

Studies on esterification reaction over aluminophosphate and silicoaluminophosphate molecular sieves

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Abstract

Di-(2-ethylhexyl) phthalate (DEP) has been synthesized using a novel silicoaluminophosphate molecular sieve CHSAPO-1 as catalyst for the esterification reaction of phthalic anhydride with 2-ethylhexanol. The effect of some factors such as reaction temperature, the molar ratio of 2-ethylhexanol/phthalic anhydride, the amount of catalyst used, the amount of cyclohexane used and reaction time on the reaction has been investigated. The yield of di-(2-ethylhexyl) phthalate obtained was over 95% when the reaction conditions used were as follows: the molar ratio of 2-ethylhexanol/phthalic anhydride = 2.8:1, the amount of cyclohexane used = 25 ml/mol phthalic anhydride, the amount of catalyst used = 1.1 g/mol phthalic anhydride, reaction temperature = 200–220°C, and reaction time = 2 h. H-CHSAPO-1 catalyst also possesses high selectivity and good activity stability for the reaction. The physical properties of the esterified product synthesized are in accordance with the literature values. For comparison, some zeolites were also tested in the esterification reactions.

Butyl pentanoate has also been synthesized by the esterification reaction of pentanoic acid with *n*-butanol over novel aluminophosphate and silicoaluminophosphate molecular sieves. The effect of the procedures of synthesizing the molecular sieves and preparing the catalysts, and reaction conditions on the yield of the ester has been systematically investigated. The yield of the ester obtained when using aluminophosphate molecular sieves as catalysts depends upon synthesis methods of the molecular sieves (mainly template and synthesis system).

The aluminophosphate and silicoaluminophosphate molecular sieves modified with Sn possess higher catalytic activity than those not modified. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aluminophosphate molecular sieve; Silicoaluminophosphate molecular sieve; Esterification; Synthesis; Catalyst

1. Introduction

Some conventional catalysts such as H₂SO₄, etc. have been used for preparation of di-(2-ethylhexyl) phthalate from the esterification reaction of phthalic anhydride with 2-ethylhexanol, and for the synthesis of butyl pentanoate from the esterification of pentanoic acid with *n*-butanol. Unfortunately, the applications of those catalysts cause some problems such as corrosion, loss of catalyst, and environment problems. However,

di-(2-ethylhexyl) phthalate and butyl pentanoate are very useful products industrially. Therefore, development of more efficient catalysts will be interesting and useful. It is well known that the use of heterogeneous catalysts for liquid phase organic synthesis reactions can give a lot of benefits [1], for example, a clean reaction product solution can be obtained after simple filtration, the catalyst is easy to be recovered and reused, and avoidance of corrosion, etc. Hence, some attention has been paid to the use of heterogeneous catalysts in the esterification reactions of carboxylic acids [2–5].

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Aluminophosphate (AlPO₄) molecular sieves are porous crystalline inorganic solid materials which are formed from alternating AlO₄ and PO₄ tetrahedra. AlPO₄ molecular sieves were first synthesized by Wilson and coworkers [6,7]. It has been shown possible to perform isomorphous substitution [8]. The materials obtained when silicon substitutes into the framework of the AlPO₄ molecular sieves are known as silicoaluminophosphate (SAPO) molecular sieves [9,10].

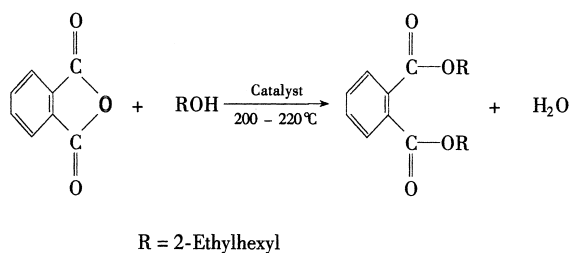
The catalytic activity of some AlPO₄ molecular sieves such as AlPO₄-12, etc. in the esterification reaction of propionic acid with *n*-butanol has been reported [11]. Now we would like to report an efficient catalyst, novel silicoaluminophosphate molecular sieve CHSAPO-1 [12] synthesized first by us, which was used for the preparation of di-(2-ethylhexyl) phthalate from the esterification reaction of phthalic anhydride with 2-ethylhexanol, and the application of some novel aluminophosphate and other silicoaluminophosphate molecular sieve catalysts in the esterification reaction of pentanoic acid with *n*-butanol.

