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Titanium silicates for carbon–carbon bond formation reactions

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Abstract

The activity of titanium silicate molecular sieves, TS-1 and aluminum-free Ti-β, has been studied for carbon–carbon bond formation reactions such as Mukaiyama-type aldol condensation and Michael addition under mild liquid-phase conditions. All the reactions were efficiently carried out in the absence of water by using dry solvents in the temperature range of 313–333 K. In the case of Mukaiyama aldol condensation, a variety of aldehydes successfully react with silyl enol ethers to give β-hydroxy esters/aldols in high yields under heterogeneous reaction conditions. Similarly in the case of Michael addition, silyl enol ethers undergo addition reactions with Michael acceptors such as acrylates and α, β-unsaturated ketones to give 1,4-addition products. The selectivity for aldol as well as Michael addition product is always 100%, regardless of conversion level, and no side products are formed. The facile formation of nucleophiles from silyl enol ethers appears to be the key step for successful carbon–carbon bond formation reactions over titanium silicates. The activity of other isomorphously substituted zeolites such as V-, Sn-, and Al-ZSM-5 as well as modified zeolites by ion exchange exhibits less activity than that observed over TS-1 and Ti-β in the aldol condensation. Among the various solvents investigated tetrahydrofuran (THF) shows the best activity. The observed catalytic activity is explained on the basis of "oxophilic Lewis acidity" of titanium silicate molecular sieves in the absence of H_2O_2 and H_2O.

Keywords: Titanosilicates; Liquid-phase; Aldol condensation; Addition reaction

1. Introduction

Nucleophilic reactions involving carbanion-type species is an important route for the formation of new carbon–carbon bonds. In zeolite catalytic systems, it is difficult to obtain direct evidence for carbanions, but their presence can reasonably be inferred from the reaction chemistry, e.g., in the aryl-ring side-chain alkylation. Several alkali-exchanged zeolites such as Rb-, Cs-, and K-X have been effectively used [1] for side-chain alkylation of toluene with methanol or formaldehyde. This type of chemistry can also be presumed for the aldol-type condensation reactions involving carbonyl compounds at high temperature in the vapor phase. Since oxygen is more electronegative than carbon, carbonyl compounds show dipole moment ($\text{–C}^{\delta+}\text{=O}^{\delta-}$), which can be attacked by other carbon nucleophiles (carbanion) on the carbon atom to give new C–C bonds. Thus, the intermolecular condensation of acetone is very well studied to give mesityl oxide, phorone, and isophorone in the vapor phase [2] using a fixed-bed reactor. Although, there are many reports on the vapor-phase condensation of acetone, and other carbonyl compounds over alkali-exchanged zeolites, and/or sodium clusters often at high temperatures in the range of 473–723 K [2–6], not much has been reported on the carbon–carbon bond formation reactions using zeolites under mild reaction conditions.

The Mukaiyama-type aldol reactions [7] between silyl enol ethers and aldehydes, a facile method for C–C bond formation, are promoted by a variety of Lewis acids such as $TiCl_4$, $SnCl_4$, and $ZnCl_2$ using either stoichiometric or catalytic amounts [8–11] under homogeneous conditions. Furthermore, it is important to note that all the homogeneously catalyzed reactions were carried out at very low temperatures between 183 and 273 K. A few heterogeneous catalysts like Nafion-117, Ca-Y, montmorillonite clay, and SiO_2–Al_2O_3 have also been reported at low reaction temperatures [12]. Similar to Mukaiyama aldol condensation, Michael addition reactions have also been carried out with a variety of homogeneous Lewis acids like $TiCl_4$, $SnCl_4$, $Ti(O\text{–}iPr)_4$, and $(Me_2N)_3S^+Me_3SiF_2{}^{4-}$ [13–15]. The successful synthesis of titanium silicate molecular sieves, TS-1

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(with a MFI structure) [16,17] and Ti-β [18], and their potential application for a variety of oxidation reactions have been extensively investigated under heterogeneous conditions using dilute H_2O_2 [19,20]. However, the utility of these titanium silicates in areas other than oxidation catalysis has not been studied in depth. We have already communicated the efficiency of TS-1 for carbon–carbon bond formation in Mukaiyama aldol condensation and Michael addition reactions [21,22]. In this paper, we report a detailed study on the activity with respect to various isomorphously substituted metallosilicates and rare-earth-modified zeolites, and the effect of various substrates and solvents and reaction times on the carbon–carbon bond formation reactions in the liquid phase over Ti-β and TS-1.

