Preparation, characterization and catalytic activity of MMT-clay exchanged sulphonic acid functionalized ionic liquid for transesterification of β-ketoesters

Rajni Ratti [a], Sukhbir Kaur [a], Michel Vaultier [b,1], Vasundhara Singh [a,*]

[a] Department of Applied Sciences (Chemistry), PEC University of Technology, Chandigarh, India
[b] UMR CNRS 6510, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

ARTICLE INFO

ABSTRACT

A novel solid acid catalyst **2** was prepared by ion exchange of sulphonic acid functionalized ionic liquid into clay interlayers as a new organic–inorganic hybrid catalytic system. The ionic tag of the imidazolium supported sulphonic acid **1** assists in the pillaring process and enhances the organophilicity of catalyst **2** in the interlayers of clay. The catalytic activity of catalyst **2** as a recyclable solid Bronsted acid has been tested for the chemoselective transesterification of ethyl/methyl β-ketoesters with various alcohols in good yields with high TON/TOF.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The development of new heterogeneous Brønsted acid catalysts as alternatives for corrosive liquid acid catalysts, which combine chemical efficiency, ease of preparation, are recyclable, safe, and economical has become important for industrial applications in the context of green chemistry [1]. The commonly used supports for acid catalysts, in particular for sulphonic acids are polymeric membranes [2], commercially available Nafion with perflourinated sulphonic acid groups [3], polystyrenes supported sulphonic acid [4] and lately, high surface area sulphonic acid functionalized mesoporous silicas have also been synthesized [5] by the condensation of alkoxy silanes and 3-mercapto propyl trimethoxy silanes, which are further oxidized to obtain the propyl sulphonic acid groups.

Heterogeneous catalysts are preferred by industries as recoverable and recyclable catalysts but suffer from problems like poor mass transfer, restricted accessibility to matrix bound acidic sites, high molecular weight/active site ratio, and rapid deactivation due to coking, while homogenous catalysts are flawed with difficulties associated with recycling and separation of products. Hence, the need to design and synthesize homogenous–heterogeneous catalysts is required to overcome the drawbacks of each system [6]. In light of this, synthesis of hybrid organic–inorganic materials as

catalysts for acid catalyzed reactions like esterification, aromatic alkylation, and etherification are attractive and their importance is increasing as new functional and nano-structured materials for developing safe industrial processes [7,8].

Research in functional ionic liquid catalysis has gained momentum due to their promising activity as efficient recoverable and recyclable catalysts [9], as the ionic support further enhances the interaction and immobilization in the ionic medium resulting in high turn over numbers, frequency and negligible metal leaching and has been recently reviewed in literature [10]. In particular, various functional acidic ionic liquids have also been synthesized and used as catalysts in numerous organic reactions as reported in literature [11–13].

Ionic liquids (ILs) have also been immobilized onto solid supports, most commonly on silica, in order to minimize the amount of ILs used, avoid the use of organic solvents and easily recover the catalyst which is desirable from an economic and toxicological point of view. These supported ionic liquid phases (SILP) possess the advantages of both ionic liquids and heterogeneous supports and has been reviewed recently [14].

Montmorillonite clay is the most important inexpensive aluminosilicate smectite clay used in catalytic applications in organic synthesis with characteristic features like cation exchange, swellability and intercalation properties [15]. Chemical modification of these clays by immobilization involves a simple ion exchange of organic and inorganic moieties which can be fine tuned as per industrial requirements and are being considered as potentially cost effective and environmentally benign nano-materials for the

---

* Corresponding author. Tel.: +91 172 275 3263.
  E-mail address: vasun7@yahoo.co.in (V. Singh).
[1] Tel.: +33 02 23 23 62 74; fax: +33 02 23 23 69 55.

future [16], especially with amines or quaternary ammonium salts which provides a simple method for the preparation of organic–inorganic hybrid materials. Recently, Kim et al. have reported the preparation of cationic nanoclays by immobilizing ionic liquids as a modifier in the interlayers of clays [17]. Supported ionic-liquid films (SILF) of nanometric thickness containing bis(oxazoline)–copper complexes in clay has been used as recoverable catalysts for enantioselective cyclopropanation reaction [18].

