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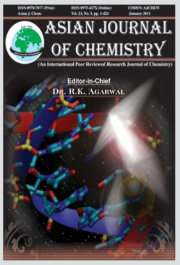

Template Effect of Pd-Pb/$CaCO_3$ Catalyst for Selective Hydrogenation of Phenylacetylene

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For investigating effects of support and ageing treatment on the capability of catalyst, conventional impregnation method was used, assist agent such as EDTA, oxalic acid on the capability of Pd-Pb/$CaCO_3$ catalyst for selective hydrogenation of phenylacetylene was investigated. The results showed that calcite, one crystal type of $CaCO_3$, presents obvious template effect in the presence of oxalic acid. In addition, dispersion measurement indicated that ageing treatment can lead to congregation of Pb particles and high selectivity (98.2 %) was also obtained.

Key Words: Lindlar catalyst, Ageing treatment, Oxalic acid, Selectivity.

INTRODUCTION

Lindlar catalyst has been widely used in fine organic synthesis in past decades because of its high selectivity of hydrocarbon synthesis[1]. For improving selectivity efficiently, many researchers are focused on catalytic mechanism and component modification and the most prominent is concerned about function of Pb in metal catalyst[2], poisoning effect of quinoline[3] and modification of Pd-Pb/$CaCO_3$[4]. However, some important problems have not yet been solved. For example, the purpose of use of the support of $CaCO_3$, ageing treatment is helpful to the improvement of selectivity of hydrocarbon synthesis and the condition requirement.

For studying catalytic mechanism and obtaining high selectivity of hydrocarbon synthesis, ageing treatment will be conducted in a certain temperature range and effect of treatment temperature on the catalytic activity of Pd-Pb/$CaCO_3$ and the selectivity of hydrocarbon synthesis will be investigated.

EXPERIMENTAL

Calcium carbonate is self-made. Palladium chloride and petroleum ether are purchased from Sinopharm Chemical Reagent Limited Company. Hydrochloric acid is purchased from chinese zhenxing second chemical factory. Sodium formate and lead acetate are purchased from Chinese Shanghai Chemical Reagent Company. Phenylacetylene is purchased from acros organics, quinoline is purchased from Shanghai Tingxin Chemical Plant. Hydrogen is purchased from Linda gas. These reagents are of analytical grade and used without further purification.

Catalyst preparation: The catalyst preparation consists of three steps: (1) 0.74 g $PdCl_2$ 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 348-358 K. (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 % $Pb(OAc)_2$ 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 333-343 K under vacuum condition for 2 h.

Catalyst evaluation: 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 383 K, detector temperature 383 K, gasification chamber temperature 413 K.

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: CuK$_\alpha$ ray, $\lambda\alpha = 0.15406$ nm, graphite monochromator, tube voltage 40 KV, tube current 30 mA, scanning rate 6 °/min.

The Pd dispersion degree of catalyst is measured using H_2-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 [H_2/Pd$_{surface}$].

RESULTS AND DISCUSSION

Nowadays, many selective hydrogenation catalysts such as Pd/C, Pd/Al_2O_3, Pd/$CaCO_3$ have been developed. Among them, Pd/$CaCO_3$ exhibits the highest catalytic activity because the support of $CaCO_3$ has the highest efficient surface area and the most suitable pore structure, which is helpful to the contact of the catalyst with the substrate. Furthermore, homodisperse of the catalyst can avoid agglomeration and improve stability.

Calcium carbonate have three crystal types and calcite is the most stable and aragonite is the most unstable. The existence of dispersant is favorable for productions of aragonite and vaterite and effect of EDTA amount on the crystal type of precipitated calcium carbonate and catalytic activity is investigated, the results are shown in Fig. 1 and Table-1. As is shown in Fig. 1, when EDTA amount is 0.2-0.25 g, calcite and aragonite are mainly produced. As EDTA amount increases, vaterite amount also increases and calcite and aragonite reduce, but the activity and the selectivity of catalyst are not affected obviously. When EDTA amount is 0.45 g, vaterite becomes the main product, which can reduce the catalytic selectivity. So the catalytic selectivity is strongly affected by the vaterite amount. Fig. 2 and Table-2 show effect of amount of oxalic acid on crystal type of calcium carbonate and catalytic activity. When oxalic acid amount is 0.2-0.4 g, the only product calcite can be obtained. At the same time, as oxalic acid amount increases, the catalyst selectivity first increases, then decreases and the maximum value (92.5 %) is achieved. For catalyst without addictive (EDTA or oxalic acid), calcite and aragonite are produced and used as a support and the selectivity is 78.89 %. Addition of EDTA into catalyst can achieve lower selectivity, while addition of oxalic acid can improve the selectivity significantly and the high selectivity (92.5 %) is reached without ageing treatment. This can be explained that addition of oxalic acid is helpful to calcite production. In addition, the change of crystal type has abduction template effect on the Pd catalyst[5], which is reflected by Pd-Pb/$CaCO_3$.