2. Results and discussion

2.1. Esterification of phthalic anhydride with 2-ethylhexanol

The esterification reaction of phthalic anhydride with 2-ethylhexanol in the presence of catalyst and in the case of heating can be represented in Scheme 1.

Table 1 shows the initial rate of the esterification reaction over various catalysts. The results indicate that the catalyst H-CHSAPO-1 is more effective than others. As can be seen from the Runs (1–4) in Table 2, the results obtained using various catalysts for the reaction indicate that the order of catalytic activity



Scheme 1. Esterification of phthalic anhydride with 2-ethylhexanol.

Table 1
Comparison of catalytic activities of various catalysts^a

Catalyst	Initial rate of esterification (mol PA/h)
H-CHSAPO-1	3.05
H-SAPO-12	2.96
HZSM-5	2.98
HY	2.91

^a Ethylhexanol:phthalic anhydride:catalyst:cyclohexane = 1 mol:3.0 mol:2.0 g:25 ml at 200–220°C.

observed within a reaction time of 2 h is as follows: H-CHSAPO-1 > H-ZSM-5 = H-SAPO-12 > HY zeolite. It is worth noting that H-CHSAPO-1 catalyst prepared by ion exchange from silicoaluminophosphate molecular sieve CHSAPO-1 possessed the highest activity for the reaction.

A series of experiments [Runs (5–10) in Table 2] has been carried out by varying the amount of the catalyst used but keeping other conditions, such as 2-ethylhexanol/phthalic anhydride molar ratio, the amount of cyclohexane used, reaction temperature and reaction time, constant. The results obtained show that the yield of di-(2-ethylhexyl) phthalate increased with increasing the amount of the catalyst used. However, when the amount of the catalyst used was varied over 1.1 g/mol phthalic anhydride, an increase in the yield was no longer evident.

A rise in 2-ethylhexanol/phthalic anhydride molar ratio (Runs 11–16) led to a slight increase in the yield because of movement of chemical equilibrium of the reversible reaction towards the direction of forming the ester. It is evident that 2.8:1 is an appropriate molar ratio of 2-ethylhexanol/phthalic anhydride.

Cyclohexane was employed as a solvent to promote separation of water formed during the esterification reaction from the reaction system. A rise in the amount of cyclohexane added led to a slight decrease in the yield (Runs 17–22). This decrease could be because the addition of the cyclohexane to the reaction system caused a decrease in the reflux temperature, i.e. reaction temperature. However, the addition of an appropriate amount of cyclohexane is necessary in order to remove the water formed during the esterification reaction from the reaction system, leading to movement of chemical equilibrium of the reversible reaction towards the direction of forming the ester to increase the yield of the ester. On the other

Table 2
Esterification of phthalic anhydride (PA) with 2-ethylhexanol (EH)

