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One-step synthesis of isoamyl butyrate from isoamyl alcohol and *n*-butyraldehyde over TS-1 in air

Rui Zhao, Yong Ding, Zhiguang Peng, Xiaolai Wang, and Jisuan Suo *

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

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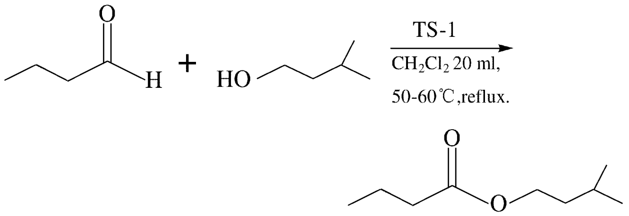
A one-step synthesis of isoamyl butyrate from isoamyl alcohol and *n*-butyraldehyde over TS-1 in air is reported. Higher aldehyde conversion and better selectivity are obtained. The mechanism of reaction over TS-1 is also investigated.

KEY WORDS: esterification; TS-1 molecular sieve; *n*-butyraldehyde; isoamyl alcohol.

1. Introduction

Organic esters represent an important class of intermediates widely used in fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals, solvents, perfumes, cosmetics and chiral auxiliaries [1]. In general, esterification of alcohols and carboxylic acids in the presence of sulfuric acid or some other Lewis acids as catalysts is one of the most important methods for the preparation of carboxylic esters [2]. However, unfortunately the use of traditional catalysts can cause problems, *e.g.*, separation and recovery of these catalysts. Furthermore, sulfuric acid is extremely corrosive and expensive durable reactors are required for its use, which limits its application in numerous industrial catalytic processes. Recently, efforts have been made to find efficient process technologies to develop clean catalytic methods. These include developing zeolite catalysts to synthesize organic esters. For example: Si-MCM-41-supported $InCl_3$ [3] catalyst for low-temperature esterification of *tert*-butanol by acetic anhydride; esterification reaction using resins as catalyst [4,5]; esterification of salicylic acid over HZSM-5 and Hβ [6]; and applications of zeolite membranes or ionic liquids to esterification reactions [7,8]. However, over zeolite catalysts there have still been some limitations in the past. A high reaction temperature is required [6], since at lower reaction temperatures poor conversion of acid may occur [3]. Also, more complex reaction equipment was required [7]. Finding an available method that requires lower reaction temperatures and gives higher conversion and selectivity for the synthesis of esters will be the major research field in zeolite sciences. On the other hand, although esterification of alcohols with carboxylic acids over zeolites has been reported, other reactions to synthesize esters have not been investigated yet, especially condensation reactions between alcohols and aldehydes over zeolites.

In this paper, a novel method of conversion of *n*-butyraldehyde to ester using TS-1 as catalyst is reported. Higher aldehyde conversion and better selectivity were obtained, and the reaction temperature was no higher than 60 °C. The mechanism of the reaction of aldehyde and alcohol to yield ester is also described.



2. Experimental

Samples of TS-1, TAPO-5, Ti-HMS and Ti-MCM-41 were synthesized according to previous reports with slight modifications [9–12]. The mole ratio of Si/Ti in all the above Ti-containing molecular sieves was about 50/1 and confirmed by XRD, SEM, UV–vis, XPS and N_2 adsorption/desorption analysis.

The reagents used for catalytic tests were isoamyl alcohol (TCI, >95%), *n*-butyraldehyde (TCI, >95%), 1,2-dichloroethylene (TCI, >95%) and tetradecane (Aldrich, >99%). The catalytic reaction of isoamyl alcohol with *n*-butyraldehyde was carried out in a four-opening flask under atmospheric pressure. Isoamyl alcohol and *n*-butyraldehyde were successively dissolved in CH_2Cl_2 and a steady flow of air at $10\,ml\,min^{-1}$ was passed over the reaction mixture through one flask opening, in order to eliminate the water formed during the reaction, which was adsorbed by means of a glass

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* To whom correspondence should be addressed.
E-mail: jssuo@ns.lzb.ac.cn

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Table 1
Results of synthesis of isoamayl butyrate from isoamyl alcohol and *n*-butyraldehyde over different Ti-containing catalysts

Entry	Catalyst	Mole ratio[a] (aldehyde : alcohol)	Time (h)	Temperature (°C)	Conversion[b] (%)	Selectivity[c] (%)
1	Blank	1.0 : 4.0	20	50–60	–	–
2	TS-1	1.0 : 4.0	2–3	50–60	100	100
3	Ti-MCM-41	1.0 : 4.0	12	50–60	100	100
4	Ti-HMS	1.0 : 4.0	14	50–60	100	98
5	TAPO-5	1.0 : 4.0	16	50–60	100	96
6	TiO_2	1.0 : 4.0	20	50–60	12	17
7	MCM-41	1.0 : 4.0	20	50–60	–	–
8	HMS	1.0 : 4.0	20	50–60	–	–
9	SiO_2	1.0 : 4.0	20	50–60	–	–
10[d]	TS-1	1.0 : 4.0	20	50–60	–	–

[a] Reaction mixture: CH_2Cl_2, 20 ml; catalyst, 0.2 g; aldehyde, 0.02 mol; alcohol, 0.08 mol.

[b] Conversion of *n*-butyric aldehyde.

[c] Selectivity to isoamyl butyrate product.

