



Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Nature of the acid sites in the metal triflates immobilized in SBA-15 and their role in the Friedel–Crafts acylation of naphthalene

S. Selvakumar, Narendra M. Gupta^{1,*}, A.P. Singh^{**}

Inorganic and Catalysis Division, National Chemical Laboratory, Pune 411008, India

ARTICLE INFO

ABSTRACT

Article history: Received 28 June 2009 Received in revised form 10 October 2009 Accepted 13 October 2009 Available online 21 October 2009

Keywords: Acylation Metal triflate Mesoporous silica Naphthalene

1. Introduction

Metal triflates and other triflate derivatives are known to serve as efficient homogeneous catalysts in the Lewis acid-catalyzed reactions for organic synthesis [1]. In addition to strong Lewis acidity, these compounds are found to exhibit a reasonably good tolerance towards water. A large number of metal triflate catalysts have therefore been reported for the Friedel-Crafts alkylation and acylation reactions. Olah et al. reported that the triflates of boron, aluminium, and gallium serve as very efficient Friedel-Crafts catalysts for the alkylation, isomerization, and acylation reactions [2]. Tsuchimoto et al. found that $Sc(OTf)_3$ was the most efficient catalyst among the rare earth metal triflates screened for the benzylation of benzene with benzyl alcohol [3]. Several studies in the last few years have reported on the heterogenization of triflic acid, in order to facilitate the separation of the catalyst from reaction medium and also to enhance the catalyst efficiency by providing a higher dispersion [4-8]. Accordingly, certain silicasupported triflates and triflic acid are found to be active and selective catalysts for certain organic synthesis reactions, such as: rearrangement of α -pinene oxide to campholenic aldehyde [6], polymerization and depolymerization of cyclic ethers [5], Friedel-Crafts reactions [7,8], and alkylation of isobutane with *n*-butene

The Zn-triflate molecules loaded (5–30 mol%) in mesoporous SBA-15 silicate exhibited considerably higher catalytic activity for liquid-phase Friedel–Crafts (FC) acylation of naphthalene with *p*-toluoyl chloride, as compared to the corresponding triflates of La, Ce and Y. In situ FTIR studies revealed that the triflate molecules occluded in the channels of SBA-15 may cause severe perturbation of surface hydroxyl groups, without undergoing an electronic binding. The metal cations of the triflate molecules, on the other hand, participated in direct bonding of the reactant molecules and also helped in the formation of some Brönsted type surface acid sites. This article discusses the role of the acid sites generated on occlusion of metal triflates in SBA-15, as monitored by using NH₃-TPD and pyridine-IR spectroscopy, in the Friedel–Crafts acylation of naphthalene.

© 2009 Elsevier B.V. All rights reserved.

[9]. There are, however, very few reports on the catalytic properties of metal triflates supported on the ordered mesoporous silica. The objective of the present study was to incorporate several metal triflates in the pores of mesoporous SBA-15. The mesoporous molecular sieve SBA-15 was chosen because of its better thermal stability and its unique pore topology comprising of the hexagonally arranged parallel mesopore channels [10,11]. Such pore structures are known to serve as ideal hosts where the mesopore channels assist in the transport of reactants or products without much diffusional resistance, and at the same time they provide a large surface area to enhance the number of the reaction sites. In this paper, we describe the catalytic properties of different metal triflates, viz. La(OTf)₃, Ce(OTf)₄, Y(OTf)₃, and Zn(OTf)₂, supported on SBA-15 for the acylation of naphthalene using ptoluoyl chloride as acylating agent to produce naphthalen-2-yl(ptolyl)methanone (2-acyl naphthalene). These compounds find application as a dye intermediate and also in the photoisomerization of cis- and trans-stilbene. In situ IR studies of pyridine adsorption could monitor the triflate-induced acid sites responsible for the FC reaction mentioned above.

2. Experimental

2.1. Materials

The precursor chemicals, i.e. Pluronic 123 (P123, average Mol. Wt = 5800), *p*-toluoyl chloride (Aldrich), tetraethylorthosilicate (Merck), metal triflates (Acros Organics) and naphthalene (S.D. fine chemical) were of research grade and were utilized without further purification.

^{*} Corresponding author. Tel.: +91 20 25902008.

^{**} Corresponding author. Tel.: +91 20 25902497; fax: +912025902633.

E-mail addresses: nm.gupta@ncl.res.in (N.M. Gupta), ap.singh@ncl.res.in (A.P. Singh).

¹ Emeritus Scientist, CSIR.

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2009.10.021

2.2. Synthesis of siliceous SBA-15

The synthesis of mesoporous SBA-15 was carried out hydrothermally under the autogeneous pressure of an autoclave. The polymer surfactant P123 was used as a template and hydrochloric acid served as a mineralizer. The following was the gel composition.

 $0.043\,TEOS:\,4.4\,g\,P123\,M_{avg}$

 $= 5800 [EO_{20} - PO_{70} - EO_{20}] : 8.33 H_2O : 0.24 HCl$

Typically, 4.4 g of tri block co-polymer dispersed in 30 g of distilled water was stirred for 1.5 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and the stirring was continued for 2 h. Finally, 9 g of TEOS was added drop wise and the mixture was maintained at 40 °C for 24 h with continuous stirring. The mass was submitted to a hydrothermal treatment (100 °C, 48 h) under static condition. The precipitate was filtered, washed with distilled water, dried in an oven (90 °C, 12 h) and then calcined in air (500 °C, 6 h) to remove the template completely.