2. Experimental

2.1. Synthesis of different metallo silicates

A typical synthesis of TS-1 [17] involves the hydrolysis of 54.2 g of tetraethyl orthosilicate (TCI, 98%) with 90 g of tetrapropylammonium hydroxide (20% aqueous solution) under vigorous stirring for 3 h. Then 2.12 g tetrabutyl orthotitanate dissolved in dry isopropanol was added slowly to obtain a clear homogeneous solution and stirred for an extended period of time to evaporate the ethanol produced from the hydrolysis. Finally, the required amount of water was added to obtain the gel composition: 0.25 SiO_2:0.008 TiO_2:0.09 TPAOH:6.3 H_2O. The gel was crystallized in a rotating autoclave at 443 K for 24 h and the product was centrifuged to remove the very fine particles, washed several times with distilled water, 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 [18]. $Ti(OBu)_4$ 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 3% dealuminated-beta seed crystals. The resulting gel (SiO_2:0.025 TiO_2:0.55 TEAOH:0.337 H_2O_2:6.3 H_2O) 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. Similarly, Al-beta was synthesized using $Al_2(SO_4)_3\cdot16H_2O$ in the absence of seed crystals.

For the synthesis of Sn-ZSM-5 [23], 27.1 g TEOS in 20 mL water was partially hydrolyzed with 48 g of tetrapropylammonium hydroxide (20% aqueous solution) and then, 0.47 g $SnCl_4$ (Aldrich, 99%) was added. The resultant clear solution was stirred for 6 h to ensure complete hydrolysis as well as to evaporate the ethanol produced from the hydrolysis. The clear homogeneous solution obtained after the addition of 16 g water was crystallized in a Teflon-lined autoclave at 443 K for 40 h. After crystallization, the white solid was washed thoroughly with distilled water, dried at 373 K, and calcined at 773 K. Similarly, Sn-ZSM-12 was synthesized using TEAOH as template instead of TPAOH, and the crystallization was carried out at 408 K for 8 days.

V-MFI was synthesized according to the procedure reported by Centi et al. [24]. $VOSO_4\cdot xH_2O$ (Aldrich, 99.9%) was used as the source of vanadium. In a typical synthesis, 21 g of TEOS in 20 mL of water was hydrolyzed with 41 g of tetrapropylammonium hydroxide (20% aqueous solution) for 3 h. Then, 0.45 of vanadyl sulfate was added, and the stirring was continued for another 3 h under a flow of helium gas in order to suppress the oxidation of V^{4+} to V^{5+} at high pH. Finally, 30 mL of water was added and the clear homogeneous solution was subjected to crystallization at 443 K for 48 h. The white solid was washed with distilled water, dried at 373 K, and calcined at 773 K under the flow of O_2 with a slowly rising oven temperature.

La-Y was prepared through ion exchange of commercial Na-Y (UCI Ltd. India) with 0.1 M solution of lanthanum nitrate at 353 K for 24 h. After the treatment, the solid was filtered, washed thoroughly with distilled water, and calcined at 773 K, and the lanthanum content (2.3 wt%) was estimated by AAS analysis. Similarly, a rare earth solution containing a mixture of La, Ce, Sm, Pr, and Nd was treated with Na-Y to get RE-Y and the amount of exchange was found to be 2.85 wt%. For the exchange of Zn metal, a 0.2 M solution of $Zn(CH_3COO)_2$ was treated with Na-ZSM-5 and this process was repeated thrice in order to get a 2.63 wt% exchange of Zn.

