

Synthesis of ceria-yttria based strong Lewis acid heterogeneous catalyst: Application for chemoselective acylation and ene reaction

Rajesh K. Pandey^a, Sharda P. Dagade^b, Kusum M. Malase^b,
Sachin B. Songire^a, Pradeep Kumar^{a,*}

^a Division of Organic Chemistry Technology, National Chemical Laboratory,
Pune, Maharashtra 411008, India

^b Catalysis Division, National Chemical Laboratory, Pune, Maharashtra 411008, India

Received 5 July 2005; received in revised form 7 October 2005; accepted 10 October 2005

Available online 11 November 2005

Abstract

The synthesis of a new ceria-yttria based strong Lewis acid heterogeneous catalyst is described and its application for the ene reaction and chemoselective acylation has been demonstrated.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ceria-yttria based Lewis acid; Ene reaction; Acylation reaction; Chemoselectivity; Heterogeneous catalysis

1. Introduction

While extensive efforts have been put in for the development of transition metal based catalyst and their subsequent application in organic chemistry, the catalytic potential of metal belonging to the lanthanide series has not been fully realized. Cerium, one of the readily available metal of the lanthanide series offers opportunities for developing strong Lewis acid sites in a heterogeneous catalyst, development of such a catalyst becomes highly desirable for organic synthetic transformations. Some of the cerium based reagents/catalysts used as a Lewis acids are cerium^{IV} acetate borontrifluoride etherate [1] cerium chloride as a mild Lewis acid [2]. Recently, we used cerium based MCM-41 catalyst for the acylation and alkylation reactions [3].

Very few reports are available in literature about the Lewis acidic properties of cerium based reagent. This prompted us to explore the Lewis acidic properties of cerium containing heterogeneous catalyst. Here we report on the synthesis and physicochemical characterization of sulfated cerium based strong Lewis acid catalyst and its applications for intramolec-

ular ene reaction and chemoselective acylation of alcohols and amines.

2. Experimental

2.1. Materials and equipment

Solvents were purified and dried by standard procedures before use according to reported procedure [4]; petroleum ether of boiling range 60–80 °C was used. The acids and alcohols were obtained from commercial sources and were purified by distillation/recrystallisation before the experiment. Infrared spectra were recorded with ATI MATT-SON RS-1 FT-IR spectrometer. Proton NMR spectra were recorded on Bruker AC-200 machine in CDCl₃ with TMS as internal standard. Mass spectra were obtained with Finnigan MAT mass spectrometer. Elemental analyses were carried out with a Carlo Erba CHNS-O analyzer. The diffractogram of X-ray powder diffraction pattern was recorded on a Rigaku diffractometer model D/Max. IIIVC with N-filtered Cu K α radiation. FTIR spectrum of pyridine adsorbed on the yttrium-based catalyst was recorded on a Nicolet 60 SXB FTIR spectrometer. TPD profile (ammonia) of the yttrium-based catalyst was recorded on a Sorbstar apparatus. Determination of specific surface area was carried out by

* Corresponding author. Fax: +91 20 25893614.
E-mail address: pk.tripathi@ncl.res.in (P. Kumar).

BET (Brunner-Emmett-Teller) N₂ adsorption using an Omnisorp 100CX apparatus.

2.2. Synthesis of the catalyst

The catalyst was prepared by employing the sol–gel technique.

A solution of cerium nitrate in isopropyl alcohol was added under constant stirring to the solution of yttrium nitrate in isopropyl alcohol. The final homogeneous solution thus formed was allowed to stand overnight. A yellowish gel was formed which was air-dried and then dried at 110 °C, ground to fine powder. The powder thus formed was added to H₂SO₄ (2N), stirred and dried on a water bath and then in oven at 110 °C for 24 h. Subsequent programmed calcination at 500 °C for 3 h at a heating rate of 2 °C min⁻¹ resulted in a highly acidic material. The chemical composition of the final catalyst (determined by X-ray fluorescence) was found to be 80 mol% of Y, 15 mol% of Ce and 5 mol% of S.

2.3. A typical procedure for acylation reaction

Acid anhydride (3.75 mmol; 1.5 equiv. per OH or NH₂) was added to a solution of alcohol or amine (2.5 mmol) in dry acetonitrile (5.0 ml) containing catalyst (15% by weight) and the mixture was refluxed for 2–15 h. The reaction was monitored by TLC. After completion of reaction (methanol (5.0 ml) was added and mixture again refluxed for 10 h (in case of pivalation) the catalyst was filtered and the filtrate was concentrated, the crude product was chromatographed on a silica gel column to afford the pure product. After the reaction, the catalyst is recovered with retention of its catalytic activity. It can be further reactivated for reuse by heating it at 500 °C in the presence of air. There was no leaching of the catalyst in the liquid phase reaction as confirmed by the atomic absorption studies of the reaction mixture.

