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Lanthanum Triflate Anchored SBA-15 is an Effective Catalyst for the Nitration of Alkyl Aromatics

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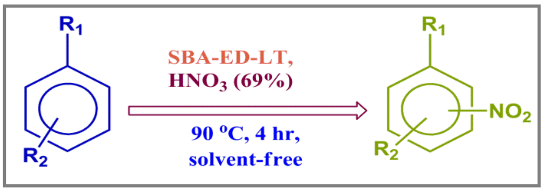
ABSTRACT

Aiming to develop an atom economic processes for efficient nitration of alkyl aromatics with minimal environmental waste with water as only by-product is an emerging trend in view of green aspects.We sought to harness in the preparation of novel solid acid catalyst with water tolerant lewis acidity and the use of catalytic quantities of lanthanum (III) triflates are studied in the nitration of alkyl aromatics. A series of lanthanum triflate loadings are anchored on diamine functionalized SBA-15 catalysts are synthesized and are well characterized by XRD, N_2 sorption, FT-IR,TGA techniques etc.These catalysts exhibited high catalytic activity with good to excellent yields using a stoichiometric amount of 69% nitric acid. Furthermore the catalyst is readily recycled by an easy separating process.

Graphical Abstract



Nitration on SBA-ED-LT catalyst.

Keywords: Lanthanum (III) triflate, SBA-15, Aromatic nitration.

INTRODUCTION

Aromatic nitration is highly important process in the chemical industries for the production of nitro intermediates that are widely used in dyes, pharmaceuticals, agro chemicals, plastics and explosives [1, 2]. The nitration procedure conventionally requires the use of potent mixture of concentrated HNO_3 as nitrating agent with concentrated sulphuric acid. This methodology is still extensively applied in manufacturing process because of its high efficiency and low cost. However, a large amount of acid waste after the tedious work-up procedures often causes serious environmental problems. To perform atom economic processes with minimal or no environmentally unfriendly by-products [3], development of novel catalyst systems that facilitate aromatic nitration in this manner should be of great importance [4].

With the increasing demand for environmentally benign processes, researchers have made extensive efforts to develop many alternative nitrating systems like modified silica [5], sulphuric acid on silica [6], boron trifluoride [7], metal exchanged clays [8, 9], acidic zeolites [10,11], sulfated titania [12, 13], metal oxide [14, 15], ionic liquids[16], and silica supported $H_4PW_{11}VO_{40}$ [17]. During recent years, the transition metallic lanthanide (III) triflates [$Ln(OTf)_3$, Ln=La−Lu] have emerged into the spotlight as novel Lewis acid catalysts for aromatic nitrations with HNO_3 and exhibited high efficiencies [18–21].

Lanthanides have found to be ever-increasing use as mild and selective reagents in organic synthesis. [22] In particular, lanthanide (III) triflates [23, 24] have been used to superior effect as Lewis acids in Diels–Alder [25], Michael [26], Friedel–Crafts [27] and Mukaiyama [28] reactions. In addition, other triflates like Zirconium and Hafnium (IV) triflates [29], scandium (III) triflate [30] and Bismuth (III) triflate [31] were reported. Unfortunately, the majority of these above catalytic nitration methods disable them for applications due to some dis-advantages such as only a little reusability or even unrecyclability of catalysts, acid anhydride involvement, poor conversion, requirements for water removing during the reactions, and complicated preparation of the catalysts. Therefore, there is need for new, environmentally friendly, economic and efficient nitration protocols under mild condition.

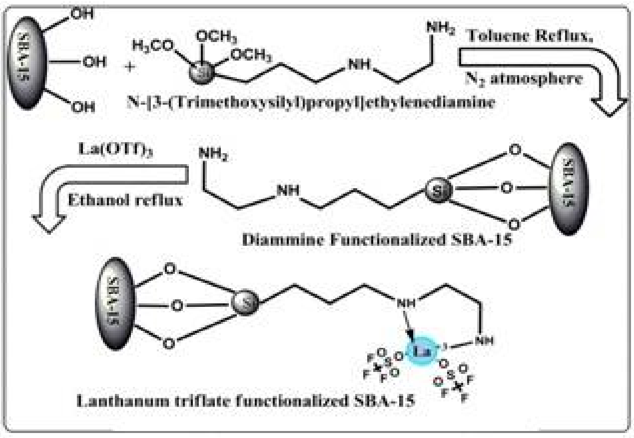
Mesoporous SBA-15 silica has been used as a potential catalyst support since its first synthesis [23, 24] because of its interesting textural properties, such as large specific surface area, uniform pore size, framework of thick walls, small crystallite size of primary particles and complementary textural porosity including its high surface-to-volume ratio, variable frame work composition and high thermal stability [25-28]. In this paper, selecting *m*-xylene as the model substrate, we investigate the catalytic performance of lanthanum triflate anchored SBA-15(SBA-ED-LT) in aromatic nitration with commercial HNO_3 as nitrating agent. We sought to harness this water tolerant Lewis acidity and herein report the use of catalytic quantities of lanthanum (III) triflates for the nitration of a range of simple aromatic compounds in good to excellent yield using a stoichiometric amount of 69% nitric acid where the only by-product is water. Furthermore the catalyst is readily recycled by an easy separating process.