2.2. Characterization of catalysts

The metallosilicates TS-1, Ti-β, Sn-ZSM-5, and Sn-ZSM-12 were thoroughly characterized by XRD, UV–vis, FT-IR, SEM, sorption and surface area measurements, and elemental analysis with ICP. Fig. 1 shows diffused reflectance spectra of TS-1 and Ti-β exhibiting a sharp ab-

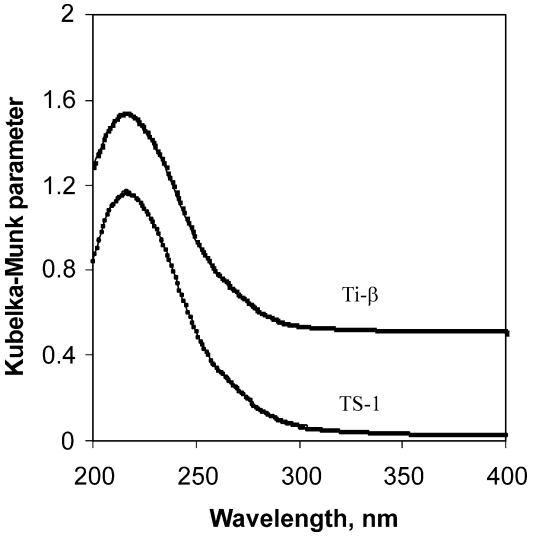


Fig. 1. Diffuse reflectance ultraviolet spectra of TS-1 and Ti-beta.

sorption band around 220 nm, characteristic of titanium present in the tetrahedral environment. The appearance of a weak shoulder at 270 nm may be due to octahedral species; however, its presence is negligible compared to tetrahedral species. Furthermore, the absence of an absorption band at 300 nm suggests that these samples are completely free from anatase. UV–visible spectra of SnZSM-5 exhibited exclusively tetrahedral species from the absorption band at 210 nm [23]; whereas in the case of SnZSM-12 the major portion of tin atoms is located in the tetrahedral position (absorption band at 212 nm) in addition to a very small amount of octahedral species (weak absorption appeared around 255–270 nm). The V-ZSM-5 was characterized by XRD, sorption and surface area measurements, SEM, and elemental analysis by AAS; however, the characterization of V-ZSM-5 was restricted to some extent under the present study since the incorporation of V^{4+} has already been proved unambiguously [20].

2.3. *Catalytic reaction procedure*

The liquid-phase catalytic reaction was performed in a two-necked glass reactor fitted with a water condenser and stirred vigorously under a N_2 atmosphere. Before the reaction, each catalyst is activated at 393 K in a vacuum oven and subsequently used for the reactions under extremely dry conditions. In a typical reaction, 150 mg of catalyst was added to a mixture of silyl enol ether (10 mmol) and an aldehyde (10 mmol) in dry THF and stirred magnetically for a period of 18 h. The reactions were carried out in the temperature range of 313–333 K. The progress of the reaction was monitored by a combination of gas chromatography and thin-layer chromatography. After completion of the reaction, the catalyst was filtered off, and the products were separated by column chromatography for quantification. The reaction products were identified through authentic samples, GC-MS splitting pattern, and ^{1}H NMR.

3. Results and discussion

3.1. *Activity of various metallosilicates for Mukaiyama aldol condensation*

Table 1
Activity of various metallosilicates over the condensation of benzaldehyde[a]

Entry	Catalyst	Si/M ratio (product)	Particle size (μm)	Micropore volume (mL g^{-1})	Yield (%)[b]	TON[d]
1	Ti-ZSM-5 (TS-1)[c]	33.5	0.1–0.2	0.138	85.0	9.2
2	Sn-ZSM-5[c]	73.5	0.2–0.4	0.132	25.0	7.35
3	V-ZSM-5[c]	86.0	0.4–0.6	0.135	10.0	1.9
4	H-ZSM-5[c]	40.0	0.3–0.5	0.153	–	–
5	Ti-β[c]	43.0	0.2–0.3	0.269	87.0	11.6
6	Al-β[c]	26.7	0.3–0.4	0.274	29.0	1.3
7	Sn-ZSM-12[c]	78.0	1–2	0.169	15.0	4.5
8	Na-Y	2.5–3.0	0.5–0.7	0.343	–	–
9	La-Y[e]	2.5–3.0	0.5–0.7	0.292	37.0	6.5[f]
10	RE-Y[e]	2.5–3.0	0.5–0.7	0.270	50.0	7.3[f]
11	Zn/ZSM-5[e]	40.0	0.3–0.5	0.141	34.0	4.4[g]

[a] Reaction conditions: 10 mmol of methyl trimethylsilyl dimethylketene acetal (silyl enol ether); 10 mmol of benzaldehyde; 150 mg catalyst; 10 mL of dry THF as dispersion medium; temperature 333 K; reaction time 18 h.