Transesterification of β-ketoesters is an important organic transformation and has been catalyzed by a number of homogenous and heterogeneous catalysts which include Bronsted and Lewis acids, bases, anion exchange resins, DMAP, titanium tetralkoxide, zeolites, clays, to list a few [19]. All previously reported procedures are flawed with one drawback or another, like volatility and toxicity of acid catalysts, long reaction times, hostility of catalysts to environmental issues, and their non-recoverability.

In continuation to our program for the development of acid catalysts based on clays and ionic liquids [20,21], we herein report the synthesis and characterization of sulphonic acid functionalized ionic liquid exchanged MMT-clay nanocomposite **2** and its application as a solid acid catalyst for transesterification of β-ketoesters. The cationic part of **1** was exchanged into the interlayer spacing of MMT clay to get catalyst **2** as a dry powder. The immobilization is by electrostatic interactions between the negatively charged interlayers and positively charged cation as shown in Fig. 1.

2. Experimental

2.1. Preparation of catalyst 2

The sulphonic acid functionalized ionic liquid **1** was prepared by ring opening of 1,3 propane sultone through the nucleophilic attack of 1-methyimidazole and subsequent anion exchange with triflic acid according to the reported procedure [22] and characterized by IR and NMR analysis [IR (KBr, cm^{-1}) 3445, 2361, 1848, 1637, 1426, 1043, 796, 623; ^{1}H NMR (D$_2$O) δ: 1.9–2.05 (m,2H), 2.62 (t, 2H, J = 7.16 Hz), 3.59 (s, 3H), 4.05 (t, 2H, J = 7.16 Hz), 7.14–7.22 (d, 2H), 8.43 (s,1H)].

To a solution of **1** (0.486 g, 1.5 mmol) in absolute ethanol (20 ml) was added Na$^+$–MMT clay (1.0 g) in small fractions with vigorous stirring at room temperature and stirring continued for 48 h. The solid was filtered and washed thoroughly with ethanol (4 × 10 ml) to remove any residual sulphonic acid functionalized ionic liquid **1**. The product was finally dried under vacuum for 24 h to get a free flowing solid and is denoted as catalyst **2**.
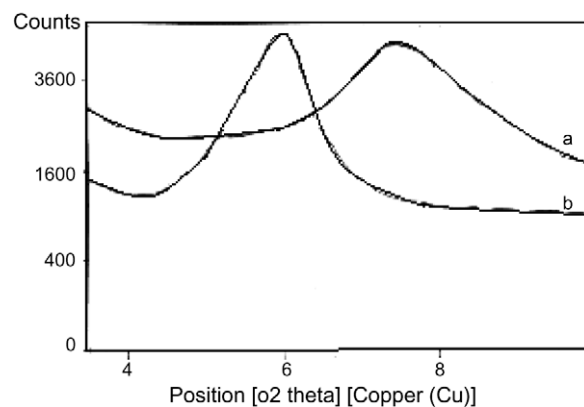

Fig. 1. Sulphonic acid functionalized ionic liquid exchanged clay nanocomposite **2**.

Fig. 2. XRD patterns of (a) Na$^+$–MMT clay, (b) catalyst **2**.

2.2. Catalyst characterization

The Na$^+$–MMT clay and catalyst **2** were characterized by using XRD, BET, and TGA analysis to determine the structure, surface area, and thermal stability respectively. The Bronsted acidity was determined by titration method. The powder XRD patterns of Na$^+$–MMT clay and catalyst **2** are presented in Fig. 2.

