

Short communication

Esterification of acetic acid with *n*-butanol over manganese nodule leached residue

S.S. Dash, K.M. Parida*

Colloids and Materials Chemistry Cell, Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India

Received 12 September 2006; received in revised form 13 October 2006; accepted 16 October 2006

Available online 20 October 2006

Abstract

Manganese nodule leached residue (MNLr) was obtained as waste material after selective extraction of Cu, Co and Ni from Indian Ocean manganese nodule. MNLr was washed with water to remove sulphate and other impurities present in its surface. The catalytic activity of the waste material was tested for liquid phase esterification of acetic acid with *n*-butanol. The effect of reaction time, catalyst amount, temperature and mole ratio of reactants on esterification was studied to optimize the reaction conditions. Water-washed manganese nodule leached residue (WMNLr) calcined at 400 °C shows highest catalytic activity with 76.6% conversion having 100% selectivity towards *n*-butyl acetate. Esterification reaction follows first order kinetics with respect to acid and 0th order with respect to *n*-butanol. Conversion of C₁–C₄ aliphatic acids with *n*-butanol follows the following order: formic > acetic > propanoic > *n*-butyric.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Esterification; Acetic acid; *n*-Butanol; *n*-Butyl acetate; Rate constant and calcination

1. Introduction

The esterification of carboxylic acids is one of the fundamental reactions in organic synthesis [1]. Liquid phase esterification is an important method for producing various esters. Esterification of acetic acid with *n*-butyl alcohol is commercially important as the product *n*-butyl acetate is widely used in the manufacture of lacquer, artificial perfumes, leather, flavoring extract, photographic films, plastics, pharmaceuticals and safety glasses [2]. It is also used as dehydrating agent. Conventional method of esterification reaction involves the use of mineral acids such as H₂SO₄, HCl, HF, H₃PO₄ and ClSO₂OH, etc. These acids are corrosive and the excess acid has to be neutralized after the reaction leaving considerable amount of salts to be disposed off into the environment. So the replacement of these conventional hazardous and polluting corrosive liquid catalysts by solid acid catalysts is the demand of the day to create a cleaner technology. Reduction of environmentally unacceptable waste to minimize environmental pollution is the crucial factor for developing environmentally friendly catalyst.

Of late a lot of effort was given to use solid wastes as catalyst that are generated from industrial process to minimize their disposal problem, pollution control and a low cost substitute for conventional catalyst. Manganese nodule leached residue is one of such material, which is obtained as a waste after extraction of Cu, Co and Ni from Indian Ocean manganese nodule through NH₃–SO₂ leaching followed by solvent extraction and electrowinning technique. This material is of interest due to its remarkable surface and texture properties to be used as a catalyst [3].

Several heterogeneous catalysts are reported in the literature for esterification including ion exchange resin [4], HZSM-5 [5], zeolites-Y [6], niobic acid [7], sulphated oxide [8], supported heteropoly acids [9] and acidic ionic liquids [10] but no work has been reported using manganese nodule leached residue as a catalyst. The present study aims to evaluate the catalytic activity of this solid waste and its calcined counterparts towards esterification of acetic acid with *n*-butanol. Further various reaction parameters such as effect of reaction time, temperature, molar ratio of the reactants and the amount of the catalyst on *n*-butyl acetate formation was evaluated to optimize the reaction conditions. The product, selectivity and rate constants were also evaluated.

* Corresponding author. Fax: +91 674 2581637.

E-mail address: kmparida@yahoo.com (K.M. Parida).

2. Experimental

2.1. Preparation of the catalyst

Manganese nodule leached residues (MNL) for the present study was collected as a residue obtained from the pilot plant studies of $\text{NH}_3\text{--SO}_2$ leaching of manganese nodule of central Indian Ocean basin. They were crushed to fine powders and sieved to different sieve fractions. The size fractions (-75 to $+50\ \mu\text{m}$) were collected for further studies. Water-washed leached residues were prepared by taking solid to liquid ratio of 1:10, stirred on a magnetic stirrer using a magnetic paddle at room temperature for 4 h, subsequently filtered and washed thoroughly in double distilled water. About 10 g of sample calcined at desired temperatures from 110 to 700 °C for 3 h in a muffle furnace with a suitable controller to maintain offset temperature $\pm 5\ ^\circ\text{C}$. Then, it was allowed to cool to ca. 50 °C and stored in a desiccator over fused CaCl_2 . The water-washed manganese nodule leached residue calcined at various temperatures was labeled as WMNLR- T , where T denotes the corresponding calcination temperature in °C.