[d] Classical esterification of isoamyl alcohol with *n*-butyacid over TS-1; reaction mixture: CH_2Cl_2, 20 ml; catalyst, 0.2 g; *n*-butyacid, 0.02 mol; alcohol, 0.08 mol.

elbow-shaped tube packed with zeolite A. The reaction typically proceeded with stirring and fluxing at 50–60 °C and was controlled by a thermometer immersed in the reaction mixture. All of the catalysts mentioned here were previously dried at 383 K for 15 h. Tetradecane (20 wt% (w/w) in the reaction mixture) was used as an internal standard for all tests. The reaction mixture was sampled at time intervals ranging between 1 and 12 h, counted after the reaction stabilized at the working temperature. After reaction, the reactants and products were directly analyzed by GC–MS and GC. For the purpose of comparison, a classical esterification of isoamyl alcohol with *n*-butyacid over TS-1 in air was also carried out under the same reaction conditions.

3. Results and discussion

The results of the reaction of *n*-butyraldehyde and isoamyl alcohol over TS-1 and other Ti-containing catalysts are outlined in table 1. For the reaction of *n*-butyraldehyde and isoamyl alcohol, the catalytic activities over TS-1 were definitely higher than those over other Ti-containing catalysts. Furthermore, the experimental results also indicated that under the same conditions there was no obvious ester formation over MCM-41, HMS and SiO_2 catalysts. Also, there was evidence to suggest that when TS-1 was used as catalyst, no reaction products were detected for acid with alcohol, which proved that acid was not the active intermediate in the reaction of aldehyde and alcohol over TS-1.

We also conducted a number of experiments to check the effects on the conversions of aldehyde of different mole ratios of aldehyde and alcohol. From table 2 it can be seen that with the alcohol overdosed the conversion and the selectivity were both higher than before. The results obtained from table 2 also showed that the reaction between aldehyde and alcohol over TS-1 was a dynamics controlled reaction.

Because we are not very sure about the mechanism of the synthesis of ester from aldehyde and alcohol over TS-1 at present, we define a turnover rate of reaction over TS-1. Table 3 and figure 1 indicate the variation in the conversion with reaction time for different amounts of

Table 2
Comparison of synthesis of isoamyl butyrate from isoamyl alcohol and *n*-butyraldehyde over TS-1 with different mole ratios of aldehyde and alcohol

Entry	Catalyst (0.2 g)	Mole ratio of aldehyde and alcohol (mol : mol)	Time (h)	Temperature (°C)	Conversion[a] (%)	Selectivity[b] (%)
1	TS-1	0.02 : 0.02	10	50–60	28	47
2	TS-1	0.02 : 0.03	10	50–60	46	68
3	TS-1	0.02 : 0.04	10	50–60	58	87
4	TS-1	0.02 : 0.06	3	50–60	100	100
5	TS-1	0.02 : 0.08	2–3	50–60	100	100

[a] Conversion of *n*-butyric aldehyde.

[b] Selectivity to isoamyl butyrate product.

Table 3
Turnover rate of *n*-butyraldehyde over TS-1

Amount of TS-1 (g)	Turnover rate[a] (mol g^{-1} h^{-1})
0.05	0.05
0.10	0.83
0.15	1.50
0.20	4.00–5.00

[a] Turnover rate of aldehyde = amount of aldehyde (mol)/amount of catalyst TS-1 (g) × reaction time (h).

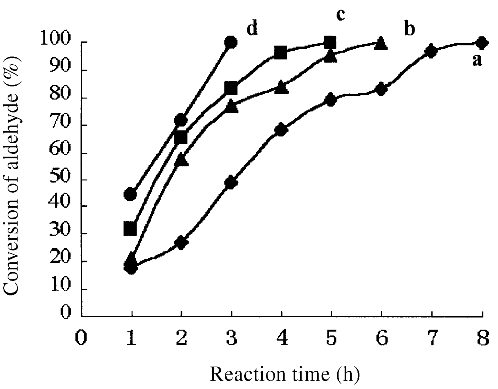

Figure 1. Variation of the conversion with reaction time for different amounts of catalyst: (a) 0.05 g, (b) 0.10 g, (c) 0.15 g, (d) 0.20 g (CH_2Cl_2, 20 ml; aldehyde, 0.02 mol; alcohol, 0.08 mol).

catalyst, which show that the more catalyst used, the shorter the reaction time required. The shortest reaction time was no longer than 3 h.

In order to determine whether molecular sieve TS-1 could be reused to catalyze the reaction, a sample of the TS-1 was recovered by filtration after the reaction and it was then reused in an identical reaction of *n*-butyraldehyde and isoamyl alcohol without regeneration.

The results listed in table 4 show that the unregenerated molecular sieve TS-1 essentially retained its catalytic activity during the period of its reuse. A small decrease in the conversion of aldehyde could be due to some loss of the catalyst during filtration and due to no addition of any fresh catalyst to keep the identical amount of catalyst used. Therefore, it could be concluded that molecular sieve TS-1 possesses good activity stability for the reaction studied.

Table 4
Investigation of reuse of molecular sieve TS-1 for the reaction[a]

Number of previous uses of molecular sieve TS-1	Conversion (%)	Selectivity (%)
0 (fresh)	100	100
1	98	100
2	>95	100

[a] Reaction mixture: CH_2Cl_2, 20 ml; catalyst, TS-1 0.2 g; aldehyde, 0.02 mol; alcohol, 0.08 mol.

Although the detailed reaction mechanism of the synthesis of ester from aldehyde and alcohol over TS-1 is not very clear at this stage, the preliminary experimental results show that TS-1 as a novel environmentally friendly catalyst is not only possible but also quite satisfactory. Further study is still ongoing.

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