The characteristic peak at 7.44° corresponds to d$_{001}$ spacing of 11.86 Å in case of Na$^+$–MMT clay. Similarly, the peak at 6.07° corresponds to a d$_{001}$ spacing of 14.52 Å in case of catalyst **2** indicating a substantial expansion of the interlayers due to exchange of smaller Na$^+$ ions with the bulkier sulphonic acid functionalized cation.

The nitrogen adsorption–desorption isotherms of MMT and catalyst **2** at 77 K were evaluated using an adsorption analyzer. The BET surface area and micropore volume increased from 11.89 to 14.37 m^2/g and 0.0452 to 0.0646 cm^3/g for MMT clay and catalyst **2** respectively, which further supports the intercalation process and remained the same after the reaction.

The cation exchange in catalyst **2** was determined by finding the Bronsted acidity using titration method which increased from 0.130 to 1.1 mmol H$^+$/g of clay for MMT clay and catalyst **2** respectively as shown in Table 1.

TGA analysis of catalyst **1** and **2** showed that catalyst **1** was thermally stable up to 280 °C after which it degraded rapidly while catalyst **2** showed thermal stability up to 300 °C and gradually degraded and continued up to 840 °C which is probably because the ionic liquid **1** is sandwiched in the layers of MMT clay in catalyst **2**.

The solid catalyst **2** was characterized by IR analysis before and after the reaction, which showed the presence of a band at 1427 cm^{-1} characteristic of (S=O) stretching vibrations of –SO$_3$H groups, similar to the one observed in catalyst **1** and is as shown in Figs. 3a and 3b.