2.2. Characterization

X-ray diffraction patterns of heat-treated samples were recorded on a Philips semiautomatic X-ray diffractometer with auto-divergent slit and graphite monochromator using $\text{Cu K}\alpha$ radiation operated at 40 kV and 20 mA.

TG–DTA of the samples (about 15 mg) was carried out using a Shimadzu DT-40 automatic thermal analyser in the temperature range 30–1000 °C at a heating rate of 10 °C min^{-1} .

The FT-IR spectra (4000–400 cm^{-1}) of the samples in KBr phase were recorded using a JASCO Model 5300 spectrometer.

The surface area of all samples was determined at liquid nitrogen temperature (77 K) by Quantasorb (Quantachrome, USA).

Brønsted acid sites was determined spectrophotometrically on the basis of irreversible adsorption of organic bases 2,6-dimethyl pyridine ($\text{p}K_b = 6.9$) [11].

2.3. Catalytic reaction

The esterification reaction was carried out taking 0.025 g of the catalyst (dried at 110 °C for 6 h in an oven), 2 mmol of acetic acid (Merck, 99.8%), 32 mmol of *n*-butanol (Merck, 98%) and 0.20 mmol of *n*-heptane (Merck, 99%) as an internal standard in a 100 ml round-bottomed flask equipped with a reflux condenser. The contents were then refluxed gently at 98 °C for 4 h. Then the reaction mixture was filtered and the products were analysed by means of gas chromatograph (GC-17A Shimadzu, Japan).

3. Result and discussion

3.1. Characterization

Powder XRD pattern shows the amorphous nature of the leached residue with some diffused broad peaks at 2.41, 3.32 and 3.18 Å indicating the presence of $\delta\text{-MnO}_2$, quartz ($\alpha\text{-SiO}_2$)

Table 1

Chemical analysis of water-washed manganese nodule leached residue (WMNLR)

Major element	%
Mn	28.8
Fe	2.55
Al_2O_3	19.8
SiO_2	0.35
SO_4^{2-}	5.58
Moisture	15.01
LOI	9.48
Minor element	ppm
Cu	0.157
Co	0.31
Ni	0.171
Zn	0.066
Cd	0.0142

and plagioclase/zeolite mineral, respectively. The peak at 110 °C in the temperature range 40–120 °C of the DTA curve corresponds to a weight loss of $\sim 12\%$, which could be due to the loss of physisorbed water. FTIR peaks show presence of Si–O–Al of silicate minerals, quartz and Mn–O vibration. The sulfate present in MNL removed by water washing was evident from FTIR spectra. Details of physicochemical characterization were given elsewhere [3]. Table 1 represents the percentage of various elements of water-washed manganese nodule leached residue. WMNLR contains Mn and Fe as major component with other trace elements. Table 2 shows the BET surface area, surface oxygen, surface hydroxyl groups and Brønsted acid sites of calcined WMNLR samples. Surface area and Brønsted acid sites increases with increase in calcination temperature up to 400 °C and decreases thereafter. Surface oxygen and surface hydroxyl group also follow a similar trend as that of surface area and Brønsted acid sites.

3.2. Application of WMNLR catalyst for esterification reaction

The esterification of acetic acid with *n*-butanol is an electrophilic substitution reaction. The reaction is relatively slow and need activation either by higher temperature or by a catalyst to achieve higher conversion to a reasonable one. Liquid phase reaction of acetic acid and *n*-butanol catalyzed by solid acids

