

Highly selective esterification of *tert*-butanol by acetic acid anhydride over alumina-supported InCl_3 , GaCl_3 , FeCl_3 , ZnCl_2 , CuCl_2 , NiCl_2 , CoCl_2 and MnCl_2 catalysts

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Abstract

Esterification of *tert*-butanol by acetic anhydride to *tert*-butyl acetate over $\text{InCl}_3/\text{Al}_2\text{O}_3$, $\text{GaCl}_3/\text{Al}_2\text{O}_3$, $\text{FeCl}_3/\text{Al}_2\text{O}_3$, $\text{MnCl}_2/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Al}_2\text{O}_3$, $\text{CuCl}_2/\text{Al}_2\text{O}_3$ and $\text{ZnCl}_2/\text{Al}_2\text{O}_3$ (metal chloride loading = 1.2 mmol g^{-1}) catalysts have been investigated. The yield of *tert*-butyl acetate obtained was over 99.5%; when the reaction conditions used were as follows: the molar ratio of *tert*-butanol/acetic acid anhydride = 1.1, the catalysts/(*tert*-butanol + acetic anhydride) wt. ratio = 0.026, reaction temperature = 30°C , and reaction time = 2 h. The esterification activity of the alumina supported metal chloride catalysts is in the following order: $\text{InCl}_3 > \text{GaCl}_3 > \text{FeCl}_3 > \text{ZnCl}_2 > \text{CuCl}_2 > \text{NiCl}_2 > \text{CoCl}_2 > \text{MnCl}_2 > \text{Al}_2\text{O}_3$. These catalysts can also be reused in the esterification of *tert*-butanol for several times. The effect of some factors such as reaction temperature, the amount of used catalyst and reaction time on the esterification has been investigated. $\text{InCl}_3/\text{Al}_2\text{O}_3$ is highly active, selective and reusable catalyst for the esterification.

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1. Introduction

Esterification of alcohols by carboxylic acids using homogeneous acid catalysts is well known [1]. For example, fluoric or sulfuric acids are used in alkylation, esterification and hydrolysis reactions [2–4]. However, these acid catalysts are toxic and corrosive and, in addition, are hard to remove from the reaction medium. So, the challenge was to replace them by solid catalysts such as zeolites, alumina or resins, which are easier to separate from the products and less toxic.

On the other hand, the preparation of *tert*-butyl ester by the esterification of *tert*-butanol using on acid catalysis very difficult because of the very high reactivity of *tert*-butanol. In the presence of acid catalyst, *tert*-butanol undergoes dehydration to *iso*-butylene, even at the room temperature. Earlier methods used for the esterification of *tert*-butanol are either

highly cumbersome or involve use of highly toxic reagents [5–8]. Recently, Choudhary et al. [9,10], used clay (Kaolin, mont-K10 and mont-KSF) supported InCl_3 , GaCl_3 , FeCl_3 and ZnCl_2 and Si-MCM-41 supported InCl_3 , GaCl_3 , FeCl_3 and ZnCl_2 catalysts at mild conditions for the esterification of *tert*-butanol by acetic anhydride. Nagasawa et al. [11,12] used activated basic alumina at mild conditions (at room temperature under argon) for the esterification of *tert*-butanol by acid chlorides or acid bromides. Although they got a good yield for *tert*-butyl ester, the amount of catalyst relative to the reactants used by them was very large. It is not of practical interest to use such a large amount of catalyst, and more over the removal of high molecular weight adsorbed products from the catalyst is quite difficult and also expensive too. Other important drawback of their butyl ester synthesis method is the use of an acid halide as esterification agent, because of which a highly toxic gaseous hydrogen halide by-product is formed, in stoichiometric quantities. Hence, there is a need to develop an environmentally benign method

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for the esterification of *tert*-butanol using more active, selective and reusable solid catalyst, having almost no activity for the dehydration of *tert*-butanol. We report here our preliminary studies indicating the use of alumina-supported InCl_3 , GaCl_3 , FeCl_3 , MnCl_2 , CoCl_2 , NiCl_2 , CuCl_2 and ZnCl_2 , as the highly selective and reusable catalysts for the esterification of *tert*-butanol by an acetic acid anhydride, producing acetic acid as a harmless by-product.