2.3. Methods and materials

^{1}H NMR was recorded in CDCl$_3$ on a 400 MHz Bruker instrument using TMS as the internal standard. IR spectra were recorded on a Bio-Rad-Win-IR spectrometer. Na$^+$–montmorillonite clay (Na$^+$–MMT) with cation exchange capacity of 120 meq/100 g clay, was provided by Kunimine Co. Ltd., Japan. XRD analysis was done using Rigaku D-Max IIIC using Ni-filtered Cu-Kα radiation. BET surface area and pore volume were determined using quantachrome autosorb automated gas sorption system. TGA analysis was carried out using TGA Mettler Toledo system. Bronsted acidity was determined by taking Na$^+$–MMT clay and catalyst **2** (250 mg each) separately and suspended in aqueous NaOH (20 ml, 0.086 N) for 24 h and filtered. The filtrate containing unreacted NaOH was titrated against standard H$_2$SO$_4$ (0.1 N) using phenolphthalein as an
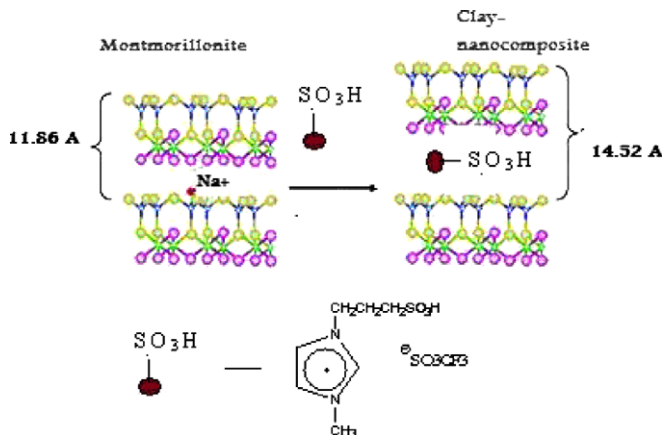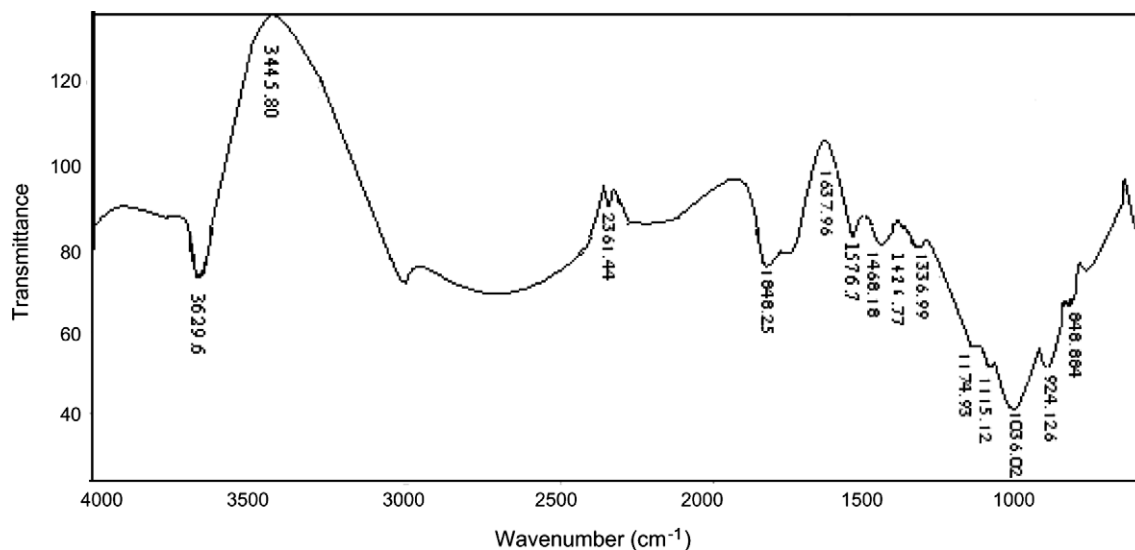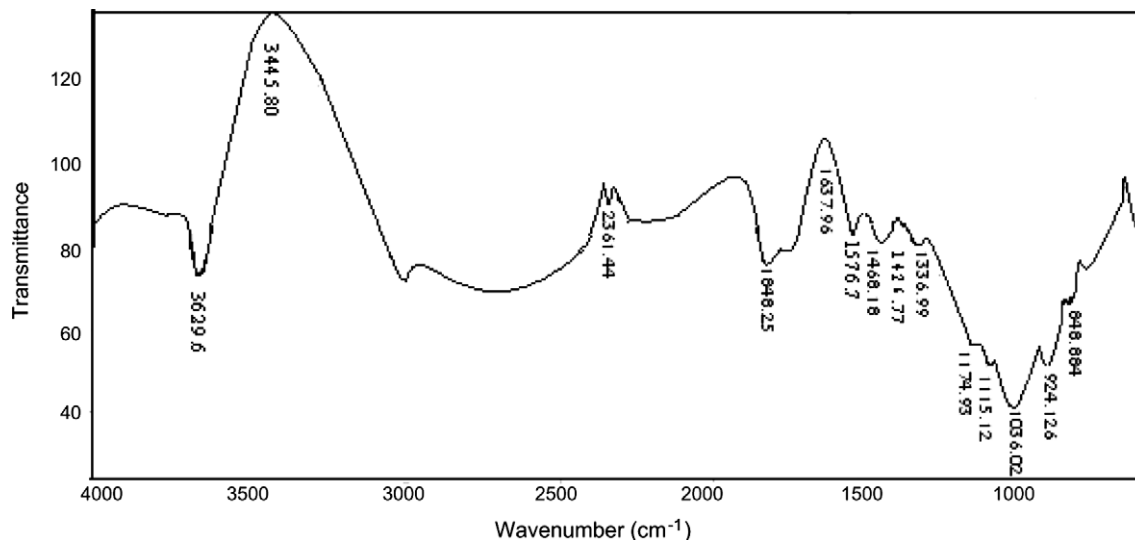
Table 1
Physico-chemical characteristics of Na$^+$–MMT clay and clay nanocomposite 2.

Sample	Basal spacing (Å)	Multipoint BET surface area (m^2/g)	Pore volume (cm^3/g)	Bronsted acidity (mmol H$^+$/g of clay)
Na$^+$–MMT clay	11.86	11.89	0.0452	0.130
Catalyst **2**	14.52	14.37	0.0646	1.110

Fig. 3a. IR spectrum of catalyst **2**.