After ageing treatment of Pd-Pb/$CaCO_3$ catalyst, the activity and the selectivity are also investigated. As is shown in Figs. 1 and 2, the selectivity of hydrocarbon synthesis can improve a lot after proper modification of EDTA and oxalic acid. The oxalic acid is more prominent and the selectivity can reach 98.2 %. Meanwhile, ageing treatment temperature has a great effect on the selectivity. As temperature increases, the

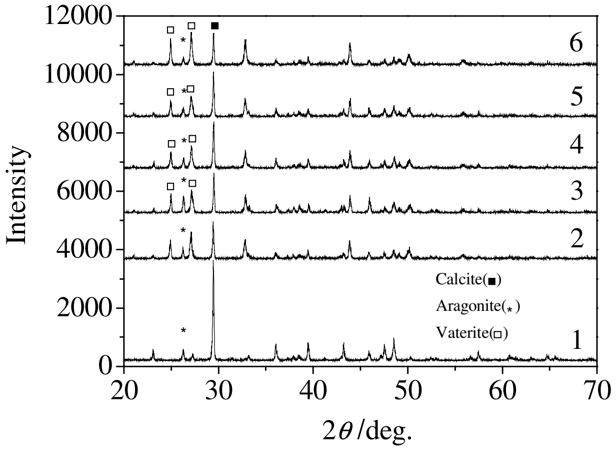

Fig. 1. XRD pattern of precipitated $CaCO_3$ in presence of EDTA. (1) 0 g (2)0.2 g (3) 0.25 g (4) 0.33 g (5) 0.4 g (6) 0.45 g

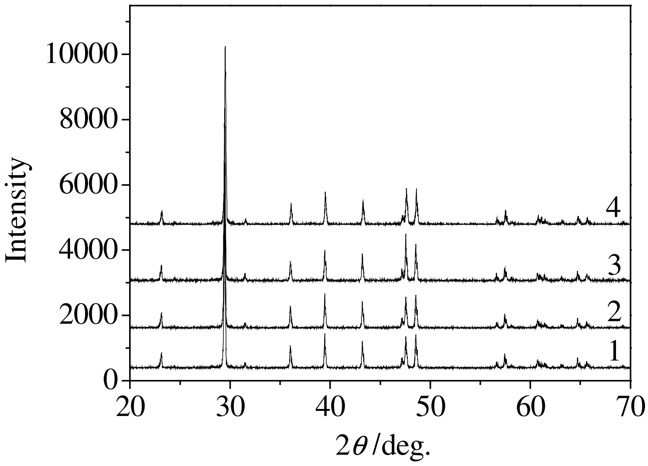

Fig. 2. XRD pattern of precipitated $CaCO_3$ in presence of oxalic acid. (1) 0.2 g (2) 0.25 g (3) 0.3g (4) 0.4 g

TABLE-1
EFFECT OF AGEING TREATMENT ON CATALYTIC PERFORMANCE OF Pd-Pb/$CaCO_3$ CATALYST IN THE PRESENCE OF EDTA

W_{EDTA} (g)	T_{ageing} (K)	$V_{hydrogen}$ (mL)	t (min)	Conv. (%)	Selectivity (%)
0.2	–	330	210	100	75.5
	633	340	180	100	72.76
	638	170	205	64.9	99.4
	643	225	210	81.7	99.4
0.25	–	300	110	100	85.7
	633	240	190	88.4	99.4
	643	185	240	67.9	98.9
	653	175	180	61.4	99.0
0.33	–	300	130	100	83.6
	638	280	120	100	92.1
	643	270	180	100	97.4
	648	250	170	90.27	97.9
0.4	–	310	160	100	84.4
	638	315	180	100	82.4
	643	290	180	100	95.5
	648	280	160	100	93.6
0.45	–	340	180	100	71.6
	638	215	180	80.8	99.41
	643	315	180	100	81.6
	648	320	180	100	77.7

Hydrogenation conditions: $W_{\Phi\text{-}C\equiv CH}$, 1.2 g; $W_{catalyst}$, 120 mg; $W_{quinoline}$, 100 mg; $V_{petroleum\ ether}$, 20 mL; temp. 301 K; pressure 1 atm.

