Titanium silicates as efficient catalyst for alkylation and acylation of silyl enol ethers under liquid-phase conditions

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ABSTRACT

The activity of titanium- and tin-silicate samples such as TS-1, TS-2, Ti-β and Sn-MFI has been investigated for acylation and alkylation of silyl enol ethers under mild liquid-phase conditions. Silyl enol ethers successfully react with acetyl chloride and *tert*-butyl chloride under dry conditions in the presence of above catalysts to produce the corresponding acylated and alkylated products, respectively. In the case of acetylation reaction, two different nucleophiles with carbon-center (C-atom) and oxygen-center (O-atom) in silyloxy group of silyl enol ether reacts with acetyl chloride to give 1,3-diketone and ketene-ester, respectively. The selectivity for alkylation is always *ca.* 100% and no side products are formed. Among the various solvents investigated, anhydrous THF was found to be the suitable solvent for alkylation; whereas dichloromethane exhibited high selectivity for diketones for acylation. The formation of nucleophiles from silyl enol ethers appears to be the key step for successful acetylation and *tert*-butylation by nucleophilic reaction mechanism. Sn-MFI showed less activity than that observed over the titanosilicates. The observed catalytic activity is explained on the basis of "oxophilic Lewis acidity" of titanium silicate molecular sieves in the absence of H_2O under dry reaction conditions.

1. Introduction

Acylation and alkylation are important synthetic reactions for synthesizing aromatic ketones, alkylated products, and a variety of key intermediates widely used in the fragrances, fine chemicals, and pharmaceuticals industries. These reactions generally use homogeneous Lewis acids such as $AlCl_3$, BF_3, $FeCl_3$, etc. or Brönsted acids like HF and polyphosphoric acid as catalysts in stoichiometric quantities [1] under homogeneous reaction conditions. The corrosive nature coupled with problems associated while disposing the spent Lewis acids and mineral acids have led to environmental concerns that have stimulated research aimed at developing safer alternate solid catalysts. Furthermore, the acylation and alkylation reactions are generally carried out through electrophilic pathway, which often leads more side products due to their severe reaction conditions at high temperature. Alternatively, nucleophilic reactions involving a nucleophile (electron rich atom or group of atoms) is an important route for formation of carbon–carbon bonds with high product selectivity under mild-conditions. In zeolite catalytic systems, although it is difficult to obtain direct evidence for carbanions participation, their presence can reasonably be inferred from the reaction chemistry, e.g., in the aryl-ring side-chain alkyla-

tion. For instance, Murakami and co-workers have proved that alkali-exchanged zeolites such as Rb-, Cs-, and K–X have been efficiently used for side-chain alkylation of toluene with methanol or formaldehyde [2]. Solid bases such as alkaline earth oxides [3,4], hydrotalcites [5,6], and aluminophosphate oxynitrides (ALPONs, prepared by nitridation of $AlPO_4$) [7] have been used for nucleophilic reactions involving nucleophile or carbanion-type species for formation of new carbon–carbon bonds through terminal alkylation like Knoevenagel and aldol condensations, and Michael addition, among others. Unlike the electrophilic reactions at high temperature, the nucleophilic reactions often lead to high conversion of substrate as well as product selectivity under mild liquid-phase conditions.

Microporous aluminosilicates, particularly MFI and Faujasite type, have been extensively investigated to catalyze the nucleophilic C–N (addition of ammonia and amines to olefins), C–O (addition of H_2O and alcohols to alkenes) and C–S (addition of H_2S to olefins) bond formation reactions [8–11] under vapor-phase conditions at high temperature. However, nucleophilic carbon–carbon bond formation reactions involving carbon-anion (carbanion) has been scarcely studied both under liquid- as well as vapor-phase conditions. The successful synthesis of titanium silicate molecular sieves such as TS-1, TS-2, and Ti-β [12–15] and their potential application for a variety of oxidation reactions have been extensively studied under heterogeneous conditions using dilute H_2O_2 as oxidant [16,17]. However, the utility of these titanium silicates in areas other than oxidation catalysis has not been stud-

ied in depth. We have previously demonstrated the efficiency of the titanium silicates for carbon-carbon bond formation reactions in Mukaiyama-type aldol condensation and Michael addition reactions [18–20] in the absence of H_2O. It was observed that titanosilicates play an important role in activating the "leaving group" and to produce the nucleophile which leads to smooth nucleophilic reactions with high product selectivity. Normally, the acylation reaction of silyl enol ethers with acid chloride [21–23] and alkylation reaction using SN_1 active *tert*-alkyl halide [24,25] are generally catalyzed by homogenous Lewis-acids such as $TiCl_4$, $SnCl_4$, $ZnCl_2$, $FeCl_3$, etc. in equimolar quantities at −40 °C to 70 °C. Here we report, titanium silicate molecular sieves as efficient Lewis acid catalysts for acylation and alkylation of silyl enol ethers with acetyl chloride and tert-butyl chloride, respectively.