Table 2

Surface area and Brønsted acid sites of calcined WMNLR samples

Catalyst	Surface area (m^2/g)	Brønsted acid sites ($\mu\text{mol}/\text{g}$)	Surface oxygen (mmol/g)	Surface hydroxyl groups (mmol/g)
WMNLR-110	108.2	60.9	5.33	0.189
WMNLR-200	119.0	64.7	7.96	0.238
WMNLR-300	135.9	72.8	9.45	0.285
WMNLR-400	175.0	89.5	10.92	0.322
WMNLR-500	149.5	67.7	6.60	0.233
WMNLR-600	69.4	53.2	5.02	0.183
WMNLR-700	49.8	45.6	1.53	0.100

Table 3
Conversion, selectivity and rate constants for esterification of acetic acid over calcined WMNLR catalyst

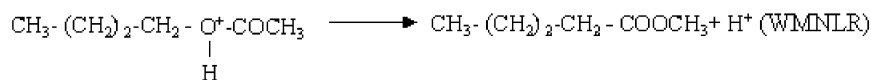
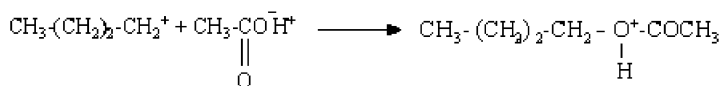
Catalyst	Conversion (%)	Selectivity (%)	Rate constant ($\times 10^{-5} \text{ s}^{-1}$)
WMNLR-110	42.4	96	3.83
WMNLR-200	55.0	98	5.54
WMNLR-300	62.2	99	6.75
WMNLR-400	76.6	100	10.12
WMNLR-500	61.3	100	6.59
WMNLR-600	47.8	98	4.5
WMNLR-700	41.5	97	3.72

Time = 4 h, reaction temperature = 98 °C, catalyst amount = 0.025 g, acetic acid:*n*-butanol = 1:16.

proceeds according to a rate equation, which is first order with respect to acetic acids and zero order with respect to *n*-butanol [12,13].

Electrophilic substitution reaction like esterification is catalyzed by strong Brønsted acid sites. It was also reported that surface hydroxyl groups are responsible for acidic nature of the catalyst [14]. Thus, the surface oxygen and surface hydroxyl group [15] plays a vital role for the catalytic activity of WMNLR. The reaction following Eley–Rideal mechanism takes place between *n*-butanol and proton chemisorbed on the active sites (Brønsted acid sites) of the catalyst surface, resulting a stable carbocation. Then, the carbocation attacks the nucleophilic center of acetic acid to form an unstable intermediate. Removal of a proton from the intermediate gives the final product, i.e. *n*-butyl acetate along with the regeneration of the catalyst. The acid catalyst facilitates the formation of the carbocation, and helps to remove OH⁻ from the alcohol [16].

The mechanism involved in the reaction is as follows:



The data on the conversion, selectivity and rate constant for esterification of acetic acid over WMNLR calcined at different temperature was given in Table 3. The analysis of reaction products showed that *n*-butyl acetate was obtained as major product with almost 100% selectivity. The catalytic activity increases with the increase in calcination temperature up to 400 °C and thereafter decreases with further rise in calcination temperature. WMNLR-400 shows highest catalytic activity with 76.6% conversion and 100% selectivity towards *n*-butyl acetate. The catalytic activity decrease beyond 400 °C calcination of WMNLR may be due to loss of Brønsted acid sites, which are responsible for esterification reaction.

3.2.1. Influence of reaction time

The influence of reaction time on the acetic acid conversion was given in Fig. 1 using WMNLR-400 as catalyst (0.025 g)

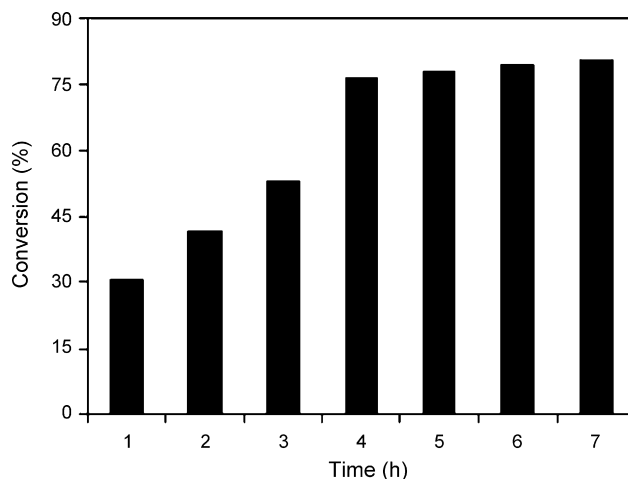


Fig. 1.

under other identical reaction conditions. A gradual rise in the conversion was seen with increase in duration of the reaction period. As seen from Fig. 1, in 4 h of reaction time, 76.6% of conversion is obtained, where as at the end of 7 h only 80% of the reaction is complete. The selectivity towards *n*-butyl acetate on the other hand remains same, i.e. 100% at 7 h. This suggests that 4 h is sufficient to achieve optimum conversion and selectivity.