The catalysts were prepared by soaking each calcined SBA-15 sample in an acetonitrile solution of a metal triflate powder, accompanied with continuous stirring for 8–10 h. The excess of acetonitrile was evaporated to dryness under reduced pressure, followed by complete drying at 120 °C. The functionalized samples are designated in the text as Zn-Tf (30)/SBA, where the number in the parentheses represents the triflate loading in mol%.

2.3. Characterization

The powder X-ray diffraction patterns were recorded by using a X'Pert Pro (M/s Panalytical) diffractometer using a Ni filter and CuKα radiation and a proportional counter as detector. A divergent slit of $1/8^{\circ}$ in the primary optics and an anti-scatter slit of $1/4^{\circ}$ in the secondary optics were employed to measure the data in the low angle region. The XRD patterns were recorded in the 2θ range between 0.5° and 5° at a scan rate of $1^{\circ}/\text{min}$. N₂ adsorption experiments were conducted at 77 K using a NOVA 1200 (Quanta chrome) apparatus for analyzing the surface area (BET) and poresize distribution in the synthesized samples. A pore-size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherms. FTIR spectra of solid samples were recorded in the range of 4000–400 cm⁻¹ to monitor the nature of the triflate bonding with the host matrix. Thin sample wafers (ca. 20 mol% of catalyst mixed with KBr powder) were used for this purpose after proper drying and the spectra were recorded in transmission mode using a Shimadzu model-8201 spectrophotometer. Thermo gravimetric analyses (TGA and DTA) were performed using a Diamond TG/DTA instrument at a heating rate of 10 °C/min under airflow. Experiments on the saturation adsorption of ammonia and its subsequent temperature-programmed desorption (TPD-NH₃) were performed on a Micromeritics Autochem 2910 instrument. About 0.1 g of a fresh sample was placed in a U-shaped, flow-through, quartz micro reactor for each experiment. The catalyst was activated at 220 °C for 2 h under helium flow (30 ml/min) and then cooled to 100 °C before being exposed to ammonia. Each sample was flushed again in He for 1 h to remove any physisorbed ammonia, and the desorption profile was then recorded by increasing the sample temperature from 100 to 900 °C at a ramp rate of 10 °C/min.

2.4. Pyridine-IR studies

The nature of the acid sites in different samples was monitored by recording the transmission-mode IR spectra of adsorbed pyridine vapor. A Thermo Nicolet (model Nexus 870) FTIR equipped with a high-pressure high-temperature stainless steel cell, fitted with water-cooled CaF2 windows and described previously in detail, was utilized for this purpose [12]. Selfsupporting wafers (~50 mg) of 25 mm diameter, placed in a sample holder block, were in direct contact with a chromel-alumel thermocouple. For acidity measurements, the samples were heated in situ for 8-10 h at 550-575 K under vacuum $(\sim 1 \times 10^{-3} \text{ Torr})$ and then exposed at 400 K to multiple doses of pyridine (\sim 1.0 µmol each) for a saturation coverage. A gas mixture comprising of nitrogen + pyridine vapor was utilized for this purpose. The gas pressure in the IR cell was monitored with the help of a digital capacitance manometer. IR spectra were plotted at 400 K after equilibrating each sample for 15-20 min subsequent to each pulse injection. Spectra were also recorded at room temperature after post-exposure cooling of the sample to room temperature, followed by pumping. A total of 300 scans were coadded for plotting of each spectrum at a resolution of 4 $\rm cm^{-1}$. The numbers given in the parentheses in some of the IR spectra represent the relative absorbance values for comparison.

2.5. Friedel–Crafts (FC) acylation reaction of naphthalene with ptoluoyl chloride

Naphthalene and p-toluoyl chloride were used without further purification. The catalyst was activated at 100 °C for 2 h and the liquid-phase FC reaction was performed in batch mode using a 50 ml round-bottom flask fitted with a condenser. The reaction vessel was maintained at a temperature between 80 and 160 °C by using an oil bath. In a typical run, a mixture of naphthalene (10 mmol), p-toluoyl chloride (10 mmol), nitrobenzene (5 ml) and activated catalyst (0.1 g), was magnetically stirred and heated to attain the desired reaction temperature. The product samples were withdrawn at regular intervals of time and analyzed periodically on a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector and a capillary column (5 µm thick crosslinked methyl silicone gum, $0.2 \text{ mm} \times 50 \text{ m}$ long). The main product, naphthalen-2-yl(p-tolyl)methanone was separated by column chromatography and confirmed by GC–MS, ¹H NMR and ¹³C NMR analyse, ¹H NMR (CDCl₃, 200 MHz) δ 2.42 (s, 3H), 7.23– 8.25 (m, 11 H) ppm. 13 C NMR (CDCl₃, 50 MHz) δ 21.71, 124.34, 125.7, 126.36, 127.08, 127.31, 128.33, 129.14, 129.17, 130.23, 130.56, 130.92, 144.20, 144.56, 197.75.

3. Results

3.1. X-ray diffraction (XRD)

Fig. 1 shows the representative XRD patterns of calcined SBA-15, without (curve (a)) and after functionalization with 30 mol% of different metal triflates (curves (b–e)). The triflate containing samples exhibited a XRD pattern similar to that of SBA-15, where three well-resolved diffraction peaks due to {1 0 0}, {1 1 0}, and {2 0 0} reflections were observed. These reflections correspond to the two dimensional hexagonal *p*6*mm* symmetry, a characteristic of well defined SBA-15 mesoporous material. The XRD patterns in Fig. 1(b–e) thus confirm the integrity of the characteristic hexagonal structure of SBA-15 in the triflate loaded samples. A progressive decrease observed in the intensity of the XRD lines, however, reveals a partial loss of long-range order of SBA-15 due to the incorporation of triflate molecules. The values of the unit cell parameter (a_0) of SBA-15 and of the corresponding triflatemodified samples are given in Table 1.