2. Experimental

2.1. Synthesis of different titanium silicates

In a typical synthesis of TS-1 [13], 45 g of tetrapropylammonium hydroxide (20% aqueous solution) was added to 27.1 g of tetraethyl orthosilicate (TCI, 98%) under vigorous stirring for 3 h. Then 1.06 g tetrabutyl orthotitanate dissolved in dry isopropanol was added slowly to obtain a clear homogeneous solution and steadily stirred for an extended period of time to evaporate the ethanol produced from the hydrolysis to obtain the gel composition: 0.25 SiO2: 0.008 TiO2: 0.09 TPAOH: 6.3 H2O. The gel was crystallized under agitation at 443 K for 24 h and the product was centrifuged to remove the very fine particles, washed thoroughly and finally calcined at 773 K for 12 h in flowing air.

Ti-β was synthesized in a basic medium by modifying the reported procedure [15]. $Ti(OBu)_4$ and H_2O_2 were mixed with water under vigorous stirring to get a titaniumperoxo complex. This complex was added to tetraethylammonium hydroxide (Aldrich, 35% aqueous solution) followed by the addition of Aerosil-200 silica and the stirring was continued until a homogeneous thick gel was obtained after the addition of 2% dealuminated-beta seed crystals. The resulting gel (SiO_2:0.025 TiO_2:0.55 TEAOH:0.337 H_2O_2:6.3 H2O) was transferred into a Teflon-lined autoclave, and the crystallization was carried out at 413 K for 5 days. The as-synthesized catalysts were dried at 373 K and calcined in O_2 flow for 12 h at 793 K.

The catalyst TS-2 was prepared using tetrbutylammonium hydroxide (40%, Aldrich) [14] according to the gel composition: SiO_2:0.025 TiO_2:0.35 TBAOH:33.3 H_2O under static condition at 443 K for 48 h.

Sn-containing microporous silica with MFI framework topology (Sn-MFI) was prepared according to the reported literature by Ramaswamy and Mal [26]. TEOS, tetrapropylammonium hydroxide, and $SnCl_4$ were used under basic medium and the gel was crystallized hydrothermally at 443 K for 40 h [26]. All the catalysts were activated at 373 K under vacuum for 3 h prior to the commencement of reaction.

2.2. Characterization of titanosilicates

Phase purity of titanosilicates was determined from powder X-ray diffraction (XRD) patterns using a Rint 2000 diffractometer with Cu Kα radiation in the region of $2\theta = 5$–50. UV–visible diffuse reflectance spectra were recorded on a JASCO V–550 spectrometer using $BaSO_4$ as a reference. Scanning electron microscopy (SEM) observation was made on a JEOL JSM–T220 instrument after suspending the sample in ethanol followed by gold sputtering. FTIR spectra were recorded on a Shimadzu FTIR-8100 spectrometer using a KBr pellet technique. The amount of Ti present in

the calcined samples was estimated by inductively coupled plasma emission spectrometry (ICP) on a Rigaku JY38S spectrometer and by using a Shimadzu AA-6300 atomic absorption spectrometer (AAS) fitted with a double beam monochromator. BET surface area and micropore volumes were measured by N_2 adsorption at 77 K on a BELSORB 28SA analyzer after evacuation at 300 °C for 3 h. The reaction products were analyzed on a Shimadzu 14B gas chromatograph equipped with OV-1 capillary column fitted with an FID detector.