Catalyst	Run	Amount of catalyst (g/mol PA)	EH/PA (mol ratio)	Amount of cyclohexane (ml/mol PA)	Reaction temperature (°C)	Reaction time (h)	Yield of DEP(%)
H-CH-SAPO-1 (HCSAP1)	1	2.0	3.0:1	25	200–220	2	97.8
H-SAPO-12	2	2.0	3.0:1	25	200–220	2	96.2
HZSM-5	3	2.0	3.0:1	25	200–220	2	96.3
HY	4	2.0	3.0:1	25	200–220	2	95.4
HCSAP1	4a	0	2.8:1	25	200–220	2	30.1
	5	1.0	2.8:1	25	200–220	2	93.1
	6	1.1	2.8:1	25	200–220	2	96.7
	7	1.5	2.8:1	25	200–220	2	96.9
	8	2.0	2.8:1	25	200–220	2	97.1
	9	2.5	2.8:1	25	200–220	2	97.2
	10	3.0	2.8:1	25	200–220	2	97.5
HCSAP1	11	2.5	2.0:1	25	200–220	1	88.7
	12	2.5	2.4:1	25	200–220	1	89.1
	13	2.5	2.8:1	25	200–220	1	90.5
	14	2.5	3.0:1	25	200–220	1	90.8
	15	2.5	3.4:1	25	200–220	1	90.8
	16	2.5	4.0:1	25	200–220	1	90.9
HCSAP1	17	1.1	2.8:1	0	190–240	1	91.2
	18	1.1	2.8:1	10	220–230	1	90.5
	19	1.1	2.8:1	15	210–230	1	90.2
	20	1.1	2.8:1	20	200–220	1	89.9
	21	1.1	2.8:1	25	200–210	1	89.4
	22	1.1	2.8:1	30	180–190	1	88.1
HCSAP1	23	3.0	3.0:1	25	150–160	1	69.2
	24	3.0	3.0:1	25	160–170	1	73.6
	25	3.0	3.0:1	25	170–180	1	77.7
	26	3.0	3.0:1	25	180–190	1	81.1
	27	3.0	3.0:1	25	190–200	1	85.6
	28	3.0	3.0:1	25	200–210	1	88.9
	29	3.0	3.0:1	25	210–220	1	90.5
HCSAP1	30	3.0	3.0:1	25	210–220	0.5	77.8
	31	3.0	3.0:1	25	200–220	1	89.9
	32	3.0	3.0:1	25	200–220	1.5	96.3
	33	3.0	3.0:1	25	200–220	2	97.6
	34	3.0	3.0:1	25	200–220	2.5	98.2
	35	3.0	3.0:1	25	200–220	3	98.7

hand, the reaction can proceed at a lower temperature, decreasing the possibility of side reactions.

An appropriate rise in the reaction temperature (Runs 23–29) can increase the yield of the ester, probably due to an increase in the activity of H-CHSAPO-1 catalyst for the reaction.

Runs 30–35 demonstrate that a rise in the reaction time led to an increase in the ester yield.

In order to establish whether the catalyst could be reused, a sample of H-CHSAPO-1 was recovered

by filtration after reaction. It was then reused in an identical reaction without further treatment for the catalyst. Table 3 lists the results obtained. The process was repeated five times, and the catalyst retained its full activity even in its fifth reuse. It is possible, therefore, that a continuous process could be utilized, although we have not attempted to carry out the reaction in this way. This illustrates that H-CHSAPO-1 catalyst possesses excellent activity stability in the esterification reaction.

Table 3

Activity stability of H-CHSAPO-1 catalyst (all reactions were carried out using 1.1 g catalyst/20 ml cyclohexane/2.8 mol 2-ethylhexanol/mol phthalic anhydride at 200–220°C for 1 h)

Times of using the catalyst	Yield of DEP (%)
First	89.8
Second	90.2
Third	89.5
Fourth	89.1
Fifth	88.7
Sixth	87.4

In addition, the esterification reactions of phthalic anhydride with *n*-butanol, *n*-pentanol, *iso*-pentanol, *n*-octanol and *iso*-octanol have also been investigated, respectively, under the same conditions as those used in the esterification reaction of phthalic anhydride with 2-ethylhexanol. The results obtained indicate that the order of the ester yield change with different alcohols is as follows: *n*-octanol > *n*-pentanol > *n*-butanol; and normal alcohols > *iso*-alcohols. For the series of normal alcohols, this could mainly be due to the difference of the boiling points amongst the alcohols having different carbon atom numbers; but for the normal and isomeric alcohols with the same carbon atom number, this could mainly be attributed to both the boiling point factor and different molecular structures and sizes.

Table 4

Esterification reaction of pentanoic acid with *n*-butanol over various aluminophosphate molecular sieves

Number of catalyst	Templating agent used in synthesis of molecular sieve	Esterification reaction time (h)	Yield of butyl pentanoate (%)
AP-9012016	Et ₃ N (Et ₃ N/Al ₂ O ₃ mol ratio = 1.5)	4	70.9
AP-89012013	Et ₃ N/Al ₂ O ₃ = 1.3	5	68.7
AP-7-24	Cyclohexamine	4	16.0
AP-89012026	Ethylenediamine	5	74.3
AP-898012031	Inorganic ammonium	5	69.8
NQ-AP-9011013	Non-aqueous system	4	61.9
AP-9002020	Non-organic system	5	60.3