3.2. Nitrogen sorption studies

The functionalized SBA-15 samples displayed type-IV isotherms with H1 hysteresis, a characteristic feature of the highly



Fig. 1. Low angle powder-XRD patterns of metal triflate loaded SBA-15. (b) Zn-Tr (30)/SBA, (c) Y-Tr (30)/SBA, (d) La-Tr (30)/SBA and (e) Ce-Tr (30)/SBA. Curve (a) is a comparative XRD pattern of pure SBA-15.

ordered mesoporous materials. The BET surface area (S_{BET}) and total pore volume (V_{total}) of SBA-15 was found to decrease progressively with increasing loading of metal triflate, as shown in the data given in Table 1. Thus, in a representative case, the loading of 30 mol% zinc triflate in SBA-15 resulted in the decrease of surface area from 684.3 to 550.3 m² g⁻¹. This trend may be attributed to the ingress of triflate molecules in the pore structure and also to the partial collapse of host structure, as revealed by the XRD results in Fig. 1.

3.3. Thermal analysis

The thermal stability of the catalysts was checked by thermo gravimetric analysis in air atmosphere from 30 to 1000 °C with a temperature ramp of 10 °C/min. That pure zinc triflate decomposes at ~540 °C, but its decomposition in the case of SBA-supported samples occurs at a lower temperature (~435 °C). A similar lowering of TG peak temperature was observed in the case of SBA-15 samples containing other metal triflates. This may be ascribed to the reaction of highly dispersed $Zn(OTf)_2$ with the surface hydroxyl groups on SBA-15 at elevated temperature to produce ZnF_2 and $ZnSO_4$ [13]. A similar observation has been reported in the earlier studies on the triflic acid supported over mesoporous materials [4,6]. The –OH groups on silica are found to promote such thermal reactions of triflic acid [14]. Since no measurable weight loss is observed at the temperatures lower than 400 °C, besides a small peak at about 100 °C due to a small amount of adsorbed



Fig. 2. Ammonia TPD profiles of (a) pure SBA-15, (b) Zn-Tr (30)/SBA, (c) Ce-Tr (30)/SBA, (d) La-Tr (30)/SBA and (e) Y-Tr (30)/SBA.

moisture (figure not shown), it is imperative that the triflate molecules are immobilized firmly in the channels of SBA-15 and are thermally stable at the temperatures up to 400 $^{\circ}$ C.

3.4. Acidity measurement

Curves (b–e) in Fig. 2 exhibit the temperature-programmed desorption (TPD) profiles of ammonia, recorded on SBA-15 samples containing different metal triflates at a uniform loading of 30 mol%. The pristine SBA-15 showed negligibly small adsorption of ammonia and the comparative TPD profile is shown in curve (a). The intensity of the TPD profiles in curves (b–e) was found to vary progressively with triflate loading. The density of acid sites in different catalyst samples, as computed from the area under each TPD profile, is included in Table 1. As shown in Table 1, the density of the acid sites is considerably higher in zinc triflate loaded SBA-15, as compared to the samples containing rare earth triflates.

Furthermore, the TPD results in Fig. 2 display the presence of at least three distinct ammonia adsorption sites. The high temperature of the desorption peaks (>325 °C) in this figure is indicative of the strong acidic character of the synthesized catalysts. These results also reveal that the acid strength distribution may depend strongly on the cation associated with a triflate molecule. For instance, the Zn-triflate containing sample exhibited a distinct NH₃ TPD peak at a higher temperature of ~450 °C (curve (b)), as compared to the samples containing similar loading of rare earth metal triflates (Fig. 2, curves (c–e)). These results conform with the pyridine-IR results described below, where the presence of distinct Lewis acid sites in Zn-Tr–SBA is demonstrated.

Table '	1
---------	---

Physico-chemical	properties (of metal	triflate-grafted	SBA-15	catalysts
------------------	--------------	----------	------------------	--------	-----------

Sample	$d_{100}({\rm \AA})$	<i>a</i> ₀ (Å) ^a	Total acidity $(mmol NH_3/g)^b$	Pore diameter (Å)	Pore volume $(cm^3 g^{-1})$	$S_{\rm BET}(m^2g^{-1})$
Calcined SBA-15	93.85	109.5	0.01	84.3	0.94	684.3
Zn-Tr (10)/SBA	100.31	115.2	2.85	81.0	0.90	628.3
Zn-Tr (30)/SBA	101.31	116.4	9.13	75.0	0.74	550.3
Ce-Tr (30)/SBA	101.31	116.4	6.96	-	-	575.3
Y-Tr (30)/SBA	101.31	116.4	6.20	_	-	525.6
La-Tr (30)/SBA	101.31	116.4	7.01	-	-	518.6

^a Unit cell parameter $(a_0) = d_{1 0 0} \times 2/\sqrt{3}$.

^b Measured by using TPD-NH₃ method.

Table 2

Assignment of IR band frequency (cm⁻¹) of zinc triflate, without and after grafting in SBA-15.