2. Experimental

2.1. Materials and physical measurements

All solvents used for synthesis and esterification reaction were purchased from Merck (pro analysis) and were dried with molecular sieves (Linde 4 Å). *tert*-Butanol and acetic anhydride were purified by standard procedures, and distilled under nitrogen stored over molecular sieves (4 Å) before use. Acidic alumina was purchased from Merck (Art. No. 1078, aluminum oxide 90 active acidic, 0.063–0.200 mm). It was activated at 500 °C for 8 h before use. InCl_3 , GaCl_3 , FeCl_3 , ZnCl_2 , CuCl_2 , NiCl_2 , CoCl_2 and MnCl_2 were obtained from Merck Chemical Co. *tert*-Butyl acetate as identified by comparisons of its retention time with that of the pure compound (obtained from Merck). The products were analyzed by GC-mass, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnigan MAT INCOF 50, 70 ev. The indium, gallium, manganese, iron, cobalt, nickel, copper and zinc contents of the samples were measured by atomic absorption spectrophotometer (AAS—Perkin-Elmer 4100–1319) using a flame approach, after acid (HF) dissolution of a known amount of the alumina material in a Parr digest pump (loading of metal chloride = 1.2 mmol g⁻¹).

2.2. Preparation of heterogeneous catalysts

Alumina supported metal chloride ($\text{InCl}_3/\text{Al}_2\text{O}_3$, $\text{GaCl}_3/\text{Al}_2\text{O}_3$, $\text{FeCl}_3/\text{Al}_2\text{O}_3$, $\text{MnCl}_2/\text{Al}_2\text{O}_3$, $\text{CoCl}_2/\text{Al}_2\text{O}_3$, $\text{NiCl}_2/\text{Al}_2\text{O}_3$, $\text{CuCl}_2/\text{Al}_2\text{O}_3$, and $\text{ZnCl}_2/\text{Al}_2\text{O}_3$) were prepared by impregnating acidic alumina with anhydrous metal chloride (purity 99.99% Aldrich) from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 120 °C for 10 h. All the catalysts were stored in desiccators.

2.3. Esterification of *tert*-butanol, general procedure

The liquid phase esterification reactions over the supported metal chloride catalysts were carried out in a magnetically stirred glass reactor (50 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture at the following reaction conditions (reaction mixture = *tert*-

butanol + acetic anhydride + catalyst; volume of reaction mixture = 10 cm³; *tert*-butanol/acetic anhydride molar ratio = 1.1; reaction time = 2 h, catalyst/(*tert*-butanol + acetic anhydride) wt. ratio 0.026). The reaction was started by injecting acetic anhydride in the reaction mixture, containing catalyst at the reaction temperature (at 30 °C) with or without solvent. The outlet of the reflux condenser was connected to a constant pressure gas collector [13]. The isobutylene formed in the reaction was measured quantitatively by collecting it in the gas collector at atmospheric pressure. The products of the esterification were analyzed by a gas chromatograph using *n*-hexane as an internal standard.

3. Results and discussion

The heterogenisation of homogeneous catalysts is a field of continuing interest [13–20]. Although some of homogeneous transition metals exhibit remarkable catalytic properties (activities and selectivity), they are unsuitable to separate intact materials from the reaction medium making their reuse difficult and contaminating the reaction products. Thus, the heterogenisation is always a toxicological and environmental challenge; moreover, it has an economical significance unless the activities of the homogeneous catalysts are exceptionally high. We have done the heterogenisation by supporting the catalysts on acidic alumina. The adsorbing tendency of the acidic alumina might arise from the presence of oxygen groups on the surface which are able to coordinate to the metal ion. This hypothesis was by the observation that a manganese complex with three bidentate ligands can not be adsorbed on the acidic alumina surface [15].

Metals contents of the alumina supported catalysts were estimated by dissolving the known amount of the catalyst in concentrated HCl and from these solution, transition metal contents were estimated by atomic absorption spectrometer. The loading of metal chlorides were 1.2 mmol g⁻¹.