3. Results and discussion

3.1. Characterization of the catalyst

The physicochemical characterization of the catalyst was carried out by TPD, SEM and N₂ adsorption techniques and TG-DTA. The X-ray powder diffraction pattern of the calcined catalyst (Fig. 1) shows the presence of both CeO₂ and Y₂O₃ reflections indicating the product as a two-phase mixed oxide. The IR spectra of pyridine adsorbed on the catalyst show strong absorption bands at 1605 and 1444 cm⁻¹ indicating the pres-

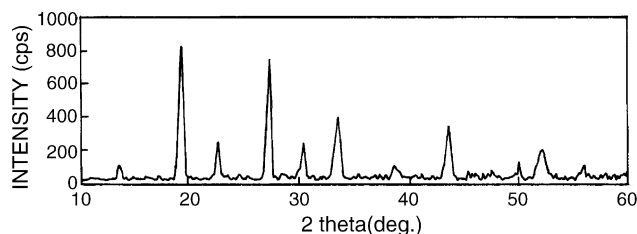


Fig. 1. X-ray powder diffraction pattern of the catalyst.

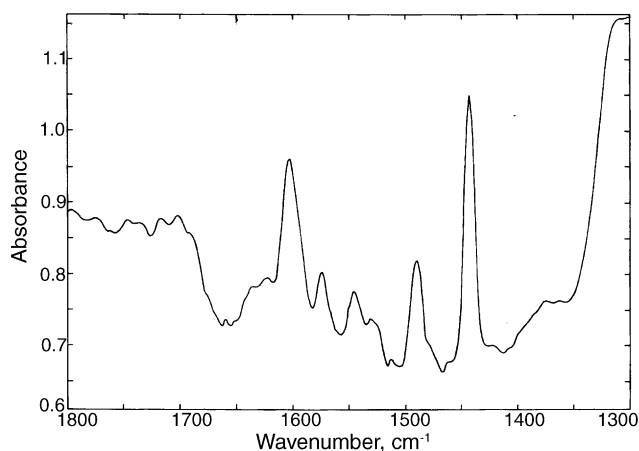


Fig. 2. FTIR spectrum of pyridine adsorbed on the catalyst.

ence of co-ordinated pyridine on the Lewis acid sites of the catalyst. The weak absorption at 1542 cm⁻¹ attributed to the pyridinium ion [5] indicates the presence of a few Brønsted acid sites (Fig. 2). Temperature programmed desorption (TPD) shows the peak maxima at 470 °C due to presence of strong acid sites as well as weak acid sites (Fig. 3) [6]. The scanning electron micrograph of sample shows the presence of uniform-sized (around 0.2–0.4 μm) particles (Fig. 4). Thermal analysis (TG-DTA) (Fig. 5) indicates that up to 200 °C there is an endothermic weight loss of 4.5% due to the adsorbed water from the surface of the catalyst. From 200–760 °C, the weight loss of only 2.3% suggests that the catalyst is thermally stable in the temperature range 200–760 °C. Final weight loss of 10% above 760 °C indicates that the catalyst is not stable above that temperature because of the structural breakdown. The surface area of the sample determined by the BET method was 100 m² g⁻¹.

3.2. Ene reaction

The very first application of Lewis acidic properties of sulfated ceria-yttria catalyst was explored for the intramolecular

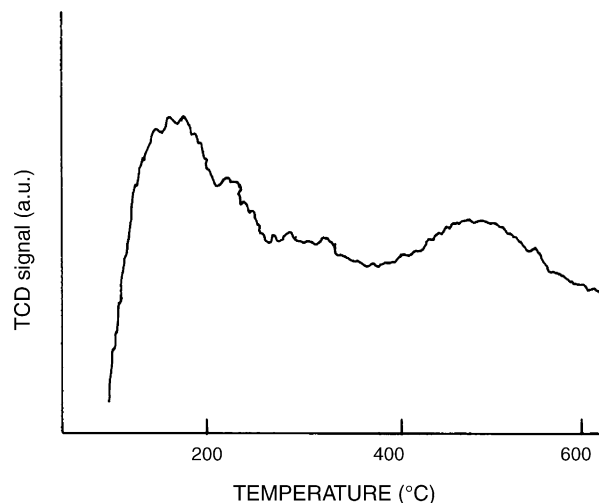


Fig. 3. TPD profile (ammonia) of the catalyst.