IR band frequency $(cm^{-1})^a$		Assignment
Zinc triflate	Zn-Tr (30)/SBA	
520	519	δ_{as} (SO ₃)
576	578	δ_{as} (CF ₃)
645	650	$\delta_{\rm s}$ (SO ₃)
768	-	$\delta_{\rm s}$ (CF ₃)+ $\nu_{\rm s}$ (CS)
1033	1035	$\nu_{\rm s}$ (SO ₃)
1180	1182	v_{as} (CF ₃)
1245	-	$\nu_{\rm s}$ (CF ₃)
1270	1270	v_{as} (SO ₃)
1346	-	ν_{as} (SO ₃)

Notations: ν , bond stretch; δ , group angle deformation; s, symmetric stretch; as, asymmetric stretch.

^a Assignments as per the references [17,18].

3.5. IR spectroscopy results

3.5.1. FTIR Spectra of triflate loaded SBA-15

The mid-IR region spectrum of a representative Zn-Tr (30)/SBA catalyst, recorded after compensating for the framework vibrational bands of pure SBA-15 in this region with pure zinc triflate, is given in Table 2. The comparison of the IR spectra reveals clearly that the frequency of different vibrational bands of zinc triflate molecules remained mostly unchanged on immobilization in mesoporous SBA-15. Significant changes are, however, noticeable in the relative intensity of different stretching and deformation mode vibrational bands arising due to SO₃ and CF₃ groups of the triflate ions. These results are indicative of certain perturbations experienced by the occluded triflate molecules, as discussed later in the text.

3.5.2. Effect of triflate and pyridine loading on hydroxyl region bands of SBA-15

The IR spectrum of calcined SBA-15, recorded at 400 K after evacuation of the sample at 525 K for 8 h, exhibited a prominent sharp band at 3740 cm⁻¹ in addition to a weak and broad absorption band in the 3650–3450 cm⁻¹ region. As is well reported, the 3740 cm⁻¹ band arises due to the non-acidic terminal silanol stretching vibrations while the lower frequency absorption band is assigned to the hydrogen-bonded internal SiOH groups in mesoporous silicates [15].

The intensity of both these $\nu(OH)$ vibrational bands was found to decrease progressively when the increasing amounts of a particular metal triflate were loaded into SBA-15. No measurable shift was observed in the frequency of these $\nu(OH)$ bands in all the samples, irrespective of the nature or the amount of triflate introduced. Plot (a) in Fig. 3 shows the progressive variation in the intensity of 3740 cm⁻¹ ν (OH) band as a function of zinc triflate loading. A decrease by a factor of \sim 70% in the intensity of 3740 cm^{-1} band is noticeable in Fig. 3(a) at the saturation loading of zinc triflate. A much smaller (~25%) decrease in the intensity of this $\nu(OH)$ band was observed for adsorption of pyridine vapor in SBA-15, even after saturation coverage. These results are presented in Fig. 3(b). Again, no shift was observed in the frequency of the ν (OH) bands. Interesting results were observed when the pyridine vapor was dosed over triflate loaded SBA-15 under the identical condition. The representative results on the relative intensity of 3740 cm⁻¹ band for different loadings of pyridine in Zn-Tr (10)/ SBA samples are shown in curve (c) of Fig. 3. We observe in this case that, even though the intensity of v(OH) band has attained a saturation after the loading of triflate alone (cf. Fig. 3(a)), a further decrease in the intensity took place as a result of subsequent pyridine loading (Fig. 3(c)). At the same time, the adsorption of pyridine over Zn-Tr/SBA gave rise to a strong band at \sim 3480 cm⁻¹,



Fig. 3. The relative intensity (absorbance) of 3740 cm⁻¹ band as a function of: curve (a) loading of zinc triflate in SBA-15, (b) pyridine adsorption over SBA-15, and (c) pyridine adsorption over Zn-Tr (10)/SBA.

the intensity increasing systematically with the increase in the amount of adsorbed pyridine. A similar trend has been reported earlier for the adsorption of pyridine over MCM-41 [15]. Fig. 4 displays the IR spectra of Zn-Tr (10)/SBA samples for the dosing of 0–7 μ mol of pyridine vapor. We observed here that the growth of the 3480 cm⁻¹ band matches well with the decrease in the intensity of the 3740 cm⁻¹ band. The intensity of this new band at ~3480 cm⁻¹ was however quite low in the case of the pyridine adsorption over triflate-free SBA-15 and it was found to merge with the broad IR band in 3700–3600 cm⁻¹ region. These results indicate that the perturbation of –OH groups in SBA-15 is more severe on occlusion of triflate molecules alone as compared to when pyridine vapor was adsorbed. The data presented in Fig. 3(c)



Fig. 4. The relative intensity of O–H stretching bands of Zn–Tr (10)/SBA on exposure to different amounts of pyridine. Amount of pyridine in μ mol: Curve (a) nil, (b) 1, (c) 3 and (d) 7. The numbers given in the parentheses represent the relative absorbance values.

further reveal that the mode of pyridine binding in the pores of SBA-15 is influenced by the presence of the triflate molecules. These aspects are discussed later in more detail.

3.5.3. IR bands of adsorbed pyridine

Exposure of SBA-15 to pyridine vapor gave rise to two symmetrical broad IR bands at 1596 and 1446 cm⁻¹. Curve (c) in Fig. 5(A) exhibits a typical IR spectrum of calcined SBA-15 sample, recorded at 400 K after an exposure to 5 μ mol pyridine. For comparison, curves (a and b) in Fig. 5(A) show the IR bands of vapor and liquid-phase pyridine in this region. Whereas spectrum (a) was recorded by introducing pyridine vapor + nitrogen in the gas cell without including a catalyst sample, spectrum (b) was plotted by placing a drop of pyridine in between the two KBr pellets.