MATERIALS AND METHODS

Preparation of Lanthanum triflate anchored SBA-15: SBA-15 was synthesized in accordance with the literature procedures [33-42].A solution of $EO_{20}PO_{70}EO_{20}$:2M HCl: TEOS:H_2O = 2:60:4.25:15 (mass ratio) was prepared, stirred for 24 h at 40°C and then hydrothermally treated at 100°C under static condition for 24 h. Subsequently it was filtered, dried at 100°C and calcined at 550°C for 6 h, to yield mesoporous silica SBA-15 as a white powder.

Prior to the functionalization procedure, the parent SBA-15 was dried in an oven at 120°C overnight under vacuum, to remove any physisorbed water. In a post synthetic approach, 1 g of degassed SBA-15 was dispersed in 50 mL of dry toluene under N_2 atmosphere, then 3 mL of N[3-(trimethoxysilyl)propyl]-ethylene diammine (TPED) was added and the mixture was refluxed for 24 h under anhydrous conditions. The solid product was recovered by filtration under vacuum, washed with 50 mL of toluene and dried at 120°C in an oven for 12 h, designated as SBA-ED.

Lanthanum Triflate SBA-15(SBA-ED-LT) was prepared through anchoring of lanthanum triflate on the surface of diammine functionalised mesoporous silica (SBA-ED) as shown in Scheme 1. Typically to 1g of SBA-NH_2, requisite amount of lanthanum (III) triflate loading was added in ethanol solution and refluxed overnight. It was then filtered, washed with ethanol to remove unanchored lanthanum triflate and dried at 100°C to yield the lanthanum triflate functionalised SBA-15(SBA-ED-LT).



Scheme 1. Synthesis of SBA-ED-LT catalyst.

Characterization: X-ray diffraction (XRD) patterns of the catalyst samples were recorded at room temperature on an X-ray diffractometer (Multiflex, Rigaku, Japan) with a nickel filtered Cu Kα radiation. N_2 adsorption-desorption isotherms were recorded on a N_2 adsorption unit at -196°C (Quadrusorb-SI V 5.06, Quantachrome Instruments Corporation, USA). The samples were out-gassed at 150°C for 4 h before the measurement. FT-IR spectra were obtained over the wave number range of 4000 to 400 cm^{-1} with a spectral resolution of 2 cm^{-1} on a Perkin Elmer FT-IR spectrometer (Spectrum GX).

Catalytic activity: All the chemicals were used without further purification. *m*-xylene (purity >99%), Lanthanum Triflate (purity >99%), from Sigma Aldrich and nitric acid (purity 69-72%), were obtained from s-d fine chemicals, India. The catalytic activity of the Lanthanum triflate functionalized SBA-15 for nitration taking *m*-xylene as a model substrate was carried out under solvent-free conditions. The following procedure is representative. Nitric acid (69%; 126 mg, 2 mmol), *m*-xylene (106 mg, 1 mmol) were added to SBDALT catalyst (50 mg,) stirred mixture was heated at 90° C for 4 h under solvent-free conditions. The product analysis was carried out using a gas chromatograph (GC-17A, Shimadzu Instruments, Japan) with an Equity-5 capillary column (0.53 mm×30 m) with FID detector. The products were confirmed using a GC-MS (QP-5050 model, Shimadzu Instruments, Japan) equipped with a DB-5 capillary column (0.32 mm dia. and 25 m length, J and W Scientific, USA).