TABLE-2
EFFECT OF AGEING TREATMENT ON CATALYTIC PERFORMANCE OF Pd-Pb/CaCO$_3$ CATALYST IN PRESENCE OF OXALIC ACID

$W_{oxalic\ acid}$ (g)	T_{ageing} (K)	$V_{hydrogen}$ (mL)	t (min)	Conv. (%)	Selectivity (%)
0	–	320	90	100	78.89
	648	310	100	100	83.68
0.2	–	320	105	100	81.3
	638	210	290	68.5	99.1
	643	200	220	80.6	98.7
	648	305	150	100	85.2
0.25	–	280	70	100	87.9
	638	285	100	100	94.5
	643	255	90	100	94.8
	648	230	170	82.6	99.1
0.3	–	275	90	100	92.5
	638	310	95	100	89.0
	643	280	120	100	94.2
	648	210	85	100	98.2
	653	210	70	100	95.3
0.4	–	335	120	100	76.0
	638	285	100	100	92.1
	643	290	95	100	90.7
	648	330	150	100	75.9

Hydrogenation conditions: see footnote to Table-1.

TABLE-3
PALLADIUM DISPERSION AND CATALYTIC PERFORMANCE OF CATALYSTS WITH DIFFERENT PREPARATION METHODS BEFORE AND AFTER AGEING TREATMENT

$W_{oxalic\ acid}$ (g)	Ageing condition	Pd dispersion (%)	Selectivity (%)	Conv. (%)
0	–	32.5	78.89	100
0	648 K, H_2, 1 h	19.8	83.68	100
0.3	–	25.6	92.5	100
0.3	648 K, H_2, 1 h	16.3	98.2	100

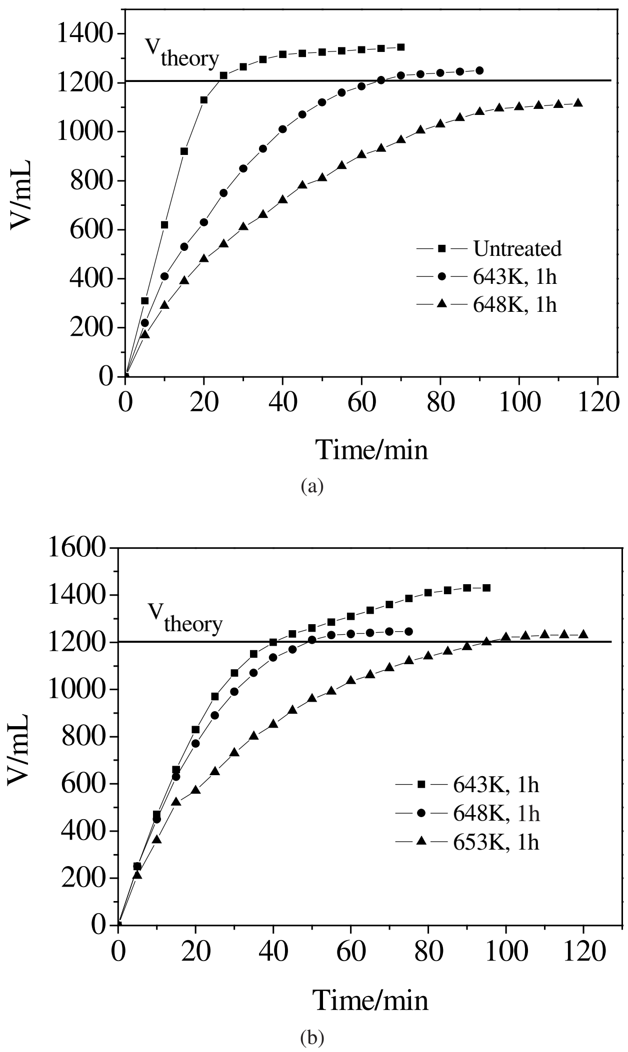

Fig. 3. Hydrogenation curves of catalysts with crystallization type modified by oxalic acid. (a) 0.25 g oxalic acid (b) 0.3 g oxalic acid. Hydrogenation conditions: $W_{\Phi\text{-}C\equiv CH}$, 6.0 g; $W_{catalyst}$, 600 mg; $W_{quinoline}$, 500 mg; $V_{petroleum\ ether}$, 30 mL; temp. 301 K; pressure 1 atm