2.3. Catalytic reaction procedure

All the catalysts were calcined at 773 K for 6 h to remove the organic templates and activated at 423 K for 2 h before the catalytic reactions. In a typical reaction for *tert*-butylation, 10 mmol of silyl enol ether was added to dry THF (15 mL) containing 20 wt% of activated TS-1. To the above mixture, 10 mmol *tert*-butyl chloride was added and the reaction temperature was raised to 333 K. The content was magnetically stirred for 16 h and the progress of the reaction was monitored by gas chromatography. In the case of acylation, dichloromethane was used as reaction medium. For acylation, the mixture of silyl enol ether and acetylchloride in dry dichloromethane was vigorously stirred at 313 K for 5 h. After completion of reaction, the catalyst was filtered and the excess acetyl chloride was removed by washing with water. The products were quantified by GC analysis and the unknown products were identified through authentic samples, and GC–MS splitting pattern.

3. Results and discussion

3.1. Activity of different titanium silicates for tert-butylation of silylenol ether

The metallosilicates were thoroughly characterized by XRD, UV–vis, and FTIR spectroscopies, scanning electron microcope (SEM), elemental analysis by ICP and AAS, and sorption/surface area measurements. Fig. 1 shows diffused reflectance spectra of TS-1, TS-2, and Ti-β exhibiting a sharp absorption band around 218 nm, characteristic of titanium present in the tetrahedral environment [13–15]. The six coordinated octahedral titanium species normally appear at 270 nm was found to be negligible for all
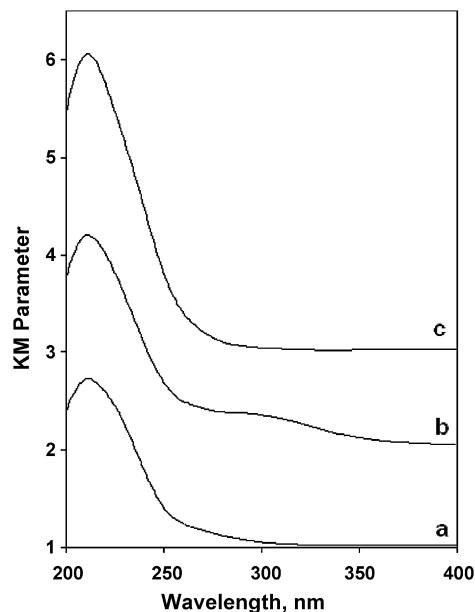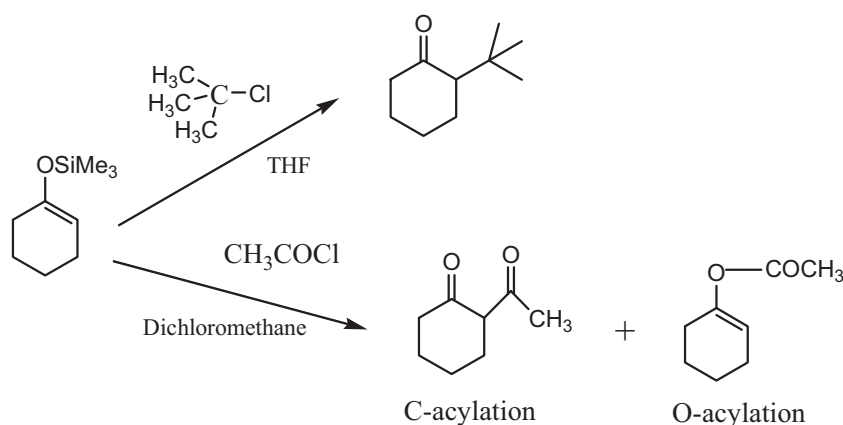

**Fig. 1.** UV–vis diffuse reflectance spectra of: TS-2 (a), Ti-β (b) and TS-1 (c).

Scheme 1. Acetylation and *tert*-butylation of silyl enol ethers over Ti-β.

the titanium silicates investigated under the present study. Furthermore, the absence of an absorption band at 300 nm suggests that these samples are completely free from bulk anatase phase. UV–visible spectrum of Sn-MFI exhibited exclusively tetrahedral species from the absorption band at 212 nm [26]. The physical characteristics of different titanosilicates and tin-silicates are listed in Table 1. The SEM pictures and XRD patterns of the metallosilicates suggest that they are highly crystalline (Figs. S1 and S2, supporting information). The FTIR spectra of these metallosilicates exhibit a band around 950–970 cm^{-1} due to M–O stretching vibrations suggesting the presence of metals in the silica network. ICP and AAS chemical analyses data revealed Si/Ti mole ratios of TS-1, TS-2 and Ti of 35.0, 47.0 and 41.0 respectively, whereas Si/Sn mole ratio in Sn-MFI was 58.0 (Table 1).