Fig. 3b. IR spectrum of catalyst **2** after the reaction.

indicator. [TMBA] NTf$_2$ (trimethylbutylammonium bis(trifluoromethylsulfonyl)imide) was prepared by quaternization of trimethylamine with butyl chloride followed by anion exchange with LiNTf$_2$ [23].

2.4. Transesterification of β-ketoesters with catalyst 1 and 2

In a typical experiment, ethylacetoacetate (0.130 g, 1.0 mmol) and octanol (0.156 g, 1.2 mmol) were added to catalyst **1** (0.05 mmol, 0.0162 g)/catalyst **2** (50 mg) in [TMBA] NTf$_2$ (1.0 ml) and heated at 80 °C for 3 h with stirring. On completion of reaction the lower alcohol formed was removed under vacuum. The product was extracted with ether (3 × 10 ml), dried and evaporation of solvent and purification after column chromatography (Pet ether/ether, 8:2) gave the desired product 0.192 g (90%)/0.196 g (92%). The catalyst and the spent ionic liquid, after removal of product, were recovered by drying at high vacuum at 80 °C and recycled for the same reaction which yielded the product with no loss in

activity and selectivity up to seven cycles. ^{1}H NMR (CDCl$_3$,) δ: 0.9 (t, 3H, J = 6.9 Hz), 1.2–1.3 (m,10H), 1.5–1.6 (m, 2H), 2.27 (s, 3H), 3.45 (s, 2H,), 4.03 (t, 2H, J = 6.8 Hz).
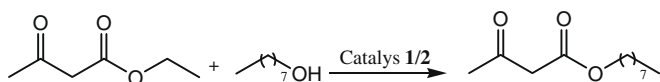
3. Results and discussion

This process illustrates a simple method of heterogenisation of an active homogeneous acid catalyst **1** on intercalating by ion exchange into the layers of inexpensive MMT clay to get a free flowing solid acid catalyst **2**. The use of the imidazolium based ionic tagged sulphonic acid helps in propping apart the layers of clay which is further assisted by the π–π interaction of the imidazole rings which acts as a template in the intercalation process. The catalyst **2** showed higher thermal stability, has greater surface area due to the presence of the ionic tag which assists in the pillaring process and increases the basal spacing. Table 1 exhibits a summary of the physico-chemical characteristics of Na$^+$–MMT clay and clay nanocomposite **2**.

In the screening and optimization of catalytic activity, a model reaction for transesterification of ethylacetoacetate and octanol (Scheme 1) at 80 °C was studied under various reaction conditions as shown in Table 2. As expected Na$^+$–MMT clay showed no catalytic activity. The acid catalyst **1** gave good yield of the desired product both under solventless conditions and in the ionic liquid [TMBA] NTf$_2$. The catalytic activity of catalyst **2** was also studied in the absence and presence of [TMBA] NTf$_2$ used as a solvent, wherein it was observed that higher conversion up to 95% after seven catalytic cycles was obtained in the presence of [TMBA] NTf$_2$ as a solvent. It is envisaged that the ammonium based ionic liquid [TMBA] NTf$_2$ assists in the transport of reactants into the layers of clay. It is evident from Table 2 that the clay nanocomposite **2** in [TMBA] NTf$_2$ proved to be the best catalytic system. The conversion were calculated from ^{1}HNMR by relative ratio of the peaks at 4.03 (t, 2H, J = 6.80 Hz) in the product and peak at 4.2 (q, 2H, J = 7.1 Hz) in ethylacetoacetate/4.03 (s, 3H) in methylacetoacetate.

Fig. 4 exhibits the progress of transesterification reaction of ethylacetoacetate and 1-octanol at 80 °C over catalyst **1** and **2** as a function of time. The reaction shows rapid progression with marginal difference in initial rate of conversion of 70 and 80% in case of catalyst **1** and **2** respectively and complete conversion was achieved in both cases in three hours.