The intensity of both the IR bands at 1596 and 1446 cm⁻¹ in Fig. 5(A), (c) followed a linear relationship with the increase in the amount of pyridine adsorbed, and no saturation was observed. A plot showing typical loading dependent variation in the intensity of 1596 cm⁻¹ band for pure SBA-15 showed progressive growth of the pyridine-IR band (figure not shown), which is in contrast to the decrease observed in the intensity of 3740 cm⁻¹ –OH band, which showed a saturation effect even at 4 µmol pyridine loading [Fig. 3(b)]. This indicates clearly that the decrease in the intensity of ν (OH) bands, as seen in Fig. 3(b), may not arise due to any direct bonding of pyridine molecules to hydroxy groups.

Several new vibrational bands were detected when a triflate containing SBA-15 was exposed to pyridine vapor. Curve (d) in Fig. 5(A) presents the IR spectrum of Zn-Tr (5)/SBA sample, recorded on exposure to 5 μ mol pyridine. We find in this figure three prominent vibrational bands at 1614, 1491 and 1454 cm⁻¹, in addition to some low intensity IR bands with the frequency maxima at 1640, 1578 and 1547 cm⁻¹. The intensity of these bands was found to increase considerably for the samples containing higher amounts of zinc triflate. For instance, curve (e) in Fig. 5(A) shows the IR spectrum of Zn-Tr (10)/SBA on exposure to 5 μ mol pyridine. The numbers given in the parentheses in this figure represent the comparative absorbance values of different IR bands. The intensity values of these IR bands, however, reached saturation for the triflate loadings of 20 mol% and above. At the same time, in case of each of the zinc triflate containing samples, the intensity of

the individual bands was found to increase progressively with the increasing amount of pyridine adsorbed.

Furthermore, the frequency and the intensity of various IR bands shown in [Fig. 5(A), (e)] were found to vary considerably when different metal triflates were dispersed in SBA-15. Curves (be) in Fig. 5B exhibit IR spectra of SBA-15 samples, loaded with 30 mol% of different metal triflates and exposed uniformly to 5 µmol pyridine. Curve (a) is again a comparative IR spectrum of pyridine adsorbed over pure SBA-15. It is important to notice that instead of a pair of weak bands at 1596 and 1446 cm^{-1} in Fig. 5(B) (b-d), a new pair of IR bands is observed at 1614 and 1454 cm⁻¹ in the case of pyridine adsorption over zinc triflate containing SBA-15, Fig. 5(B) (e). Moreover, the intensity of the 1546 cm^{-1} band is found to be much smaller in the IR spectrum in Fig. 5(B) (e) as compared to that in Fig. 5(B)(b-d). A weak and overlapping IR band at ${\sim}1618~\text{cm}^{-1}$ is also noticeable (figure not shown). The IR bands shown in Fig. 5(B) were found to be fairly stable when the samples exposed to pyridine vapor at 425 K were cooled to room temperature followed by 15 min pumping.

3.6. Catalytic reactions

3.6.1. Effect of triflate loading and reaction temperature

The host material SBA-15, with no triflate loading, showed no measurable catalytic activity for acylation of naphthalene under the reaction conditions of this study. In the case of triflatefunctionalized SBA-15, the conversion of naphthalene was found to increase progressively with the increase in the triflate loading. Also, the best results were obtained by using the equi-molar mixture of the reactants, i.e. naphthalene + p-toluovl chloride (p-TC). The conversion of naphthalene was found to decrease drastically for smaller amounts of *p*-TC taken for a reaction. In the representative experiments conducted at 140 °C over zinc triflate loaded SBA-15 and using an equi-molar mixture of naphthalene + *p*-toluoyl chloride (*p*-TC), the overall conversion of naphthalene was found to increase progressively from \sim 35 to 55% for the increase in the triflate loading from 5 to 30 mol%. The 2acyl naphthalene was the major reaction product (\sim 92% yield), the minor product being 1-acyl naphthalene. However, similar product selectivity was obtained by using the catalyst samples containing different loadings of a particular triflate.



Fig. 5. (A) Comparative IR Spectra of pyridine (5 μmol) adsorbed at 125 °C over (c) pure SBA-15, (d) Zn-Tr (5)/SBA and (e) Zn-Tr (10)/SBA catalysts. Curves (a and b) show the characteristic IR spectra of vapor and liquid states of pyridine, respectively. (B) Comparative FTIR spectra of pyridine (5 μmol) adsorbed at 125 °C over (a) pure SBA-15, (b) La-Tr (30)/SBA, (c) Ce-Tr (30)/SBA, (d) Y-Tr (30)/SBA, and (e) Zn-Tr (30)/SBA.

The increase in the reaction temperature gave rise to higher conversions and also in the increase in the rate of FC reaction of naphthalene with *p*-toluoyl chloride. Taking Zn-Tr (30)/SBA-15 as a model catalyst again, the effect of the rise in reaction temperature on the time-dependent conversion of naphthalene is depicted in Fig. 6. These results show that the equilibrium conversion of naphthalene increases from 12.2 to 53.6 wt% with the increase in reaction temperature from 80 to 160 °C. At the same time, the rate of the reaction also increased considerably with the increase in reaction temperature. Thus, while an equilibrium conversion was achieved in ~24 h at 80 °C (curve (a)), the reaction was complete in about 3 h time at the temperatures above 120 °C (curves (d and e)). However, the selectivity for 2-acyl naphthalene remained nearly unchanged with the increase in reaction temperature.