3.2.2. Influence of catalyst amount

The amount of catalyst (WMNLR-400) was varied from 0.01 to 0.03 g while keeping the molar ratio of acid:alcohol at 1:16 and reaction temperature at 98 °C. The reaction was carried out for 4 h and the products were analyzed. The results are represented

in Fig. 2. With the increase in catalyst amount from 0.01 to 0.03 g, the conversion of acetic acid increases from 32.5% to 80.2%. This is due to the availability of large surface area and acid sites, which favors the dispersion of more active species. Therefore, the accessibility of the large number of molecules of the reactants to the catalyst surface is favored. The selectivity towards butyl acetate is nearly 100% in all cases.

3.2.3. Influence of reaction temperature

Fig. 3 illustrates the effect of reaction temperature on the esterification of acetic acid with *n*-butanol. The reaction was carried out in the temperature region 80–110 °C taking WMNLR-400 as catalyst without altering other reaction parameters. The conversion of acetic acid increases (40–81%) with increase in reaction temperature having nearly 100% selectivity. This suggests that increase in reaction temperature favors the

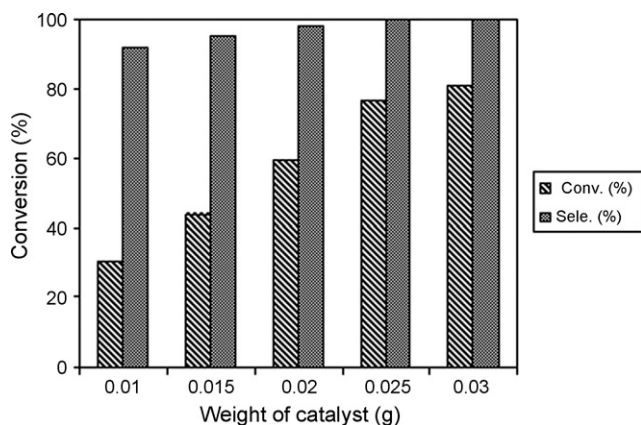


Fig. 2.

formation of carbonium ion from *n*-butyl alcohol, which reacts with acetic acid to produce *n*-butyl acetate.

3.2.4. Influence of molar ratio of reactants

Mole ratios of acetic acid to *n*-butanol were varied from 1:10 to 1:18 and the result is shown in Fig. 4. In all cases, *n*-butyl acetate was observed as the main product. The conversion increased from 48.7% to 76.6% with a change in mole ratio of acetic acid to *n*-butanol from 1:10 to 1:16. With further increase in mole ratio of acetic acid to *n*-butanol, a decrease in conversion was observed. Decrease in conversion in higher molar ratio of acid to alcohol (1:18) may be due to the saturation of the catalytic surface with the alcohol or prevention of nucleophilic attack by shielding protonated alcohol by its own excess. This confirms Eley–Rideal mechanism with chemisorption of alcohol on the Brønsted acid sites of the catalyst. This result is very similar to Kirumakki et al. [17] who used zeolite as catalyst over esterification of benzyl alcohol with acetic acid and Jermy and Pandurangan, who used Al-MCM-41 catalyst over esterification of acetic acid with *n*-butyl alcohol, although in both the cases the experiments were performed in a lower molar ratio of acid and alcohol compared to the present work.