The results of recycling experiments with catalyst **1** under solventless conditions (entry 2) and catalyst **2** in [TMBA] NTf$_2$ (entry 4) are shown in Fig 5. Best results were observed with catalyst **2** in [TMBA] NTf$_2$ up to seven cycles where both the catalyst and ionic liquid were efficiently recycled.

The plausible mechanism for the transesterification reaction is as shown in Scheme 2.

The reaction using different alcohols and methylacetoacetate were also studied to determine the efficacy of the catalytic systems **1** and **2** and it was found that the reaction goes smoothly with high yields and TONs above 15,000 as shown in Table 3. Moreover, catalyst **1** provides the opportunity to carry out the reaction under solvent-free conditions and the novel heterogenous catalytic sys-
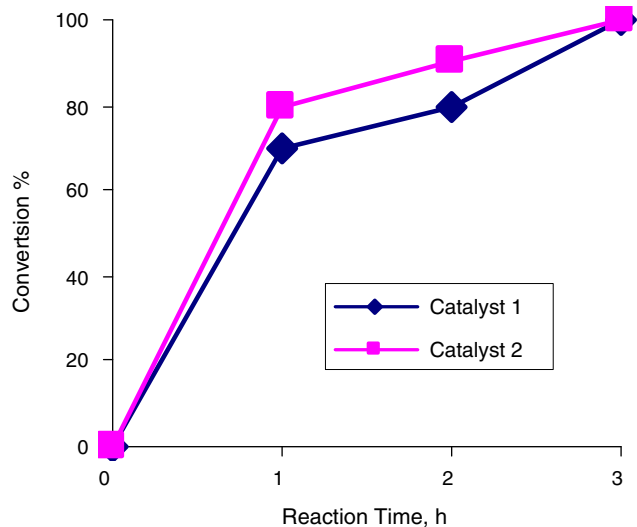

Fig. 4. Kinetic curves for the transesterification of ethylacetoacetate with 1-octanol using catalyst **1** and **2**.
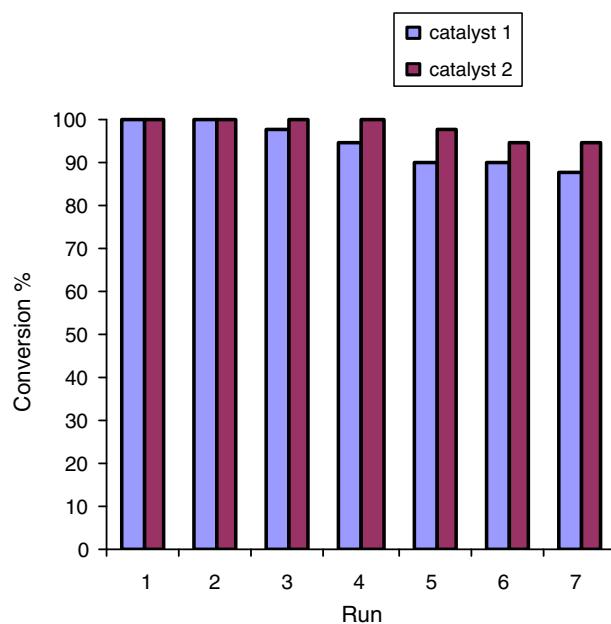

Fig. 5. Recycling experiments of ethylacetoacetate and 1-octanol using catalyst **1** and **2**.

Scheme 1. Transesterification reactions catalyzed by catalyst **1** and **2**.

Table 2
Optimized results for transesterification of ethylacetoacetate and octanol at 80 °C under various reaction conditions.