selectivity of Pd-Pb/CaCO$_3$ catalyst first increases, then decreases. For 0.3 g oxalic acid, when temperature increases from 643-653 K, the selectivity increases from 94.2-98.2 % and then decreases to 95.3 %. Compared with oxalic acid, catalyst after EDTA modification is more sensitive to heat treatment and conversion efficiency after ageing treatment is less than 100 %. That is because that high temperature can reduce surface active sites of the catalyst. In addition, low catalytic activity can lead to high selectivity of hydrocarbon synthesis and roasting of catalyst at proper temperature can enhance its selectivity. However, if roasting temperature is too high, catalytic activity decreases dramatically, which can be reflected by the reduction of absorption rate of hydrogen and incompletion of hydrogenation, *etc*, which is shown in Figs. 3 and 4. Therefore, high selectivity can be obtained mainly by modification of Pd-Pb/CaCO$_3$ catalyst.

Effect of structure on alkyne hydrogenation is not strong and Pd crystal with low energy is propitious to the reaction. On the contrary, alkene hydrogenation is sensitive to crystal structure. Kink type atoms can exist in small particles easily, terrace type atoms are distributed to the big metal particle surfaces and medium size particles are mostly step type atoms. Hydrogen and nitrogen are selected as ageing treatment environment and the results show that the selectivity obtained at proper temperature is almost the same, which indicated that roasting affected stability of the catalyst significantly. Fig. 3 shows Pd dispersion degree of the catalyst before and after ageing treatment. When 0.3 g oxalic acid was added, the Pd dispersion degree is 25.6 % and the selectivity was 92.5 % before ageing treatment and after ageing treatment at 648 K the Pd dispersion degree was 16.3 % and the selectivity was 98.2 %. The decrease of the Pd dispersion degree after ageing treatment showed that roasting can make particles grow larger and the selectivity can enhance a lot while the activity remained unchanged, which indicated that the amount of terrace type Pd in the catalyst after ageing treatment increases dramatically and the terrace type surface is just active site and selective site of alkyne hydrogenation.

Palladium-based multiphase hydrogenation reaction is sensitive to surface structure and configuration of catalyst[6]. Palladium can change and recombine in hydrogen because that β-hydrid of Pd can be produced[7-9], which is similar to functions of most metallic salt and drug substance and they can improve Pd catalyst selectivity by modifying configuration, size and surface structure. Heat treatment in hydrogen environment can make Pd particles in the catalyst reunite and the number of terrace type Pd atoms increases and smooth surface can be formed with the increase of particle size, which can hold back active sites of Pd catalyst, reduce the catalytic activity and enhance selectivity significantly.

Conclusion

Calcite, one of three crystal types of $CaCO_3$, is the most helpful to phenylacetylene hydrogenation than the other two crystal type aragonite and vaterite. Additives affected the crystal types significantly and addition of oxalic acid as an additive was helpful to formation of calcite. When 0.3 g oxalic acid was added and heat treatment lasted for 1 h at 648 K, the selectivity of Pd-Pb/$CaCO_3$ catalyst can reach 98.2 %. In addition, high selectivity of Pd-Pb/$CaCO_3$ catalyst was obtained by conventional impregnation method. Also, the treatment method is simple and maneuverability is strong, which showed a promising prospect.

REFERENCES

1. H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).
2. J.G. Ulan, W.F. Maier and D.A. Smith, *J. Org. Chem.*, **52**, 3132 (1987).
3. T. Fukuda, *Bull. Chem. Soc. (Japan)*, **32**, 420 (1959).
4. J. Rajaram, A.P.S. Narula, H.P.S. Chawla and S. Dev, *Tetrahedron*, **39**, 2315 (1983).
5. L.F. Yang, C.K. Shi and X.E. He, *Appl. Catal. B*, **38**, 117 (2002).
6. W.F. Maier, *Chem. Ind. (Dekker)*, **33**, 211 (1988).
7. Z. Paal and P.G. Menon, *Catal. Rev.-Sci. Eng.*, **25**, 229 (1983).
8. W. Palczewska, *Adv. Catal.*, **24**, 243 (1975).
9. R.K. Nandi, P. Georgopoulos and J.B. Cohen, *J. Catal.*, **77**, 421 (1982).