Table 5

Esterification reaction of pentanoic acid with *n*-butanol over various aluminophosphate molecular sieve catalysts modified with Sn

Number of catalyst	Type or synthetic system of AlPO ₄ before modifying with Sn	Esterification reaction time (h)	Yield of butyl pentanoate (%)
AP-9012016M	Et ₃ N system	4	89.5
AP-9003026M	Ethylenediamine	4	81.0
AP-7-24M	CHNUAP-7	4	74.9
NA-AP-9011013M	Non-aqueous system	4	63.6

2.2. Esterification of pentanoic acid with *n*-butanol

In the case of pentanoic acid/*n*-butanol molar ratio = 1:1.2, the amount of catalyst used = 1.0 g/mol pentanoic acid, the amount of cyclohexane used = 5 ml/mol pentanoic acid, and reaction temperature = 140–150°C, the aluminophosphate and silicoaluminophosphate molecular sieve catalysts prepared by various methods were used for the esterification reaction of pentanoic acid with *n*-butanol. Tables 4–6 list the results obtained.

As shown in Table 4, the catalyst prepared from the AlPO₄ molecular sieve synthesized using ethylenediamine as a templating agent possesses the highest activity for the esterification reaction. The AlPO₄ molecular sieves synthesized in different systems possess some differences in their crystal structures, leading to slightly different catalytic activities.

It can be seen from comparison of Table 5 with Table 4 that the AlPO₄ molecular sieve catalysts modified with Sn exhibit higher catalytic activity, in particularly the modified CHNUAP-7, than those not modified.

The results given in Table 6 indicate that H form SAPO molecular sieves possess higher catalytic activity than non-H form SAPO. Both the H form and non-H form SAPO molecular sieves modified with Sn

Table 6

Esterification reaction of pentanoic acid with *n*-butanol over various silicoaluminophosphate molecular sieves

Number of catalyst	Type or preparation conditions of catalyst	Esterification reaction time (h)	Yield of butyl pentanoate (%)
H-CHSAPO-1	H form	4	76.0
H-CHSAPO-1M	H form, modified with Sn	4	81.5
H-SAPO-12028	H-SAPO-12	5	74.5
H-SAPO-12D	H-SAPO-12 modified	5	95.2
N-HSAPO-CH-1-28	Synthesized in non-aqueous system	5	65.4
N-HSAPO-CH-1-28M	Synthesized in non-aqueous system, H form and modified	5	91.7
N-HSAPO-CH-1-26	Synthesized in non-organic system	3.5	66.5
N-HSAPO-CH-1-26M	Synthesized in non-organic system, H form and modified	3.5	74.6
CHSAPO-7-17	CHSAPO-7, no ion exchange	3.5	60.0
CHSAPO-7-17M	CHSAPO-7, no ion exchange, modified	3.5	76.4
CHSAPO-8-28	CHSAPO-8, no ion exchange	4	67.6
CHSAPO-8-28M	CHSAPO-8, no ion exchange, modified	3.5	71.8
CHSAPO-9-20	CHSAPO-9, no ion exchange	4	64.5
CHSAPO-9-20M	CHSAPO-9, no ion exchange, modified	4	83.1
SAPO-9012002	SAPO-17, no ion exchange	4	65.7
SAPO-9012002M	SAPO-17, no ion exchange, modified	4	79.2
CHSAPO-10-4	CHSAPO-10, no ion exchange	4	59.1
CHSAPO-10-4M	CHSAPO-10, no ion exchange, modified	4	83.8

exhibit higher activity than the SAPO not modified. The H form SAPO molecular sieves modified with Sn possess higher activity than the non-H form SAPO modified with Sn.

3. Conclusions

H-CHSAPO-1 is an effective catalyst with high activity, excellent selectivity and activity stability for the esterification reaction of phthalic anhydride with 2-ethylhexanol.

The catalytic activities of different AlPO_4 molecular sieves in the esterification reaction depend upon the synthesis methods of these molecular sieves.

The modification of the AlPO_4 and SAPO molecular sieves with Sn can markedly increase the catalytic activities of these catalysts in the esterification reactions.

4. Experimental

4.1. Catalyst

Syntheses of AlPO_4 molecular sieves were carried out according to the procedures described by Zhao et al. [11], using phosphoric acid (85% H_3PO_4) and aluminium hydroxide as the sources of phosphate and alumina, respectively.