Entry	Catalyst	[TMBA] NTf$_2$ (ml)	Time (h)	Yield (%)	TON	TOF (h^{-1})
1	Na$^+$–MMT clay	0.5	3	Nil	–	–
2	**1**	Nil	3	90	18,000	6000
3	**1**	0.5	3	92	18,400	6133
4	**2**	0.5	3	95	19,000	6333
5	**2**	Nil	3	Nil	–	–
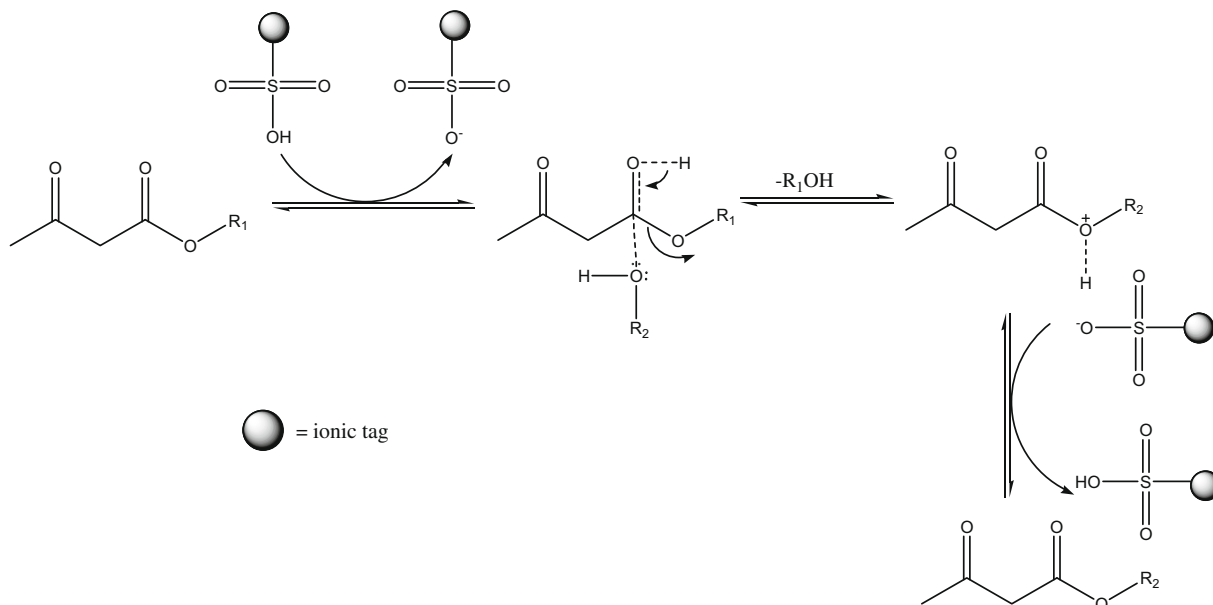
Scheme 2. The plausible mechanism for transesterification reaction catalyzed by sulphonic acid functionalized ionic liquid and its nanocomposite.

Table 3
Transesterification of methylacetoacetate with different alcohols using catalyst **1** and **2**.

Entry	Catalyst	Alcohol	Time (h)	Yield (%)	TON	TOF (h^{-1})
1	**1**	Butanol	3	90	18,000	6000
	2	Butanol	3	85	17,000	5666
2	**1**	Isobutanol	3	80	16,000	5333
	2	Isobutanol	3	90	18,000	6000
3	**1**	Allyl alcohol	3	75	15,000	5000
	2	Allyl alcohol	3	88	17,600	5866
4	**1**	Benzyl alcohol	3	72	14,400	4800
	2	Benzyl alcohol	3	80	16,000	5333
5	**1**	Cyclohexanol	3	75	15,000	5000
	2	Cyclohexanol	3	80	16,000	5333

tem **2** can be used in flow reactors in industry [24,25]. Both the catalysts showed good catalytic activity with high conversion and reasonable yields. The catalysts were recovered after the reaction and reused subsequently. In comparison to the existing studies the current protocol has the advantages of high TON/TOF, recyclability and recoverability of the catalytic system.

