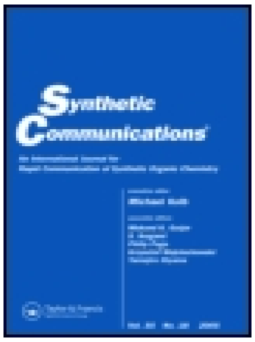

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MONTMORILLONITE SUPPORTED PHASE TRANSFER CATALYST IN REDUCTION OF CARBONYL GROUPS.

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Abstract:*Silylpropyltrimethylammonium iodide covalently anchored onto montmorillonite shows good catalytic activity in carbonyl reduction under triphase catalysis. Selectively trans-t-butylcyclohexanol was formed selectively in good yield in the reduction of 4-t-butylcyclohexanone. The catalyst was reused for several cycles.*

Quaternary ammonium salts immobilised on insoluble synthetic polymers and inorganic oxides, such as silica and alumina, have been widely explored as triphase catalysts[1-4]. Inherent disadvantages, such as low physical strength, alkali instability, and acid instability, respectively, with polymers, silica, and alumina[3], render these catalysts unsuitable for many reactions. Montmorillonite is a support of current interest for pillared[5], immobilised[6], and anchored catalysts[7] and has been found to be an excellent template for selective organic transformations. In view of the inherent advantages associated in the use of montmorillonite such as large source of natural abundance that can give an inexpensive material, with high physical strength and relatively high resistance towards acid and alkali treatment, montmorillonite was chosen as a support in our studies. In earlier studies, onium salts were intercalated by exchange in montmorillonite, but their applicability was limited to a few reactions in phase transfer catalysis[8,9]. We recently reported the synthesis of covalently bound

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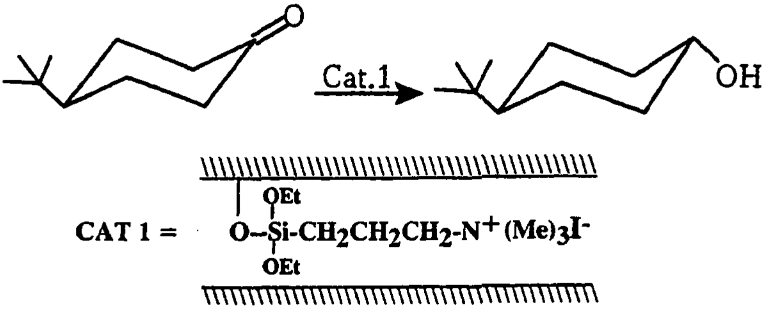

CAT 1 = $\text{O--}\overset{\text{OEt}}{\underset{\text{OEt}}{\text{Si}}}\text{-CH}_2\text{CH}_2\text{CH}_2\text{-N}^+(\text{Me})_3\text{I}^-$

Scheme.

Table: Reduction of Carbonyl compounds

Entry No	Substrate	Time(hrs)	Yield(%)
1	C_6H_5CHO	7	98
2	$C_6H_5COCH_3$	11	97
3	$(p\text{-}OMe)C_6H_4COCH_3$	11	90
4	$C_6H_5CH_2COCH_2C_6H_5$	13	84
5	$(p\text{-}OMe)C_6H_4CH_2COCH_3$	8	89
6	$C_6H_5COCH_2CH_2COOEt$	10	92
7	$C_6H_5COC_6H_5$	7	94
8	$(OMe)_3C_6H_2CHO$	4	96
9	4-t-Butylcyclohexanone	6	98
10	$CH_3(CH_2)_5COCH_3$	10	79

onium salts in the interlamellar region of montmorillonite and their wide applicability as phase transfer catalysts[10]. In this communication, we present results on the reduction of a variety of carbonyl groups in excellent yields(Table),which includes the stereoselective reduction of 4-t-butylcyclohexa--none predominantly to trans 4-t-butylcyclohexanol(scheme) with $NaBH_4$ in benzene and water catalysed by montmorillonitesilylpropyltrimethylammonium iodide(**Cat 1**) under triphase conditions.

The synthesis of **cat 1** was first effected by reacting the H-montmorillonite with 3-aminopropyltriethoxysilane in toluene and subsequent quaternisation with methyl iodide.The amount of iodide was titrated and found 0.5 mmol/g.

The $NaBH_4$ reductions of carbonyl groups catalysed by **cat 1** are simple and fast. It is generally observed that reduction of aldehydes is faster than ketones, whereas the ester groups were unreactive under these conditions. The remarkable feature of the present work is the display of the high stereoselectivity in the reduction of 4-t-butylcyclohexanone to trans4-t-butylcyclohexanol in 90% yield. Further, the phase transfer catalyst has displayed consistent activity for four recycles on reuse after simple filtration.The catalyst was unchanged after reuse as was indicated by XRD and spectral analysis. The catalyst is also stable under storage for several months.Therefore the present method described here represents a practical and viable alternative to reported methods[11,12], since it offers the following advantages: a) requirement of catalytic amount of phase transfer agent,and reuse for number of recycles, b) easy separation of the catalyst from the reaction medium, c) comparable stereoselectivity and high catalytic activity even with lower liphophilic onium salts thus dispensing with the use of expensive tetraalkylonium salts containing long chain hydrocarbons.

Experimental

The **cat 1** was synthesised as described earlier[10]. H-montmorillonite(5g), prepared from commercial montmorillonite K10, was refluxed with 3-aminopropyltriethoxysilane(0.78 g,3.5 mmol) in dry toluene for 48 hrs.Then it was filtered and washed with toluene and ether and dried.For quaternisation,3g of amino functionalised montmorillonite was suspended in 30 ml of ethanol and cooled to $0^{o}C$, 10 ml of methyl iodide was added and allowed to reach room temprature. Then the mixture was refluxed for 5 hrs and diluted with ether. The catalyst was filtered,washed with ehanol and ether,and dried under high vacuum.

In a typical experiment a 50 ml round bottom flask was charged with **cat 1** (100mg, 0.05mmol), p-methoxyacetophenone(375mg, 2.5mmol) and $NaBH_4$(106mg, 2.8mmol) followed by benzene(4.5ml) and water(1.5ml). Then the reaction mixture was stirred and the reaction was followed by GC and TLC. After completion of the reaction,the mixture was just filtered through a sintered funnel, the catalyst was washed with ether and kept aside for reuse.The filtrate was concentrated and the product, 1-p-methoxyphenylethanol(342mg, 90%) was analysed by NMR and Mass.

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