The alkylation, more specifically, α-*tert*-butylation of silylenol ethers of ketones with *tert*-butyl chloride is depicted in the Scheme 1. It is worthy to point out that, primary and secondary alkyl halides undergo reactions by SN_2 pathway; however in the present study, *tert*-butyl chloride was used as alkylating agent, which is expected to react by SN_1 reaction mechanism. Fig. 2 exhibits the reaction progress with time for the *tert*-butylation of silyl enol ether over various metallosilicates and separate experimental runs were carried out at each point of graphs. Among the various titanosilicates investigated, large-pore Ti-β shows the best activity (59.1%) than the other metallosilicates. Interestingly, the medium-pore TS-1 also exhibited comparable activity to that of Ti-β; however, the activity of TS-2 (Si/Ti = 47) and Sn-MFI (Si/Sn = 58) show relatively lower activities in accordance with lower metal contents. However, the intrinsic activity of all the metallosilicates increases rather linearly as the reaction progress.

3.2. Tert-butylation of various silyl enol ethers

Table 2 shows the *tert*-butylation of various silyl enol ethers. The SN_1 reaction involves the attack of carbon-nucleophile on either side of stable planar electrophilic-carbon of *tert*-butyl chlo-
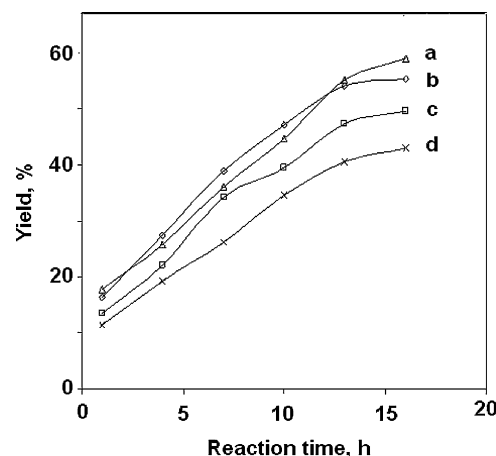
Fig. 2. Effect of reaction time over conversion for *tert*-butylation of cyclohexyl silyl enol ether using different metallosilicates: Ti-β (a), TS-1 (b), TS-2 (c) and Sn-MFI (d).

ride leading to the formation of SN_1 substitution products. The interaction of Lewis acid oxo-philic sites of titanium-silicates with silylenol ether leads to the formation of carbon-nucleophiles under dry conditions. The nucleophilic species then attacks the carbocation (*tert*-butyl chloride) in SN_1 fashion as observed under homogeneous condition [24,25]. Entries 1–3 in Table 2 show the suitability of different dry solvents for *tert*-butylation of silyl enol ether with *tert*-butyl chloride and THF showed better activity than dichloromethane or acetonitrile. The α-*tert*-butyl ketones were the sole reaction products and no side products were observed. The remaining material was the unreacted starting materials. The reactivity of different silyl enol ethers for *tert*-butylation is shown in entries 3–6. The cyclohexanone (entry 3) and 4-methylcyclohexanone (entry 4) derivative of silyl enol ethers exhibit higher conversion of 59.1 and 54.8%, respectively, than the cyclopentanone derivative (entry 5, 47.3%). The open-chain methyl trimethylsilyl dimethylketene acetal (entry 6) also pro-

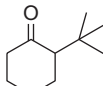**Table 1**
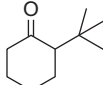Physiochemical characteristics of metallosilicates.
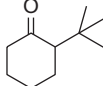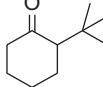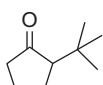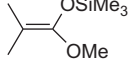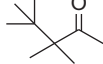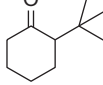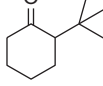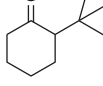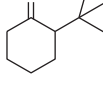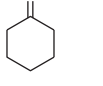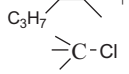
Catalyst	Si/M mole ratio (product)[a]	Particle size (μm)[b]	BET surface area[c] ($m^2 g^{-1}$)	Micropore volume[c] ($mL g^{-1}$)
TS-1	35.0	0.1–0.2	535	0.15
TS-2	47.0	0.3–0.4	469	0.13
Ti-β	41.0	0.2–0.3	648	0.28
Sn-MFI	58.0	0.2–0.4	451	0.14

[a] Si/M was calculated from elemental analysis by ICP and AAS.
[b] Particle size was estimated from SEM analysis.
[c] BET surface area and micropore volume were calculated from N_2 sorption analysis.