[b] The yield was estimated by isolation of product.

[c] The metal atom is substituted in the tetrahedral position.

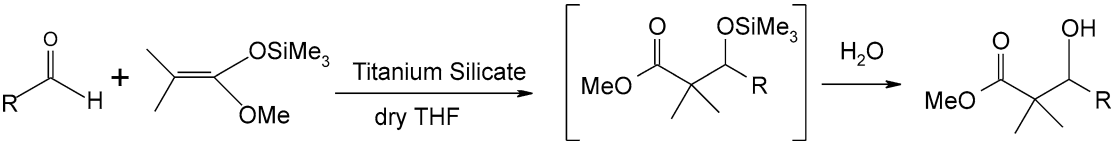
[d] Number of moles of product per mole of metal per hour.

[e] La = 2.3 wt%; combination of all the rare-earth metals = 2.85 wt%; and Zn = 2.63 wt%.

[f] TON based on rare-earth metals.

[g] TON based on Zn.

Table 1 shows the efficiency of various isomorphously substituted as well as modified metallosilicates for the condensation of methyl trimethylsilyl dimethylketene acetal (silyl enol ether) with benzaldehyde (Scheme 1) to produce the corresponding β-hydroxy esters (aldol). It is important to note that after completion of the reaction, water was added and shaken thoroughly to get the final aldol product as shown in Scheme 1. Entries 1–4 exhibit the activity of different isomorphously substituted metals in the ZSM-5 structure, and Ti-ZSM-5 (TS-1) with titanium in the tetrahedral sites exhibits the best activity, whereas Sn- and V-silicalite display poor activity and no activity was observed over H-ZSM-5. The TON for different isomorphously substituted metallosilicates follows the order Ti > Sn > V > Al. Entries 5–7 show the activity of large-pore metallosilicates and Ti-β realized only marginally higher conversion than that of TS-1, but the turnover number of Ti-β (11.6) is higher than that of TS-1 (9.2) and reveals that large pore size still favors increased activity. However, the overall difference in activity between large-pore Ti-β and medium-pore TS-1 is much less, in contrast to the liquid-phase oxidation reactions, where the efficiency of the former is considerably high for bulky substrates. Thus, the activity trend observed over TS-1 and Ti-β indicates that the carbon–carbon bond formation may probably follow a different reaction pathway from that of conventional oxidation reactions involving H_2O_2. Furthermore, the activity per active site is consistently higher for titanium than the other metals such as Sn or Al, regardless of the pore size. The difference in activity between Na-Y (entry 8) and lanthanum-exchanged Y-zeolites (La-Y, entry 9) suggests that Lewis acids (since the exchange of rare earths



Scheme 1.

Table 2
Reactivity of various aldehydes with silyl enol ether over Ti-β and TS-1[a]

Entry	Substrate	Temperature (K)	Product yield (%)[b]	
			Ti-β	TS-1
1[c]	Benzaldehyde	313	69.0	–
2[d]	Benzaldehyde	313	76.0	–
3[e]	Benzaldehyde	313	87.0	85.0
4	4-Nitrobenzaldehyde	313	92.0	90.0
5	4-Cyanobenzaldehyde	333	89.5	82.0
6	Furfuraldehyde	333	86.0	84.5
7	Propionaldehyde	333	73.0	70.0
8	Isobutyraldehyde	313	68.0	67.0
9	Octylaldehyde	333	81.5	71.0
10[f]	Benzaldehyde	333	–	21.0
11[g]	Benzaldehyde	313	–	49.0

[a] Reaction conditions: 10 mmol of methyl trimethylsilyl dimethylketene acetal (silyl enol ether); 10 mmol of aldehydes; 150 mg catalyst; 10 mL of dry THF as solvent; reaction time, 18 h.