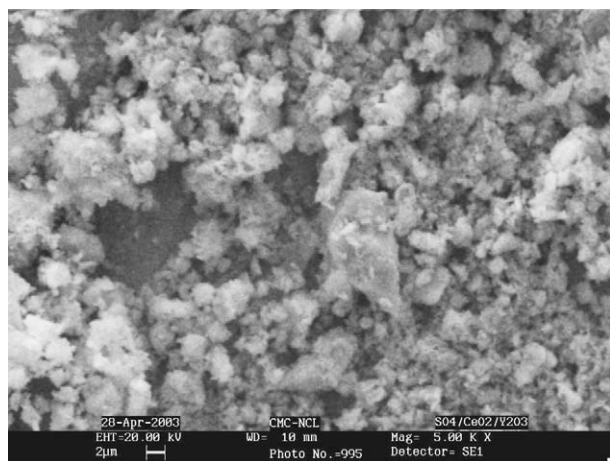


Fig. 4. Scanning electron micrograph of the catalyst.

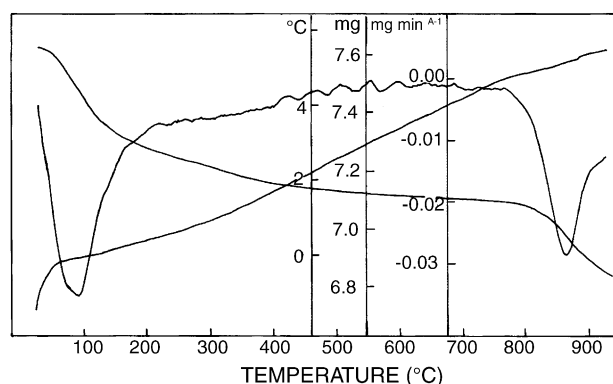


Fig. 5. Thermal analysis (TG-DTA) of the catalyst.

ene reaction. This study revealed that isopulegol can be conventionally prepared from citronellal using catalytic amount (15%, w/w) of sulfated ceria-yttria Lewis acid catalyst in acetonitrile at reflux temperature in 65% yield. It should be noted that the reaction either in acetonitrile solvent or under neat conditions without catalyst did not show the formation of any product. The other catalysts for this reaction were also screened and the results of such study are summarized in Table 1. Thus, ceria-yttria based Lewis acid catalyst was found to be the best catalyst for the conversion of citronellal to isopulegol compared to H-mordenite and H-beta zeolite. We also studied the effect of different solvents such as hexane, tetrahydrofuran, acetone and acetonitrile for the conversion of citronellal to isopulegol. The results are

Table 1
Effect of different catalyst for the conversion of citronellal to isopulegol in acetonitrile^a

Entry	Catalyst	Reaction time (h)	Yield (%) ^b
1	Ceria-yttria based Lewis acid	10	65
2	H-Beta	14	35
3	H-Mordenite	30	25 ^c

^a Product was characterized by spectroscopic data and also by comparison with authentic sample.

^b Yields refer to pure and isolated product.

^c 50% catalyst was used.

Table 2

Effect of various solvent for the synthesis of isopulegol^a

Entry	Solvent	Reaction time (h)	Yield (%) ^b
1	Hexane	20	40
2	Acetonitrile	10	65
3	Acetone	11	60
4	Tetrahydrofuran	14	55

^a Product was characterized by spectroscopic data and also by comparison with authentic sample.

^b Yields refer to pure and isolated product.

summarized in Table 2. It is clear from the Table 2 that polar solvents were proved to be better than nonpolar solvent.

3.3. Acylation reaction

As the ceria-yttria based Lewis acid developed by us was found to be an extremely efficient catalyst for the ene reaction, we thought of employing this catalyst as test case for acylation reaction. Though the acylation of alcohols and amines under basic conditions is a well established reaction [7], there are sufficient drawbacks to most of the reported procedures [8] to justify the need for a general, selective and practical method for acylation reaction. Initially the acylation of hexanol with various acylating agent using varied amount of acylating agents was examined (Table 3). From Table 3 it is clear that 10% catalyst is sufficient to catalyse the reaction. However, the use of 15% of catalyst (w/w) proved to be the best with regard to the reaction time and yield of the product. The advantage of this procedure is that catalyst can be reused without loss of activity (Table 3, entry 13). In order to see the effect of the catalyst, blank experiments were carried out under solvent-free and catalyst-free conditions [9]. Thus, the heating of cyclohexanol with acetic anhydride at 80 °C under neat conditions without catalyst for 2 h or even a prolonged reaction time did not afford any product. Similarly acetylation of benzyl alcohol under neat conditions without cat-