RESULTS AND DISCUSSION

The synthesis procedure is depicted in scheme 1. At first, the mesoporous SBA-15 was functionalized with TPED followed by anchoring with lanthanum triflate led to the formation of SBA-ED-LT. Low-angle X-ray diffraction (XRD) patterns of the functionalised SBA-15 catalysts along with the parent SBA-15 are shown in figure 1, which exhibited three typical diffraction lines at 0.91°, 1.57° and 1.82° respectively on the 2θ scale that are indexable as

(100), (110) and (200) reflections associated with p6 mm hexagonal symmetry. The mesoporous structure is well retained in all the functionalized catalysts. The decrease in the intensity of (110) and (200) planes are observed which indicates the partial lowering of degree of orderness.

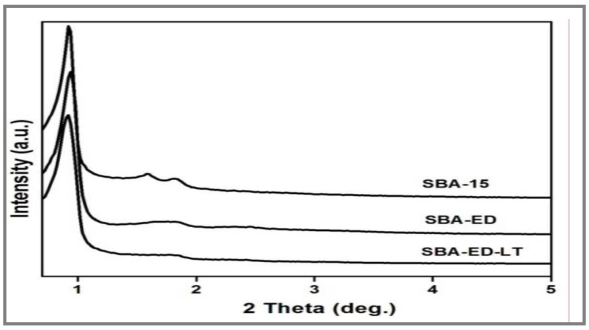


Figure 1. Low angle XRD patterns of SBA-15 and functionalized SBA-15 catalysts.

Table 1. Textural and structural parameters of functionalized SBA-15 samples obtained from N_2 sorption data

Catalyst	S_{BET} [a] (m^2/g)	V_t [b] (cc/g)	d [c] (nm)
SBA-15	635	1.086	7.233
SBA- ED	320	0.476	5.245
SBA-ED-LT	148	0.201	4.560

[a] BET surface area; [b] Total pore volume; [c] BJH pore diameter.

Figure 2 shows the N_2 adsorption-desorption isotherms of SBA-ED-LT catalysts together with that of pure SBA-15. The isotherms obtained for pure SBA-15 and functionalized catalysts are of type IV and exhibited a hysteresis loop of H1 type and a sharp capillary condensation step in the P/P_0 range of 0.6-0.8, which is a characteristic of large channel-like pores with a narrow pore size distribution (PSD). The surface area is calculated by using the BET model and pore size is estimated by BJH method as shown in table 1. The total volumes of mesopores are calculated from the amounts of nitrogen adsorbed at P/P_0 of 0.98, assuming that adsorptions on the external surface were negligible compared with the adsorption in pores. The PSD curves of all the catalysts are shown in figure 3. There is a decrease in the total pore volume of the SBA-ED-LT sample as compared with that of pure SBA-15 due to pore blockage by functionalizing ligand and Lanthanum triflate on the framework of SBA-15.

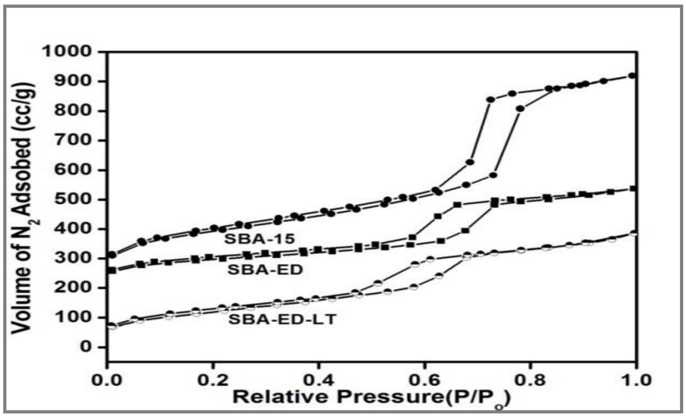


Figure 2. N_2 adsorption-desorption isotherms of SBA-15 and functionalized SBA-15 catalysts.

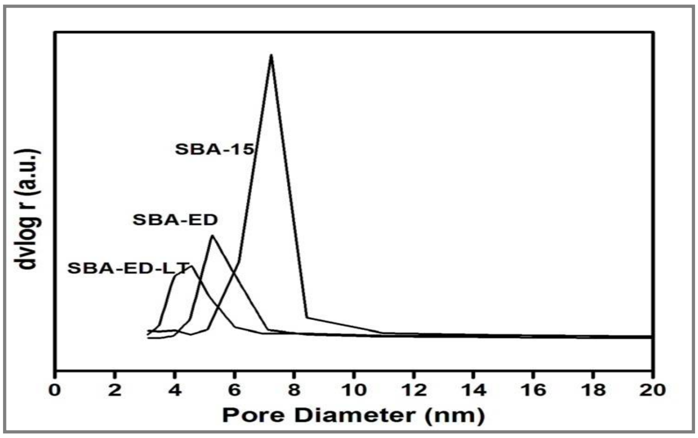


Figure 3. Pore size distribution curves of SBA-15 and functionalized SBA-15 catalysts.