[b] The product was isolated by column chromatography and quantified; the rest is unreacted starting material.

[c] Dichloromethane was used as solvent.

[d] Nitromethane was used as solvent.

[e] THF was used as solvent.

[f] The reaction was carried out over uncalcined TS-1.

[g] Small amount of water was added to dry THF.

imparts Lewis acidity) play an important role by facilitating the nucleophile formation in the condensation between silyl enol ether and aldehydes. Also, the rare earth-exchanged zeolites exhibit comparatively better TON than that of isomorphously substituted Al- or V-silicates. Therefore, the moderate activity of Lay, RE-Y, and Zn-ZSM-5 (entries 9–11) may also be due to increased Lewis acidity of these modified zeolites after exchange with rare-earth and zinc metals. Thus, the above results clearly distinguish the efficiency of titanosilicates over other isomorphously substituted and/or modified metallosilicates, and therefore, further detailed investigation has been effected over Ti-β and TS-1.

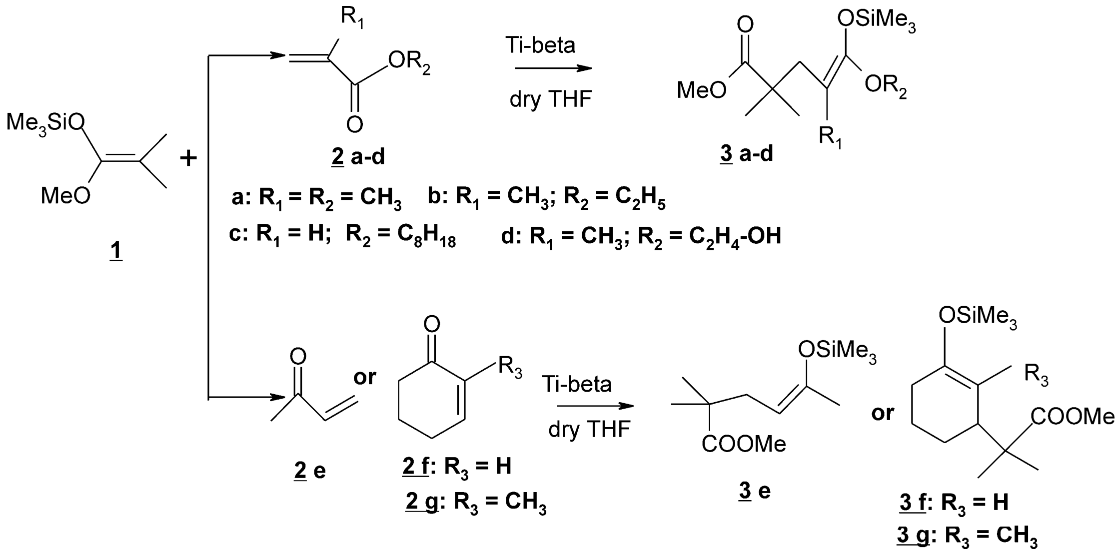
3.2. *Condensation of methyl trimethylsilyl dimethylketene with various aldehydes over Ti-β and TS-1*

Entries 1–3 in Table 2 show the suitability of different dry solvents for aldol condensation of silyl enol ether with benzaldehyde over Ti-β, and THF gives better activity than dichloromethane or nitromethane. The activity of different aromatic aldehydes with methyl trimethylsilyl dimethylketene acetal (Scheme 1) is shown in entries 3–5. The conversion of 4-nitrobenzaldehyde (entry 4) is higher than that of benzaldehyde (entry 3), suggesting that the electron-withdrawing group on the benzene ring increases the electrophilicity of carbon of the carbonyl group (–C=O) by delocalization of electron results in facile nucleophilic reactions. The reactivity of 4-cyanobenzaldehyde with the –C≡N group on the para position (entry 5) is also slightly increased over that of benzaldehyde. However, heteroaromatic aldehyde (entry 6) is comparatively less reactive than the benzaldehyde. Possibly the electrophilicity of the –C=O group may be controlled by the oxygen in the furan ring. The observed reactivity for different aliphatic aldehydes (entries 7–9) is less than that for the aromatic aldehydes. The decreased reactivity of open-chain aldehydes may partly be accounted for by reduced electrophilicity realized at the –C=O due to the electron-releasing nature of alkyl groups.