3.6.2. Acylation of naphthalene over SBA-15 loaded with different metal triflates

The comparative catalytic activity values of different metal triflates (Ce, La, Y and Zn, loaded at 30 mol% on SBA-15) for FC reaction of naphthalene with p-toluoyl chloride are shown in Fig. 7. The results reported in this figure are for the reaction conducted at 140 °C over a period of ca. 9 h, using the reactants in an equi-molar ratio. As mentioned above, the main reaction product was naphthalen-2-yl(p-tolyl)methanone. Also, the product distribution was almost independent of the catalyst used. As seen in Fig. 7, the Zn-Tr (30)/SBA catalyst showed much higher catalytic activity as compared to the catalysts containing rare earth triflates, even though the selectivity for 2-acyl naphthalene production was almost similar (94–98%). In order to demonstrate a relationship between the activity and the acidic strength, the number of acid sites in different catalysts (TPD results) is plotted in Fig. 7. We may add that all the triflate based catalysts showed remarkable stability and reproducibility in catalytic activity when utilized for 5-6 consecutive test runs, the activity loss in the process being ca. 5%.

4. Discussion

The results presented in Fig. 7 exhibit a direct relationship between the naphthalene conversion and the density of the acid sites in a particular catalyst sample. Thus, the almost 5-times higher



Fig. 6. Conversion of naphthalene over Zn-Tr (30)/SBA catalyst as a function of time and at different reaction temperatures: curve (a) 80, (b) 100, (c) 120, (d) 140 and (e) 160 °C. Reaction parameters: catalyst amount = 0.1 g; naphthalene = 10 mmol; p-TC = 10 mmol; nitrobenzene = 5 ml.



Fig. 7. Comparative catalytic activity for the naphthalene acylation reaction carried out using different metal triflate loaded (30 mol%) SBA-15 catalysts. Reaction parameters: catalyst amount 0.1 g; naphthalene = 10 mmol; *p*-TC = 10 mmol; nitrobenzene = 5 ml; reaction temperature = $140 \degree$ C; reaction time = 9 h.

conversion obtained by using Zn-Tr (30)/SBA, as compared to the rare earth triflate containing samples, is reflected in the considerably higher acidity of this catalyst (Table 1). On the other hand, the almost identical activity of the three rare earth-based catalysts is in consonance with the number of the acid sites present in these samples. The higher activity of zinc containing samples can be explained by visualizing the mode in which triflate molecules are bonded in the channels of the SBA host. The IR spectra assignments in Table 2 help us in establishing the binding states of a grafted triflate molecule. As is well known, the non-coordinated triflate ion (i.e. $CF_3SO_3^{-}$) has a point-symmetry $C_{3\nu}$, where the antisymmetric stretching mode, $v_{as}(SO_3)$, with E-symmetry is doubly degenerate, while the A1 symmetric mode, $v_s(SO_3)$, is non-degenerate [16]. Both these modes are IR active. The coordination of triflate ion causes the lowering of the symmetry and this causes the splitting of the antisymmetric SO_3^- stretching mode into two components [17]. The extent of this splitting will depend upon the physical state of the molecules. The overlapping IR bands at 1270 and 1340 cm⁻¹ are thus assigned to the antisymmetric SO3 stretching, following the assignments reported in the previous studies [16-18]. Based on the studies conducted on ¹⁸O-labeled triflates [18], the strong IR bands appearing at 1245 and 1180 cm⁻¹ in Table 2 for pure zinc triflate are assigned to the symmetric and antisymmetric stretching modes of (CF₃) groups. The corresponding asymmetric deformation band appears at 576 cm⁻¹. No appreciable shift in these frequencies is observed when the zinc triflate molecules are grafted on to SBA-15A (Table 2). No significant electronic interaction is therefore envisaged between the guest molecules and the surface of the host silicate. At the same time the relative intensities of the IR bands due to (SO_3) and (CF_3) groups undergo considerable changes. Thus, the comparison of spectra of pure zinc triflate and of zinc triflate loaded SBA-15 reveals a drastic decrease in the intensity of the IR bands, both symmetric and antisymmetric modes, related mainly to the CF₃ groups. These observations point to a significant perturbation of triflate molecules as a result of their occlusion in the channels of SBA-15. The nature of this perturbation becomes clear when we take onto account the changes occurring in the stretching vibrations of the hydroxyl groups.

Fig. 3(a) shows that the intensity of the 3740 cm^{-1} band, arising due to the O-H stretching of the isolated silanols in SBA-15, decreases progressively with the increasing loading of the zinc triflate. No shift was, however, observed in the frequency of this band as a result of triflate loading (figure not shown). This behavior has been attributed earlier to the interaction of triflate molecules with surface OH groups; both the (SO_3) and the (CF_3) groups are shown to participate individually in such interactions [19-22]. Various possible binding modes of triflate ion $(CF_3SO_3^{-})$ at the surface silanols, viz. monodentate, bidentate, tridentate and tetradentate, have also been postulated in an earlier publication [4]. We may, however, point out that an electronic interaction between the triflate ions with the surface sites of SBA-15 is likely to change the frequency of the bonded guest molecules, as has been discussed in our earlier publication [23]. Similarly, the ν (OH) frequency is expected to increase because of the increased electron density along the hydroxyl group. Therefore, the spectroscopy results of our study cannot be ascribed to any electronic interaction between the triflate ions and the surface hydroxyl groups. On the other hand, the results reported here are akin to the findings of our previous studies on the occlusion of small molecules, such as methanol, benzene and cyclohexane, in the channels of micro- and mesoporous silicates [23,24]. Based on the detailed discussion presented in these references, the removal of 3740 cm⁻¹ band on triflate or pyridine loading can be attributed to the physical perturbation or the displacement of the -OH groups. This may facilitate a weak van der Waals type interaction between the two displaced hydroxyl groups, leading to the progressive removal of 3740 cm⁻¹ band and the development of a new lower frequency band at \sim 3485 cm⁻¹ (Fig. 4). This is shown graphically in Fig. 8. This mode of triflate occlusion in SBA-15 would thus enable a metal cation to serve as a distinct Lewis acid site for the activation of a reactant molecule, as shown in Fig. 8. The reaction mechanism for the acylation of naphthalene can thus be expressed by two reaction steps. The first step consists of an interaction of toluoyl chloride with the metal triflate to form an acyl cation-zinc triflate activated complex. This transient complex may promote the formation of some highly active species, e.g. acylium ion. In the second step the acylium ion may react with the naphthalene, giving rise to the formation of 2-acyl naphthalene and eventual regeneration of the catalyst.