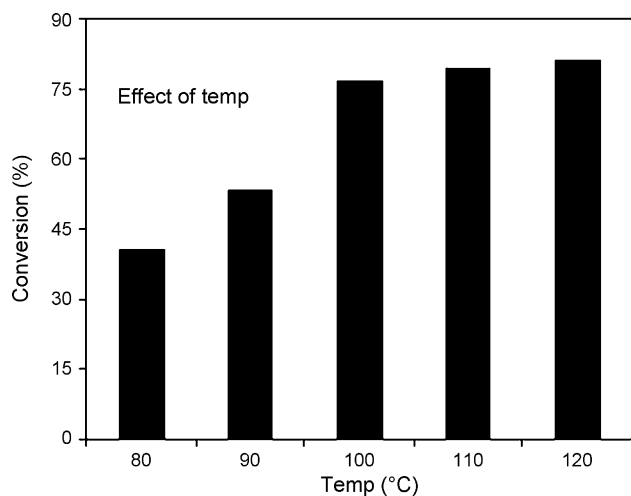


Fig. 3.

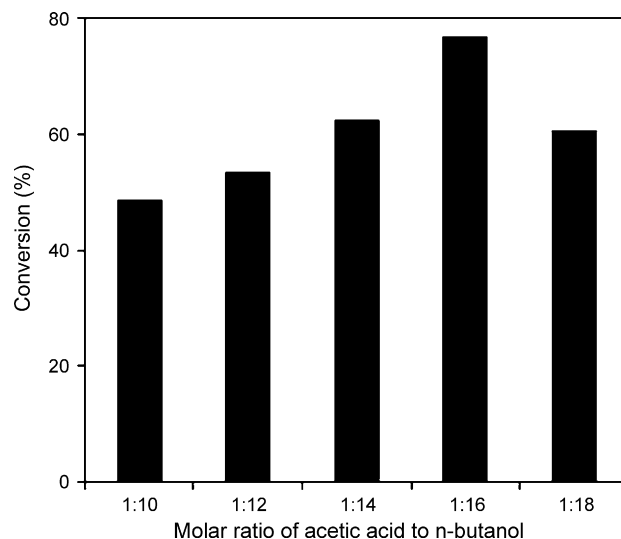


Fig. 4.

3.2.5. Kinetics of esterification of acetic acid with *n*-butanol

Fig. 5 shows the first order nature of the esterification reaction, which gives a straight-line plot of $-\ln(1 - \text{conversion})$ versus reaction time for the reactions carried out at 98 °C. Similar type of result was shown by Namba et al. [13] the reaction between acetic acid and *n*-butanol proceeds according to a rate equation, which is first order with respect to acetic acid and 0th order with respect to *n*-butanol.

Formic acid, propanoic acid and *n*-butyric acid were subjected to the esterification reaction with *n*-butanol under identical condition using WMNLR-400 as catalyst to test the generality of this method and the results are summarized in Table 4. The percentage conversion of acids can be explained on the basis of the strength and size of the reacting acids. Strength of these aliphatic acids follows the following order: formic > acetic > propanoic > *n*-butyric due to the +I effect of the alkyl group of the acids. Also the removal of proton decreases with increase in length of carbon chain. Hence, conversion of these acids follows the same order as that of acid strength of these acids.

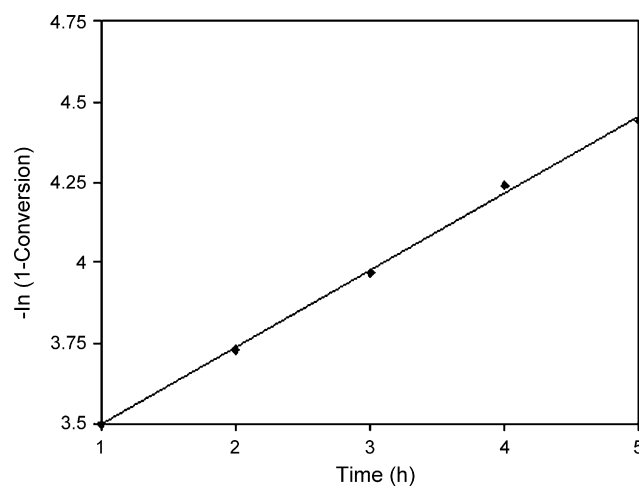


Fig. 5.