A novel SAPO molecular sieve, CHSAPO-1, was synthesized in the system triethylamine– Al_2O_3 – P_2O_5 – SiO_2 – H_2O [12]. The synthesis of other SAPO molecular sieves were performed according to Lok et al. [9].

The synthetic products were characterized using powder X-ray diffraction (XRD), SEM, IR, DTA, chemical analysis and adsorption measurement.

The chemical composition and adsorption data of a novel SAPO molecular sieve, CHSAPO-1, were given in Table 7.

Table 7

Chemical composition and adsorption data of CHSAPO-1

Weight loss after calcination (%)	Composition (wt.%)			Molar composition $\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:\text{SiO}_2$	Adsorption data (wt.%)	
	Al_2O_3	P_2O_5	SiO_2		H_2O	Cyclohexane
13.41	32.68	37.36	16.55	1:0.82:0.86	9.3	9.5

H-SAPO catalyst was prepared by a series of treatments. The SAPO molecular sieve was first calcined at 540°C in order to remove the organic template, it was then ion-exchanged with an aqueous solution of 0.5 M NH₄Cl. H-SAPO was prepared by calcining the NH₄-SAPO at 540°C. Finally, 25 wt.% of a binder (Al₂O₃) was added to the H-SAPO, and H-SAPO catalyst was prepared after further a series of treatments including crashing, sieving and calcination at 540°C for 3 h.

SAPO catalysts modified with Sn were prepared by impregnation or mechanical mixing.

4.2. Esterification procedures

General procedures for catalytic esterification were described as follows. A freshly activated molecular sieve catalyst was added to a mixture of phthalic anhydride, 2-ethylhexanol (or pentanoic acid and *n*-butanol) and cyclohexane in a three necked round-bottomed flask equipped with a thermometer, a reflux condenser and a separator of water. The suspension was stirred under reflux for a few hours to obtain a satisfactory yield. The progress of the reaction was examined by determining the conversion of the phthalic anhydride or pentanoic acid using acid–base titration. After a certain reaction time, the reaction mixture was cooled, and filtered. The filtrate was neutralized by saturated Na₂CO₃ solution. A pure ester product was obtained by distillation under reduced pressure.

4.3. Analysis

The yields of the esterified products were determined by GC or weighing the purified product. IR spectra of the products were recorded on a Perkin-Elmer 783 FTIR spectrometer.

4.4. The reaction rate measurements

The rate measurements of esterification reactions were made by determining the concentration of phthalic anhydride at different reaction periods with chemical analysis, and then by drawing the concentration of phthalic anhydride (C_A) versus reaction time (t). Thus, the reaction rate is equal to $-dC_A/dt$.

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References

- [1] K. Smith (Ed.), Solid Supports and Catalysts in Organic Synthesis, Ellis Horwood, Chichester, UK, 1992.
- [2] Z.H. Zhao, R.L. Zhao, Z. Sheng, Nat. Sci. J. Hunan Normal Univ. 4 (1993) 332–337.
- [3] Z.H. Zhao, R.L. Zhao, S.F. Jiang, Cuihua Xuebao 13 (1992) 237–240.
- [4] Z.H. Zhao, M. Zhang, Cuihua Xuebao 12 (1991) 328–332.
- [5] Z.H. Zhao, Y.Q. Wang, Nat. Sci. J. Hunan Normal Univ. 1 (1990) 61–64.
- [6] S.T. Wilson, B.M. Lok, E.M. Flanigen, US Patent 4,310,440 (1982).
- [7] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannen, E.M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1146.
- [8] E.M. Flanigen, B.M. Lok, R.L. Lyle, S.T. Wilson, Stud. Surf. Sci. Catal. 28 (1986) 103–112.
- [9] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannen, E.M. Flanigen, US Patent 4,440,871 (1984).
- [10] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannen, E.M. Flanigen, J. Am. Chem. Soc. 106 (1984) 6092–6093.
- [11] Z.H. Zhao, R.L. Zhao, Zeolites 13 (1993) 634–639.
- [12] Z.H. Zhao, R.L. Zhao, Shiyu Huagong 10 (1991) 676–681.