IR results in Fig. 5(A) confirm that the acid density in a catalyst was directly related to the loading of a metal triflate. Moreover, the



Fig. 8. Schematic presentation of the perturbation of –OH groups caused by the confinement of a metal triflate molecule in a silicate channel, and the postulated binding mode of a reactant molecule.

nature of the acid sites in a catalyst sample may depend considerably on the cation associated with a metal triflate, as can be seen clearly in Fig. 5(B). A pair of strong IR bands observed at 1614 and 1454 cm⁻¹ in the case of pyridine adsorption over zinc triflate loaded SBA-15 [Fig. 5(B), (e)] arises due to well reported 8a ν (C–C) and 19b ν (C–C) vibrations of pyridine adsorbed at the Lewis acid (designated as L1) sites [15,25]. Another pair of bands observed at 1640 and 1546 cm⁻¹ in this figure is known to arise due to the vibrations of pyridine molecules bound at bridgebonded Brönsted (B) sites. The band appearing at 1491 cm⁻¹ is attributed to the adsorption of pyridine at both the Lewis and Brönsted acid sites. In the case of SBA-15 samples containing the triflates of Y, La and Ce, instead of a pair of bands at 1614 and 1454 cm⁻¹ we observe two low intensity bands at 1597 and 1447 cm⁻¹ [Fig. 5(B), (b–d)], similar to the IR bands observed for pure SBA-15 [Fig. 5(B), (a)]. As discussed in our earlier paper in detail [25], these bands are attributable to weak Lewis acid sites (designated as L2), a characteristic feature of the siliceous mesoporous silicates having a weak acid character. The higher intensity of the 1546 cm⁻¹ band in curves (b–d) of Fig. 5(B) indicates that the samples loaded with the triflates of La, Ce and Y exhibit much higher Brönsted acidity and at the same time a lower Lewis acidity, as compared to the zinc triflate containing sample. The ratio B/L (L1 or L2) follows a trend La (9.5) > Y (4.7) > Ce(3.0) = Zn (0.3), and this matches well with the catalytic activity results of Fig. 7.

The important role played by the metal cation in an occluded triflate molecule becomes apparent when we compare the IR bands in spectra (c-e) in Fig. 5(A) with the corresponding spectra of pyridine in its vapor (curve (a)) and liquid (curve (b)) forms. In the case of pyridine adsorption over pure SBA-15 [Fig. 5(A), (c)], the two observed bands are quite broad and at the same time they lack any splitting of the bands, a characteristic feature of the IR spectrum of pyridine vapor [cf. Fig. 5(A), (a)]. Further, the full width at half maximum (FWHM) of the IR bands seen in Fig. 5(A), (c) is \sim 15 cm⁻¹, and this lies in between the FWHM values for IR bands of vapor ($\sim 28 \text{ cm}^{-1}$) and liquid ($\sim 4 \text{ cm}^{-1}$) phases of pyridine. This indicates that the pyridine molecules entrapped in SBA-15 may exist in a non-equilibrium state, in between the vapor and the liquid form. In this adsorbed state, the pyridine molecules are likely to retain their rotational motion without any strong bonding at the SBA sites. On the other hand, a considerable shift is observed in the frequencies of v8a and v19b C–C bands for the adsorption of pyridine molecules in Zn-Tr/SBA samples [Fig. 5(A), (d and e)]. In addition, significant narrowing of the peaks (FWHM \sim 6 cm⁻¹) is noticeable in spectra (d) and (e) of Fig. 5(A), as compared to the IR bands of pyridine vapor [Fig. 5(A), (a)]. This represents an immobile state of pyridine molecules having no rotational motion. It can thus be concluded that the triflate metal cations may participate in the direct binding of a guest molecule, a situation similar to that presented schematically in Fig. 8. Further, the systematic increase in the intensity of pyridine bands as a function of increasing triflate loading in SBA-15 [Fig. 5(A), (d and e)] and the dependence of Lewis acidity in the functionalized silicate samples on the nature of the occluded metal cation [Fig. 5(B)] also serve as evidence for the direct participation of the triflate cation in binding of the pyridine molecules. Logically, other reactant molecules are likely to undergo similar binding at the cation sites, as depicted in Fig. 8. The binding of the pyridine molecules at triflate metal cations may eventually lead to further perturbation of the surface hydroxyl groups in the host matrix, thus giving rise to some synergistic changes in the intensity of v(OH) band, as shown in Fig. 3(c). We surmise that the perturbed -OH groups may give rise to certain bridge bonded hydroxyl species with the participation of a triflate metal cation, and these species may be associated with a broad IR band observed at 3485 cm⁻¹ in Fig. 4. These bridge bonded

hydroxyl groups may in turn serve as new Brönsted acid sites, the presence of which is seen clearly in IR spectra in Fig. 5(A), (d and e). The very small intensity of 3485 cm^{-1} band in case of pyridine adsorption over triflate-free SBA-15, as mentioned above, and the near absence of the Brönsted acid sites in Fig. 5(A), (c) are in conformity with our ideas.