Table 2
Tert-butylation of silyl enol ethers over various metallosilicates.[a]

| Entry	Catalyst	Metal content, wt.%	Reactant	Product	Yield, mole%
1[b]	Ti-β	1.88			42.6
2[c]	Ti-β	1.88			35.3
3	Ti-β	1.88			59.1
4	Ti-β	1.88			54.8
5	Ti-β	1.88			47.3
6	Ti-β	1.88			46.7
7	TS-1	2.19			55.4
8	TS-2	1.64			49.6
9	Sn-MFI	3.27			43.1
10	No catalyst	–			Nil
11	SiO$_2$ + H-ZSM-5	2.28			87.0
12[d]	Ti-β	1.88		No alkylation	–

[a] Reaction conditions: silyl enol ether = 10 mmol, *tert*-butylchloride = 10 mmol, catalyst = 20 wt%, THF = 15 mL, temperature = 333 K, and reaction time = 16 h.
[b] Acetonitrile as solvent.
[c] Dichloromethane as solvent.
[d] *tert*-butylation of 2-methyl-2-hexene under identical reaction conditions.

duced the corresponding alkylated product with moderate yield (46.7%). Entries 7–9 exhibit the activities of TS-1, TS-2, and Sn-ZSM-5. Similar to Ti-β, the medium-pore titanium silicates (entries 7 and 8) also lead to facile reaction with good yield; however, Sn-MFI realized lower yield than the medium-pore titanium silicates. As expected, the reaction fails to undergo in the absence of catalysts (entry 10). To obtain more insight over the role of Brönsted acid-sites, the reaction was carried with a mixture of silica and H-ZSM-5 catalyst (entry 11, Al = 2.28 wt%) but no desired product was obtained. Only cyclohexanone was formed due to cleavage of silyl enol ethers. In order to prove the nucleophilic reaction indirectly, *tert*-butylation was attempted with 2-methyl-2-hexene (entry 12) instead of silyl enol ethers under identical

reaction conditions but no alkylation was noticed. The above result unambiguously proves nucleophilic alkylation over the titanium- and tin-silicates. Furthermore, the similarity between medium-pore TS-1 and large-pore Ti-β in their activity leads to whether the reaction is intra porous or surface assisted. However, the basic aspects regarding the nucleophilic reactions under homogeneous conditions suggest that the formation of nucleophile is a key step [27] and the charged nucleophiles can travel through the reaction medium to attack the electron deficient or electrophilic carbon center to give the desired product. Therefore, the facile formation of nucleophile from silyl enol ethers by the catalytic action of titanosilicates could be the key step for successful *tert*-butylation of silyl enol ethers.

Table 3
Acylation of silyl enol ethers over various metallosilicates.[a]

| Entry	Catalyst	Reaction		Product distribution	
				Diketone (C-acylation)	Ketene-ester (O-acylation)
1[b]	Ti-β	OSiMe₃ / OMe + CH₃COCl		82.4	17.6
2[c]	Ti-β	OSiMe₃ / OMe + CH₃COCl		79.5	20.5
3[d]	Ti-β	OSiMe₃ / OMe + CH₃COCl		68.5	31.5
4	Ti-β	OSiMe₃ / OMe + CH₃COCl		89.7	10.3
5	TS-1	OSiMe₃ / OMe + CH₃COCl		87.2	12.8
6	TS-2	OSiMe₃ / OMe + CH₃COCl		85.8	14.2
7	Sn-MFI	OSiMe₃ / OMe + CH₃COCl		84.1	15.9
8	Ti-β	OSiMe₃ + CH₃COCl		83.5	16.5
9	Ti-β	OSiMe₃ + CH₃COCl		86.0	14.0
10	Ti-β	OSiMe₃ + CH₃COCl		80.2	19.8
11	Ti-β	OSiMe₃ / OMe + CH₃CH₂COCl		86.3	16.7
12[e]	Ti-β	OSiMe₃ / OMe + CH₃COCl		83.9	16.1
13[f]	Ti-β	OSiMe₃ / OMe + CH₃COCl		63.6	36.4

[a] Reaction conditions: Silyl enol ether = 10 mmol, acetyl chloride = 10 mmol, catalyst = 20 wt%, dichloromethane = 15 mL, temperature = 313 K, and reaction time = 5 h.
[b] THF.
[c] Nitromethane.
[d] Acetonitrile.
[e] Reaction was performed with uncalcined Ti-β and 16.3% conversion was observed.
[f] Small amount of water was added during the reaction and the conversion was 42.9%.