The FT-IR spectra of SBA-15, SBA-ED and SBA-ED-LT are depicted in figure 4. The band at 1630 cm^{-1} may be assigned to the O–H vibrations of physisorbed water. The Si–O–Si bands originate from SBA-15 and are observed around 1085, 805, and 462 cm^{-1}. The peaks positioned at 972 $cm^{-1}$is assigned to the vibration of the silanol groups (Si–OH) in SBA-15. The bands at 694, 1475, 3270cm^{-1} correspond to bending and stretching vibrations of the N–H bond. The band at 2944 cm^{-1} assigned to the stretching vibration of $–CH_2$ group. The decrease in intensity of the peaks at 972 and 1635 cm^{-1} with generation of new bands at 694 cm^{-1} confirms the consumption of surface –OH groups and formation of covalent anchoring with TPED functionalizing ligand. The band at 1420 cm^{-1} was assigned to the stretching vibration of S=O, which attributed to the sulfonate group of lanthanum (III) triflate loaded on SBA-ED. The SBA-ED-LT sample showed four characteristic bands at 1470 cm^{-1}(C-N), 763 cm^{-1} (C-S), 642 cm^{-1} ($>SO_2$). The appearance of new bands at 642 and 763 cm^{-1} and an increase in the intensity of the IR bands at 1085, 805, and 462 cm^{-1} compared with SBA-ED may be considered as a proof for the successful incorporation of lanthanum triflate in the channels of SBA-ED-LT. Further, CHNS elemental analysis confirmed amount of lanthanum triflate.

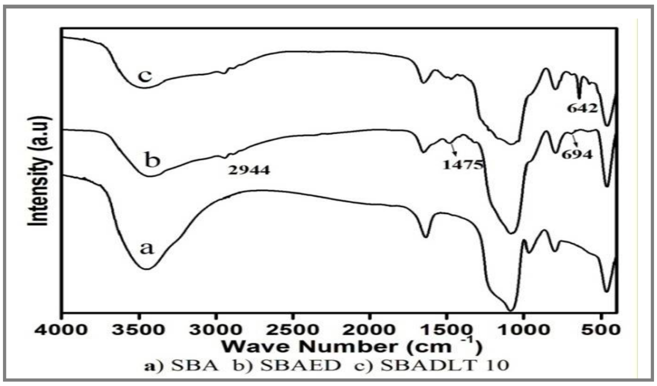


Figure 4. FTIR Spectrum of functionalized SBA-15 samples.

The thermal stability of the catalyst is studied by thermo gravimetric analysis (TGA). The thermal behavior of SBA-15, SBA-ED and SBA-ED-LT are shown in figure 5. A marginal weight loss is observed in SBA-15. For the samples SBA-ED and SBA-ED-LT, two weight loss stages are observed in the TGA curve. The first region, which occurred below 130°C was corresponded to the loss of physisorbed water from the catalyst. In the second stage, weight loss was about 12.5 wt%, which could be attributed to the loss of organic components attached to the surface. The major weight loss is observed in SBA-ED-LT catalyst from 280 to 500°C due to the decomposition of anchored lanthanum triflate. From the above results, it is concluded that the metal triflate moiety was covalently anchored on the surface of SBA-ED.

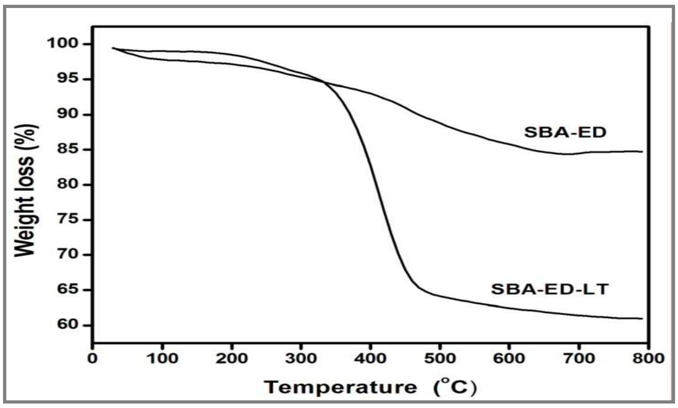
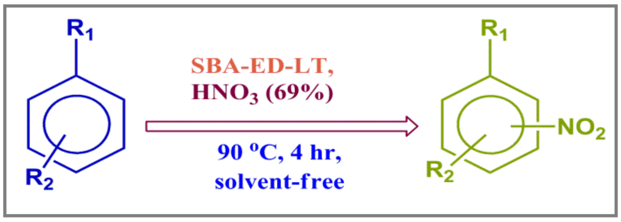