The distinctive acid character exhibited by zinc as compared to other metal triflates may be related to various factors, such as electronic configuration of the cation, coordination number and cationic radius. These factors may influence the overall configuration of the particular triflate molecules entrapped in the silicate pores, thus deciding the acidic character of a functionalized silicate. Studies are now underway to further understand these important observations.

5. Conclusions

The zinc triflate molecules entrapped in the pores of mesoporous SBA-15 exhibit considerably high acid strength and also a high catalytic activity for acylation of naphthalene, as compared to the samples containing triflates of Y, La or Ce. The results of our IR studies reveal that, while large triflate groups may assist in the geometric confinement within the pores of the mesoporous SBA-15, the metal cations are basically responsible for the direct binding of the reactant molecules and hence for the catalytic properties. We surmise that the confinement of a large molecule such as metal triflate may cause significant physical perturbation to the surface hydroxyl groups of the host matrix and this in turn may give rise to the formation of certain Brönsted type surface acid sites.

Acknowledgements

Our thanks are due to Dr. V.B. Kartha, former Head Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, for helpful discussion. SK thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, for a fellowship and NMG thanks the CSIR for an Emeritus Scientist research grant.

References

- F. Sainte, B. Serckx-Poncin, A.-M. Hesbain-Frisque, L. Ghosez, J. Am. Chem. Soc. 104 (1982) 1428–1430.
- [2] G.A. Olah, O. Farooq, S. Morteza, F. Farmina, J.A. Olah, J. Am. Chem. Soc. 110 (1998) 2560–2565.
- [3] T. Tsuchimoto, K. Tobita, T. Hiyama, S. Fukuzawa, Synlett (1996) 557–559.
- [4] M. Chidambaram, D. Curulla-Ferre, A.P. Singh, B.G. Anderson, J. Catal. 220 (2003) 442–457.
- [5] N.E. Drysdale, N. Herron, WO Patent 9502625 (1994).
- [6] K. Wilson, A. Renson, J.H. Clark, Catal. Lett. 61 (1999) 51-55.
- [7] S. Kobayashi, S. Nagayama, J. Am. Chem. Soc. 120 (1998) 2985-2986.
- [8] F. Schager, W. Bonrath, Appl. Catal. A: Gen. 202 (2000) 117-120.
- [9] M.G. Clerici, C. Perego, A. De Angelis, L. Montanari, European Patent 638363
- (1995).
 [10] A. Sakthivel, S.-J. Huang, W.-H. Chen, W.-H. Chen, Z.-H. Lan, K.-H. Chen, T.-W. Kim, R. Ryoo, A.S.T. Chiang, S.-B. Liu, Chem. Mater. 16 (2004) 3168–3175.
- 11] Z. Yang, Y. Xia, R. Mokaya, Adv. Mater. 16 (2004) 727–732.
- [12] N.M. Gupta, in: B. Viswanathan, S. Sivasanker, A.V. Ramaswamy (Eds.), Catalysis: Principles and Applications, Narosa, New Delhi, 2002, pp. 127–144.
- [13] C.N. Trung, J.C. Bryan, D.A. Palmer, Struct. Chem. 15 (2004) 89-94.
- [14] K. Wilson, J.H. Clark, Chem. Commun. (1998) 2135-2136.
- [15] A. Jentys, N.H. Pham, H. Vinek, J. Chem. Soc. Faraday Trans. 92 (17) (1996) 3287– 3291.
- [16] H. Burger, H. Burezyk, A. Blaschette, Monatshefte fur Chemie 101 (1970) 102–119.
 [17] A. Wendsjo, J. Lindgren, J.O. Thomas, G.C. Farrington, Solid State Ionics 53–56 (1992) 1077–1082.
- [18] D.H. Johnston, D.F. Shriver, Inorg. Chem. 32 (1993) 1045-1047.
- [19] S.M. Coman, M. Florea, V.I. Parvulescu, V. David, A. Medvedovici, D.D. Vos, P.A. Jacobs, G. Poncelel, P. Grange, J. Catal. 249 (2007) 359-369.
- [20] C. Paze, G.T. Palomino, A. Zecchina, Catal. Lett. 60 (1999) 139-143.
- [21] A. de Angelis, C. Flego, P. Ingallina, L. Montanari, M.G. Clerici, C. Carati, C. Perego, Catal. Today 65 (2001) 363–371.
- [22] O. Mouhtady, H.G. Iloughmane, N. Rogues, C.L. Roux, Tetrahedron Lett. 44 (2003) 6379–6382.
- [23] M.D. Kadgaonkar, M.W. Kasture, V.B. Kartha, R. Kumar, N.M. Gupta, J. Phys. Chem. C 111 (2007) 9927–9935.
- [24] A. Sahasrabudhe, S. Mitra, A.K. Tripathi, R. Mukhopadhyay, N.M. Gupta, Phys. Chem. Chem. Phys. 5 (2003) 3066–3075.
- [25] P. Kalita, N.M. Gupta, R. Kumar, J. Catal. 245 (2007) 338-347.