3.3. Acylation of silyl enol ethers

Table 3 exhibits the acylation of silyl enol ethers with acetyl and propionyl chloride over different metallosilicates under mild liquid-phase conditions (Scheme 1). All the reactions were performed under perfectly dry conditions as that of alkylation, and all the catalysts invariably show quantitative conversion. Similar to nucleophilic alkylation, the acylation over microporous metallosilicates produces diketones as the major product through carbon–carbon bond formation. However, ketene-ester is also formed as the minor side-product through carbon–oxygen bond formation. Among the various dry solvents investigated for reaction between methyl trimethylsilyl dimethylketene acetal and acetyl chloride (entries 1–4), dichloromethane was found to be an efficient solvent as it leads to significantly less amount of the side-product ketene–ester and therefore, dichloromethane was used as solvent for further investigation. The acylation reaction also proceeds smoothly over different titanosilicates as well as Sn-silicates (entries 5–7); the conversion of silyl enol ether is

always quantitative although there is a variation in product distribution. Among the titanosiliates, the Ti-β and TS-1 showed high tendency for carbon–carbon bond formation with minor portion of ketene–ester formation. The acetylation of different silyl enol ethers under standardized reaction conditions produced the corresponding diketones from 80.2 to 86.0% (entries 8–10). The use of other acylating agent such as propionyl chloride also produced a mixture of diketone and ketene–esters with similar product selectivity (entry 11). On contrary to homogeneous Lewis acids catalyst [21,28], the Brönsted acidity originating from silanol groups cannot be neglected over heterogeneous catalysts and produces appreciable amount of O-acylated products. The product distribution in the acylation reaction suggest that the carbanion (nucleophile) formed from silyl enol ether reacts with the electron deficient carbon of −C=O of acid chloride to give desired diketones. On contrary, Brönsted acid promoted reaction of chloride ions (of acetyl chloride) with SiMe₃ (leaving group) to form neutral SiMe₃Cl prior to double bond migration in the silyl enol ether leads to the formation of carbon–oxygen bond to give ketene–esters. In order to obtain
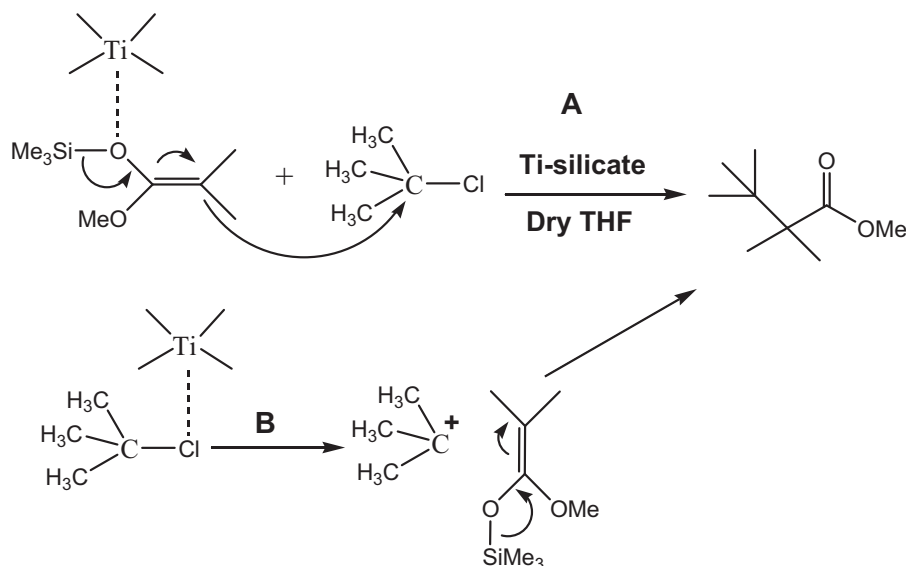
Scheme 2. Formation of nucleophile and subsequent carbon–carbon bond during alkylation and acylation over titanium silicates.

