CaCO<sub>3</sub>/10 mL EDTA b. 10 g CaCO<sub>3</sub>/15 mL EDTA c. 10 g CaCO<sub>3</sub>/6 mL EDTA d. 10 g CaCO<sub>3</sub>/35 mL EDTA e. 10 g CaCO<sub>3</sub>/25 mL EDTA

## Conclusion

Based on the above analysis, the paper gave the following explanation with regard to EDTA promotion of catalytic performance: commercially available heavy CaCO<sub>3</sub> was a single crystal of calcite, but the shape was not regular. That is to say, there were some deficiencies on the surface of CaCO<sub>3</sub> particles and Pd was loaded onto the rough surface of all parts of CaCO<sub>3</sub> in conventional impregnation, which inevitably resulted in ups and downs of the surface for the loaded metal Pd. In the double impregnation method, a large number of small EDTA molecules were coated on the surface of CaCO<sub>3</sub> particles at the initial stage and largely filled the position of the defects in the surface of CaCO<sub>3</sub> to form a relatively smooth coating. The surfaces of EDTA and CaCO<sub>3</sub> were formed to be surface complexation centers; when palladium salt solution was used to immerse, the adsorption center of the carrier interacts with complex center, which made the load Pd has relatively flat surface. According to the Maier theory, terrace type surface was helpful to selective hydrogenation of alkynes, and the side reaction such as *cis* and *trans* isomerization, valence bond isomerization, excessive hydrogenation was sensitive to surface structure and can happen on the rough surface of step type or kink type. Therefore, Pd-Pb/CaCO<sub>3</sub> catalyst prepared by double impregnation method had more prominent improvement in selectivity compared with that prepared by conventional impregnation method, and the processing condition was gentle and simple.

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