Table 3

Acylation of hexanol with various amount of catalyst and with different acylating agent

Entry	Acylating agent	% of catalyst (w/w)	Reaction time (h)	Yield (%) ^a
1	Acetic anhydride	5	8	80
2	Acetic anhydride	10	6	92
3	Acetic anhydride	15	3	93
4	Acetic anhydride	20	3	94
5	Propionic anhydride	15	3.5	90
6	Pivalic anhydride	15	5	90
7	Benzoic anhydride	15	8	80
8	Acetic acid	15	4	92 ^b
9	Propionic acid	15	5	90 ^b
10	Benzoic acid	15	10	78 ^b
11	Acetyl chloride	15	2.5	94
12	Benzoyl chloride	15	4	85
13	Acetic anhydride	15	3	93 ^c

^a Yields refer to pure and isolated product.

^b Reaction carried out with 12.5 mol acid at 130 °C without any solvent.

^c Catalyst recycled four times.

Table 4

The ceria-yttria based Lewis acid catalyzed acylation of alcohols, polyols and amines

Entry	Alcohol/amines	Anhydride	Reaction time (h)	Yield (%) ^a
1	Cyclohexanol	Acetic	5	95
2	Cyclohexanol	Pivalic	4	91
3	Menthol	Acetic	4	96
4	Menthol	Pivalic	5	86
5	Benzyl alcohol	Acetic	4	94
6	Benzyl alcohol	Propionic	4.5	90
7	Benzyl alcohol	Pivalic	6	85
8	Geraniol	Acetic	5	90
9	Geraniol	Pivalic	6	87
10	Furfuryl alcohol	Acetic	5	84
11	Prenyl alcohol	Acetic	6	70
12	Linalool	Pivalic	15	40
13	Phenol	Acetic	10	85 ^b
14	Catachol	Acetic	9	98 ^c
15	Glycerol	Acetic	6	96 ^d
16	Glycerol	Pivalic	8	75 ^d
17	D-Mannitol	Acetic	10	94 ^e
18	Butyl amine	Pivalic	5.0	90 ^f
19	Cyclohexyl amine	Acetic	3.5	97 ^f
20	Diisopropylamine	Acetic	2.5	90 ^f
21	Diisopropylamine	Pivalic	2	91 ^f
22	Benzyl amine	Acetic	4.5	95 ^f
23	Aniline	Acetic	3	99 ^f
24	Aniline	Pivalic	5	95 ^f

^a Yields refer to the pure and isolated product.

^b 5 Equiv. Acetic anhydride used.

^c Diacetate isolated.

^d Triacylated product isolated.

^e Hexaacetate product isolated.

^f Reaction performed at room temperature.

alyst gave only 50% of the acylated product whereas the use of ceria-yttria catalyst under our conditions afforded the corresponding acylated compounds in excellent yield (Table 4, entry 1, 5). Further, the scope of this reaction was extended to a variety of other amines and alcohols using various acylating agents (Table 4). The present procedure for acylation is quite general as a wide range of structurally varied alcohols such as open chain, cyclic, allylic, aromatic ones and polyols underwent acylation with excellent yields. Notable feature of this methodology is that wide range of structurally varied alcohols underwent pivalation reaction (Table 4, entries 2, 4, 7, 9, 12 and 16). The procedure has been extended to a variety of amines. Thus, the aromatic and aliphatic amines were successfully acetylated/pivalated at room temperature in the presence of a ceria-yttria based Lewis acid catalyst (Table 4, entries 18–24). The noteworthy feature of this reaction is that even a hindered amine was acylated in very high yield (Table 4, entries 20–21). It may be noted that the *N*-acylation of aniline with acetic anhydride under solvent-free and catalyst-free conditions gave only the moderate yield of product at our hand [9], the use of ceria-yttria catalyst under our conditions has significant effect on the reaction (Table 4, entry 23). It was observed that the reaction is chemoselective for the amino alcohols giving the *N*-acetate product only (Table 5, entry 1). Similarly the hydroxyl group of 2-mercapto ethanol reacted preferentially over the thiol (Table 5, entry 2). In the case of 1,2-diol, we observed preference in the acylation for primary alcohol over

Table 5

Chemoselective acetylation of amino alcohol, mercapto alcohol and diol catalyzed by ceria-yttria based Lewis acid catalyst

Entry	Substrate	Reaction time (h)	Product	Yield (%) ^a
1	2-Aminoethanol	4	<i>N</i> -Acetate	98 ^b
2	2-Mercaptoethanol	12	<i>O</i> -Acetate	84 ^c
3	2-Methyl-1,3-propanediol	10	Mono-acetate Di-acetate	80 ^d 10

^a Yields refer to the pure and isolated product.