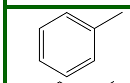
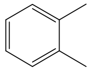
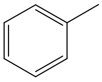
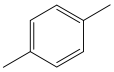
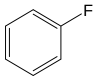
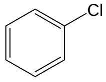
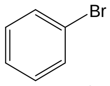
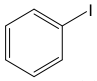
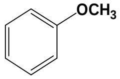
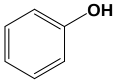
Figure 5. TGA curves of functionalized SBA-15 samples.



Scheme 2. Nitration on SBA-ED-LT catalyst.

The nitration of various aromatic substrates over SBA-ED-LT catalyst has been schematically presented in Scheme 2. To understand the nature of lanthanum triflate on SBA-15 catalyst, initial experiments were conducted using *m*-xylene as a substrate and 69% HNO_3 as a nitrating agent under solvent-free conditions. Subsequently, the reaction parameters like *m*-xylene-to-HNO_3 mole ratio, amount of catalyst, reaction time and reaction temperature are optimized. As per the results obtained, it is found that the optimum reaction time is 4hr, amount of catalyst is 50 mg and *m*-xylene -to -HNO_3 molar ratio is 1: 2 and it gives maximum conversion of 98% with selectivity of 1,3-Dimethyl- 2-nitrobenzene 14% and 1,3-dimethyl-4-nitrobenzene 86% as nitration products are obtained. No di-nitrated products are observed. To authenticate the superior activity of SBA-ED-LT catalyst, the SBA-ED and SBA-15 materials were also studied and their activity details are presented in Table 6. In order to check the recyclability of SBA-ED-LT catalyst, the catalyst was isolated from the product mixture by centrifugation, washed with acetone, dried at 120°C for 6 h and re-used under the above mentioned optimized reaction conditions (Figure 6). It is found that there is no considerable efficiency loss in activity for at least for five repeated cycles. The scope of SBA-ED-LT catalyst for the nitration of aromatic compounds other than *m*-xylene has also been verified taking substituted arenes such as toluene, ortho, para xylenes and halo benzenes. It is found that all the substrates were smoothly converted into their respective mononitrated products with traces of oxidized products. The details of the different substrate conversions under optimized conditions are displayed in table 2.

Table 2. Nitration of different aromatic substrates

Substrate	Conversion (%)	Selectivity (%)		
		a	b	c
	100	63	36	01
	92	54	46	--
	98	86	14	--
	95	98	--	02
	98	89	10	01
	51	54	38	08
	38	85	10	05
	16	82	11	07
	72	78	22	--
	86	13	87	-

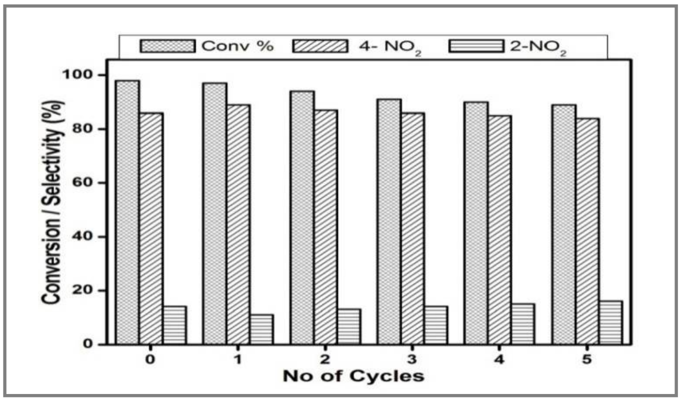


Figure 6. The recyclability of SBA -ED-LT catalyst.

APPLICATION

We believe this to be a significant step forward in the area of clean technology for aromatic nitration. This programme of research has in addition had many spin-off discoveries and developments of significance to green chemistry.

CONCLUSION

We have developed an environmentally acceptable nitration procedure with our initial investigations commencing with the commercially available lanthanum (III) triflate, which is anchored on SBA-15 and used for nitration under solvent-free conditions. Maximum conversion of reaction was achieved for SBA-ED-LT. In all cases the nitration systems use a double equivalent of nitric acid, the only side-product is water and the catalysts may be recycled and reused.

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