4. Conclusion

This is a simple method to prepare a MMT-clay exchanged sulphonic acid functionalized ionic liquid nanocomposite as a hybrid organic–inorganic heterogeneous catalyst with high acidity, as a free flowing solid with the homogenous acid catalyst sandwiched between the layers of clay. It combines the advantages of both heterogeneous and homogenous catalytic system for effective mass transport of reactants and product molecules. The ionic tag improves intercalation and organophilicity and the catalyst exhibits good activity for the transesterification of β-keto esters with various primary, secondary, cyclic and benzylic alcohols. The catalytic activity of catalyst **2** will be studied for other important organic reactions enabling its usage for the industrially preferred fixed bed technology.

References

[1] M.A. Harmer, W.E. Farneth, Q. Sun, Adv. Mater. 10 (1998) 1255.
[2] L. Guerreiro, J.E. Castanheiro, I.M. Fonseca, R.M. Martin-Aranda, A.M. Ramos, J. Vital, Catal. Today 118 (2006) 166.
[3] S.L. Jain, B. Sain, Appl. Catal. A: Gen. 301 (2006) 259.
[4] S. Iimura, K. Manabe, S. Kobayashi, Org. Biomol. Chem. 1 (2003) 2416.
[5] R.I. Kureshy, I. Ahmad, K. Pathak, N.H. Khan, S.H.R. Abdi, R.V. Jasra, Catal. Commun. 10 (2009) 572.
[6] A. Corma, H. Garcia, Top. Catal. 48 (2008) 8.
[7] S. Jaenicke, G.K. Chuah, X.H. Lin, X.C. Hu, Micropor. Mesopor. Mat. 35–36 (2000) 143.
[8] J.M. Notestein, A. Katz, Chem. Eur. J. 12 (2006) 3954.
[9] X. Li, J. Zhou, X. Guo, M. Liu, X. Ma, C. Song, C. Wang, Ind. Eng. Chem. Res. 47 (2008) 5298.
[10] R. Sebesta, I. Kmentova, S. Toma, Green Chem. 9 (2008) 484.
[11] F. Dong, L. Jun, Z.X. Li, L.Z. Liang, Catal. Lett. 116 (2007) 76.
[12] K.E. Johnson, R.M. Pagni, J. Bartmers, Monatsh. Chem. 138 (2007) 1077.
[13] L. Zhang, M. Xian, Y. He, L. Li, J. Yang, S. Yu, X. Xu, Bioresour. Technol. 100 (2009) 4368.
[14] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, Top. Catal. 40 (2006) 91.
[15] R.S. Varma, Tetrahedron 58 (2002) 1235.
[16] R.A. Schoonheydt, Clays Clay. Miner. 50 (2002) 411.
[17] N.H. Kim, S.V. Malhotra, M. Xanthos, Micropor. Mesopor. Mat. 96 (2006) 29.
[18] M.R. Castillo, L. Fousse, J.M. Fraile, J.I. García, J.A. Mayoral, Chem. Eur. J. 13 (2007) 287.
[19] W. Bo, Y.L. Ming, S.J. Shuan, Tetrahedron Lett. 44 (2003) 5037. and references cited therein.
[20] V. Singh, V. Sapehiyia, G.L. Kad, J. Mol. Catal. A-Chem. 210 (2004) 119.
[21] V. Singh, S. Kaur, V. Sapehiyia, J. Singh, G.L. Kad, Catal. Commun. (2005) 57.
[22] A.C. Cole, J.L. Jensen, I. Ntai, K. Loan, T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 5962.
[23] C. Tiyapiboonchaiya, D.R. Mac Farlane, D.R. Sun, M. Forsyth, Macromol. Chem. Phys. 203 (2002) 1906.
[24] K. Bunyakiat, S. Makmee, R. Sawangkew, S. Ngamprasertsith, Energy Fuel 20 (2006) 812.
[25] C. Wiles, P. Watts, Eur. J. Org. Chem. (2008) 1655.