Results of Table 1 show the catalytic activity of InCl_3 as homogeneous catalysts. Comparing between neat and alumina supported complexes as catalyst evidence that alumina-supported catalysts gave higher conversion of substrate than their corresponding neat complexes. The higher activity of supported complexes is because of site isolation of the complexes. Among the supported metal chloride catalysts, the $\text{InCl}_3/\text{Al}_2\text{O}_3$ showed both high conversion and high selectivity in the esterification (Table 1). All the alumina supported metal chloride catalysts show high selectivity (≥ 99.1) but they differ significantly in their esterification activity. The $\text{InCl}_3/\text{Al}_2\text{O}_3$ shows the best performance, giving 99.5% selectivity for *tert*-butyl acetate at 100% and 94.6% conversion of acetic anhydride and *tert*-butanol, respectively. The esterification activity of the alumina supported metal chloride catalysts is in the following order: $\text{InCl}_3/\text{Al}_2\text{O}_3 > \text{GaCl}_3/\text{Al}_2\text{O}_3 > \text{FeCl}_3/\text{Al}_2\text{O}_3 > \text{ZnCl}_2/\text{Al}_2\text{O}_3 > \text{CuCl}_2/\text{Al}_2\text{O}_3 > \text{NiCl}_2/\text{Al}_2\text{O}_3 > \text{CoCl}_2/\text{Al}_2\text{O}_3 > \text{MnCl}_2/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3$.

Table 1

Results of the esterification of *tert*-butanol by acetic anhydride over different metal chloride supported on alumina catalysts at 30 °C

Catalyst (g)	Conversion (%)		Selectivity (%)	
	<i>tert</i> -Butanol	Acetic anhydride	<i>tert</i> -Butyl acetate	Isobutylene
InCl ₃ /Al ₂ O ₃	94.6	100	99.5	0.5
InCl ₃ /Al ₂ O ₃ ^a	94.1	97.4	99.1	0.9
InCl ₃ /Al ₂ O ₃ ^b	93.7	95.3	98.4	1.6
InCl ₃ /Al ₂ O ₃ ^c	93.1	94.2	97.6	2.4
GaCl ₃ /Al ₂ O ₃	83.7	96.5	99.4	0.6
FeCl ₃ /Al ₂ O ₃	79.7	84.9	99.3	0.7
ZnCl ₂ /Al ₂ O ₃	75.3	83.7	99.1	0.9
CuCl ₂ /Al ₂ O ₃	47.5	58.7	99.6	0.4
NiCl ₂ /Al ₂ O ₃	40.6	56.5	99.7	0.3
CoCl ₂ /Al ₂ O ₃	35.5	55.3	99.7	0.3
MnCl ₂ /Al ₂ O ₃	30.2	54.2	99.8	0.2
InCl ₃ ^d	89.8	98.6	99.1	0.9
Al ₂ O ₃	14.5	16.8	100	0.0

(Reaction mixture = *tert*-butanol + acetic anhydride (acetic anhydride) + catalyst; volume of reaction mixture = 10 cm³, *tert*-butanol/acetic anhydride molar ratio = 1.1; reaction time = 2 h; catalyst/(*tert*-butanol + acetic anhydride) wt. ratio = 0.026.

^a First reuse of the catalyst.

^b Third reuse of the catalyst.

^c Seven reuse of the catalyst.

^d Homogeneous catalyst [13].

At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by AAS showed little reduction in the amount of metal ions, they showed a slightly lower catalytic activity (0.5%). Results showing the reuse of the InCl₃/Al₂O₃ catalyst.

The reaction data using different amounts of InCl₃/Al₂O₃ catalyst revealed that selectivity to *tert*-butyl acetate was higher at a lower concentration (Table 2). At the higher concentration of the InCl₃/Al₂O₃, the conversion of *tert*-butanol increased to an optimum value but formation of isobutylene product also increased simultaneously. Hence, an optimum of 0.4 g of catalyst in the reaction mixture was ideal for achieving better conversion (94.6%) and selectivity for *tert*-butyl acetate (99.5%).