information on the role of external surface, the uncalcined Ti-β was used in the acetylation (entry 12) and the observed conversion was very low due to absence of reaction inside the pores and channels (since they are filled with template). Hence, the small amount of product formed over the uncalcined Ti-β is attributed to catalytic activity of surface titanyl groups. Furthermore, decreased activity was observed on addition of a small amount of water in the reaction medium (entry 13). This result suggests poisoning of Lewis acid sites, which are primary responsible for the nucleophilic reactions. In addition, the presence of a little H_2O could promote Brönsted acid sites, which may possibly increase the O-acylated product. Furthermore, the stability of Ti-β and TS-1 were also studied by successive reuse of these catalysts for four times after activating the catalyst at 623 K for 3 h in air to remove the occluded solvent and organic molecules present in the pores and channels. In the case of *tert*-butylation after four successive reuses, the activities of Ti-β and TS-1 were found to be 97.2 and 98.0%, respectively. In addition, the analysis of reaction mixture after evaporation of solvents by AAS indicates a negligible amount of leaching of metals and thus confirms that the titanium active sites are quite stable under the alkylation and acylation conditions.

3.4. Probable reaction pathway over titanium silicates

In the absence of water TS-1 shows oxophilic Lewis acidic property [29,30] while the possibility of Brönsted acid sites has been suggested in the presence of H_2O_2 and H_2O [31–35]. Since both alkylation and acylation reactions were carried out under absolutely dry conditions, Lewis acidity can play an important role in the formation of nucleophiles according to our previous reports [18–20]. The probable reaction mechanism may involve the activation of enolic-oxygen of silyl enol ethers followed by the migration of a double bond, thus facilitating the formation of nucleophilic moiety at the β-carbon (Scheme 2, pathway A), which subsequently lead to carbon–carbon bond formation [36,37]. In addition, the observed activity of Ti-β with large-pore size is only marginally higher than that of TS-1 (Table 2, entries 3 and 7) indicating that a concerted mechanism involving delocalized charges on the silyl enol ether and tertiary-carbon or carbonyl carbon induced by Ti-sites would be less operative, although such a process cannot be ruled out completely. On the other hand it may be probable that Lewis acid sites present in the

titanium- and tin-silicates can activate C–Cl bond of $(CH_3)_3C$–Cl (making Cl^- a better leaving group) and generate carbocation $(CH_3)_3C^+$, which could be attacked by nucleophile silyl enol ether to yield the α-alkylated ketone (Scheme 2, path B). Therefore, in either case as soon as carbon-nucleophile is formed, it can travel through the reaction medium to attack electron deficient or electrophilic carbon either inside the channel or outside pores to give final product. Furthermore, when the nucleophilic reaction occurs before the migration of double bond, as in the case of acylation, the ultimate product is ketene–ester due to carbon–oxygen bond formation. As expected, the addition of small amount of water decreased the conversion (Table 3, entry 13) probably by poisoning the Lewis acid sites. Thus it confirmed the role of Lewis acid sites in these catalytic reactions. Ti^{4+} in the titanium silicates with its d^0 configuration behaves as oxophilic site to activate the O–Si bond in silyl enol ethers even though some Lewis acid sites are poisoned in the presence of water. Thus, the Lewis acidity of titanium silicates in the complete absence of H_2O would promote carbon–carbon bond formation reactions in the alkylation and acylation of silyl enol ethers under liquid-phase conditions.

4. Conclusions

The titanium silicates Ti-β, TS-1, and TS-2 in the absence of H_2O successfully catalyze the carbon–carbon bond formation in SN_1 type *tert*-butylation and acetylation reactions using silylenol ethers of ketones as nucleophilic reagent. *Tert*-butylation of silyl enol ethers produced the corresponding α-*tert*-butyl ketone as the sole product through carbon–carbon bond formation and no side-products were observed. Among the various metallosilicates investigated, Ti-β exhibited best activity in the alkylation reaction. All the metallosilicates exhibited a facile reaction between silyl enol ethers and acetyl chloride and led to quantitative conversion. Diketone and ketene esters were formed due to the reaction of C-nucleophile and O-nucleophile with –C=O acetyl chloride, respectively. The titanium silicates were reused four times with negligible loss of activity and no leaching of titanium was observed during the reactions. The titanium silicates with "oxophilic Lewis acidity" promote nucleophilic *tert*-butylation and acetylation of silylenol ethers under mild liquid-phase conditions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.06.013.

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