Table 4
Conversion, selectivity and rate constants for esterification of acids with *n*-butanol over WMNLR-400 catalyst

Acids	Conversion (%)	Selectivity (%)	Rate constant ($\times 10^{-5} \text{ s}^{-1}$)
Formic	81.1	100	11.56
Acetic	76.6	100	10.12
Propanoic	73.0	100	9.1
<i>n</i> -Butyric	68.5	98	8.02

Time = 4 h; reaction temperature = 98 °C; catalyst amount = 0.025 g; acid:*n*-butanol = 1:16.

Table 5
Conversion of acetic acid with recovered catalyst

Cycle	Conversion (%)
1	76.6
2	75.4
3	72.0

Time = 4 h; catalyst = 0.025 g; reaction temperature = 98 °C; acetic acid:*n*-butanol = 1:16.

As the bulkiness of the acids increases, the steric hindrance also increases which results decrease in acid conversion.

3.3. Recyclability of the catalyst

The catalyst WMNLR-400 was used for recycling study. In order to regenerate the catalyst after 4 h reaction, the catalyst was separated by filtration, washed with conductivity water several times, dried at 110 °C and used in the esterification reaction with a fresh reaction mixture. In the regenerated sample after two cycles, the yield decreases by 4.6%. The results obtained are shown in Table 5.

4. Conclusions

From the studies on esterification of acetic acid with *n*-butanol over WMNLR calcined at various temperatures the following conclusions were drawn.

1. *n*-Butyl acetate was obtained as the major product which is facilitated by Brønsted acid sites.
2. Less amount of catalyst (0.025 g) and low reaction period (4 h) is required for converting a major amount of reactants to product with high selectivity.
3. WMNLR calcined at 400 °C showed highest catalytic activity with 76.6% conversion of acetic acid having 100% selectivity towards *n*-butyl acetate.
4. The reaction is proposed to occur mainly within the pores of the catalyst.

Acknowledgment

The authors are thankful to Prof. B.K. Mishra, Director, RRL for his interest, encouragement and kind permission to publish this work. One of the authors S.S. Dash is obliged to CSIR for a senior research fellowship.

References

- [1] R.C. Larock, Comprehensive Organic Transformations, VCH Publishers, New York, 1989 (Chapter 9).
- [2] B.R. Jermly, A. Pandurangan, J. Mol. Catal. A: Chem. 237 (2005) 146.
- [3] K.M. Parida, S.S. Dash, S. Mallick, J. Colloid Interf. Sci. 290 (2005) 431.
- [4] J. Gimenez, J. Costa, S. Cervera, Ind. Eng. Chem. 26 (1987) 198.
- [5] H.B. Zhang, B.Z. Zhang, H.X. Li, J. Nat. Gas Chem. (1992) 49.
- [6] A. Corma, H. Garcia, S. Iborra, J. Primo, J. Catal. 120 (1989) 78.
- [7] Z.H. Chen, T. Lizuka, K. Tanabe, Chem. Lett. (1984) 1085.
- [8] M. Hino, K. Arata, Chem. Lett. (1981) 1671.
- [9] J.M. Verhoef, J.P. Kooyman, A.J. Peters, H. van Bekkum, Micropor. Mesopor. Mater. 27 (1999) 365.
- [10] J. Gui, X. Cong, D. Liu, X. Zhang, H. Zhide, S. Zhaolin, Catal. Commun. 5 (2004) 473.
- [11] I.V. Kozhevnikov, Russ. Catal. Rev. Sci. Eng. 37 (1995) 311.
- [12] S.K. Samantray, K.M. Parida, Appl. Catal. A 211 (2001) 175.
- [13] S. Namba, Y. Wakashima, T. Shimizu, H. Masumoto, T. Yashim, Catalysis by Acids and Bases, Elsevier, Amsterdam, 1989.
- [14] Y. Wang, W. Li, React. Kinet. Catal. Lett. 69 (2000) 169.
- [15] H. Knzinger, H. Buhl, K. Kochlotl, J. Catal. 24 (1972) 57.
- [16] A.K. Chakraborty, A. Basak, V. Grover, J. Org. Chem. 64 (1999) 8014.
- [17] S.R. Kirumakki, N. Nagraraju, S. Narayanan, Appl. Catal. A 273 (2004) 1.