Table 2

Esterification of *tert*-butanol with acetic anhydride at different InCl₃/Al₂O₃ concentration (conditions: reaction time = 2 h; volume of reaction mixture = 10 cm³; temperature = 30 °C; *tert*-butanol/acetic anhydride mole ratio = 1.1)

Catalyst (g)	Conversion (%)		Selectivity (%)	
	<i>tert</i> -Butanol	Acetic anhydride	<i>tert</i> -Butyl acetate	Isobutylene
0.1	69.7	71.6	100	–
0.2	81.6	89.5	100	–
0.3	90.6	94.3	100	–
0.4	94.6	100	99.5	0.5
0.5	98.5	100	94.3	5.7
0.6	100	100	90.6	9.4
0.9	100	100	83.2	16.8

Table 3

Esterification of *tert*-butanol with acetic anhydride at different temperatures over InCl₃/Al₂O₃ catalyst (conditions: reaction time = 2 h; volume of reaction mixture = 10 cm³; *tert*-butanol/acetic anhydride mole ratio = 1.1; catalyst/(*tert*-butanol + acetic anhydride) wt. ratio = 0.026)

Temperature (°C)	Conversion (%)		Selectivity (%)	
	<i>tert</i> -Butanol	Acetic anhydride	<i>tert</i> -Butyl acetate	Isobutylene
25	86.7	93.2	99.9	0.1
30	94.6	100	99.5	0.5
40	96.5	100	62.8	37.2
50	98.5	100	29.6	70.4
60	99.5	100	16.8	83.2
80	100	100	4.0	96.0

The results of the temperature studies are shown in Table 3. Reaction was carried out using InCl₃/Al₂O₃ in the temperature range of 25–80 °C. It was found that conversion were low at 25 °C. On increasing the temperature from 50 to 80 °C, the formation of *tert*-butyl acetate decreased as expected. High reaction temperatures favor the formation of isobutene.

A comparison of the conversion of each catalyst for the esterification and dehydration reactions at 30 °C (Tables 1 and 2) shows that all the alumina supported metal chloride catalysts have lower activity for the dehydration of *tert*-butanol to isobutylene. The dehydration conversion, however, increased exponentially upon with increasing the temperature (Table 3).

In the esterification of *tert*-butanol by acetic anhydride, acetic acid in stoichiometric amounts is formed as a by-product. However, it has a commercial value and moreover it can be converted back to acetic anhydride and recycled in the process. Thus, this process is free from any serious problem of handling and/or treating highly corrosive and toxic by-product, such as hydrogen halide produced in the process based on the use of an acid halide as an esterification agent [3,4]. Also the amount of catalyst used relative to the reactant is much smaller.

4. Conclusions

The esterification of *tert*-butanol with acetic anhydride over InCl₃, GaCl₃, MnCl₂, FeCl₃, CoCl₂, NiCl₂, CuCl₂ and ZnCl₂ supported on alumina catalysts has been investigated. Homogeneous indium chloride, gave lower conversions than to the supported catalyst. The following points may be noted:

1. The major product of esterification of *tert*-butanol with acetic anhydride in this study is *tert*-butyl acetate.
2. The catalysts did not undergo any color change during the reaction and could be easily separated and reused many times. In contrast, the homogeneous indium chloride active in the first cycle were completely destroyed during the first run and changed color.

3. The alumina alone in the absence of metals was not catalytically active.
4. The activity in *tert*-butanol esterification with acetic anhydride decreases in the series: $\text{InCl}_3/\text{Al}_2\text{O}_3 > \text{GaCl}_3/\text{Al}_2\text{O}_3 > \text{FeCl}_3/\text{Al}_2\text{O}_3 > \text{ZnCl}_2/\text{Al}_2\text{O}_3 > \text{CuCl}_2/\text{Al}_2\text{O}_3 > \text{NiCl}_2/\text{Al}_2\text{O}_3 > \text{CoCl}_2/\text{Al}_2\text{O}_3 > \text{MnCl}_2/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3$.

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