^b Reaction performed at room temperature.

^c Reaction carried out at 40 °C.

secondary; however a mixture of mono and di-acylated product was obtained (Table 5, entry 3). It may be pertinent to mention here that there was no selectivity observed in the chemoselective acylation of 2-aminoethanol under solvent-free and catalyst-free conditions [9].

4. Conclusion

In conclusion, we have synthesized heterogeneous, recyclable sulfated ceria-yttria based strong Lewis acid catalyst for the first time and fully characterized by XRD, SEM, TG-DTA and BET surface area studies. Its Lewis acidity has been demonstrated by FT-IR spectrum of pyridine and desorption of ammonia studies. The Lewis acidic properties were successfully explored for the intramolecular ene reaction, chemoselective acylation of alcohol and amines.

Acknowledgements

RKP thanks the Council of Scientific and Industrial Research (CSIR), Government of India, for financial assistance.

References

- [1] S.J. Danishefsky, M. Barbachyn, J. Am. Chem. Soc. 107 (1985) 7761; S.J. Danishefsky, M.P. DeNinno, S. Chen, L. Biosvert, M. Barbachyn, J. Am. Chem. Soc. 111 (1989) 5810; S.J. Danishefsky, M.P. DeNinno, Angew. Chem. Int. Ed. Eng. 26 (1987) 15.
- [2] A.L. Germal, J.-L. Luche, J. Org. Chem. 44 (1979) 4187.
- [3] S.C. Laha, R.K. Pandey, M.D. Kadgaonkar, P. Kumar, R. Kumar, Bull. Catal. Soc. India 1 (2002) 38; M.D. Kadgaonkar, S.C. Laha, R.K. Pandey, P. Kumar, S.P. Mirajkar, R. Kumar, Catal. Today 97 (2004) 225.
- [4] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell (Eds.), Vogel's Textbook of Practical Organic Chemistry, fourth ed., ELBS, Longman, London, 1978.
- [5] N. Mizuno, H. Fujii, H. Igarashi, M. Misono, J. Am. Chem. Soc. 114 (1992) 7151.
- [6] M.J.F.M. Verhaak, A. vanDillen, J.W. Geus, Appl. Catal. 105 (1993) 251.
- [7] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, John Wiley and Sons, Inc, New York, 1991; E.F.V. Scriven, Chem. Soc. Rev. 12 (1983) 129; G. Hofle, V. Steglich, H. Vorbruggen, Angew. Chem. Int. Ed. Eng. 17 (1978) 569.
- [8] P. Sarvanan, V.K. Singh, Tetrahedron Lett. 40 (1999) 2611; S. Chandrasekhar, T. Ramchander, M. Takhi, Tetrahedron Lett. 39 (1998) 3263;

- P.A. Procopiou, S.P.D. Baugh, S.S. Flack, G.G.A. Ingliss, J. Org. Chem. 63 (1998) 2342;
- K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, J. Am. Chem. Soc. 117 (1995) 4413;
- G.M. Barrett, D.C. Braddock, Chem. Commun. (1997) 351;
- J. Iqbal, R.R. Srivastva, J. Org. Chem. 57 (1992) 2001;
- E. Vedejs, S.T. Diver, J. Am. Chem. Soc. 115 (1993) 3358;
- A. Orita, C. Tanahashi, A. Kakuda, J. Otera, Angew. Chem. Int. Ed. 39 (2000) 2877;
- S.P. Chavan, R. Anand, K. Pasupathy, B.S. Rao, Green Chem. (2001) 320;
- P. Kumar, R.K. Pandey, M.S. Bodas, M.K. Dongare, Synlett (2001) 206;
- P. Kumar, R.K. Pandey, M.S. Bodas, S.P. Dagade, M.K. Dongare, A.V. Ramaswamy, J. Mol. Catal. A: Chem. 181 (2002) 207;
- R. Gosh, S. Maiti, A. Chakraborty, Tetrahedron Lett. 46 (2005) 147.
- [9] B.C. Ranu, S.S. Dey, A. Hazra, Synlett 5 (2003) 44.