Furthermore, the similarity between medium-pore TS-1 and large-pore Ti-β in their activity leads to speculation whether the reaction is really intra porous or surface assisted. However, the basic aspects regarding the nucleophilic condensation or addition in homogeneously catalyzed reactions suggest that the formation of nucleophile is a key step [25], and the charged nucleophiles can travel through the reaction medium to attack the electrophilic carbon of –C=O groups. Thus, under the present investigation using titanium silicates, the speculated major reaction path would be the interaction of silyl enol ether with Ti sites in the framework to produce the nucleophiles, which can attack the electron-deficient carbon of –C=O either in the channels or the bulk reaction medium. However, one cannot completely neglect the possibility of a concerted mechanism involving delocalized charges on silyl enol ether and carbonyl group induced by Ti sites, particularly in the case of Ti-β with large micropore volume and pore size. The extent of surface-catalyzed reactions was assessed by carrying out the reaction over uncalcined TS-1 (filled with organic templates, entry 10), and the observed activity clearly suggests that the titanyl groups (possibly with different configuration) located on the surface can also facilitate the formation of nucleophiles. As expected, the addition of water to the reaction medium during the initial period decreased the activity (entry 11), since the addition of water leads to poisoning of Lewis acid sites. All the above results suggest that Lewis acidity plays a prominent role in the aldol condensation reaction in the absence of H_2O and H_2O_2.

3.3. *Michael addition of silyl enol ether with various α,β-unsaturated carbonyl compounds over TS-1 and Ti-β*

Table 3 exhibits a 1,4-addition of various α,β-unsaturated carbonyl compounds (Scheme 2) with methyl trimethylsilyl dimethylketene acetal (silyl enol ether). All the reactions were performed under perfectly dry conditions as that of aldol condensation, and both TS-1 and Ti-β show good activity. Among the various substrates investigated, methyl methacrylate (entry 1) reacts readily with silyl enol ether to give high conversion. The difference in reactivity of substituted methyl methacrylate (entries 2–4) may be due to an electronic effect, although a steric effect cannot be neglected altogether particularly in the case of TS-1 with medium-pore openings. The minor difference in activity between large-pore Ti-β and medium-pore TS-1 can safely be considered as a result of a steric effect arising from the bulky substrates. Methyl vinyl ketone (entry 5) undergoes facile addition to give a 1,4-addition product. The activity of cyclic α,β-unsaturated ketones (entries 6 and 7) is however



Scheme 2.

Table 3
Michael addition of various α,β-unsaturated carbonyl compounds to silyl enol ether over Ti-β and TS-1[a]

Entry	α,β-Unsaturated carbonyl compounds	Product	Product yield (%)[b]	
			Ti-β	TS-1
1	Methyl methacrylate, **2a**	**3a**	53.0	47.0
2	Ethyl methacrylate, **2b**	**3b**	41.0	35.0
3	2-Ethylhexyl acrylate, **2c**	**3c**	39.0	36.0
4	2-Hydroxyethyl methacrylate, **2d**	**3d**	41.0	39.0
5	Methyl vinyl ketone, **2e**	**3e**	45.0	49.0
6	Cyclohexenone, **2f**	**3f**	39.0	36.0
7	2-Methylcyclohexenone, **2g**	**3g**	35.0	33.0

[a] Reaction conditions: 10 mmol of methyl trimethylsilyl dimethylketene acetal (silyl enol ether); 10 mmol of α,β-unsaturated carbonyl compounds; 150 mg catalyst; 10 mL of dry THF; reaction temperature 333 K; reaction time, 14 h.

[b] Isolated yield by column chromatography and the rest is unconverted starting material.

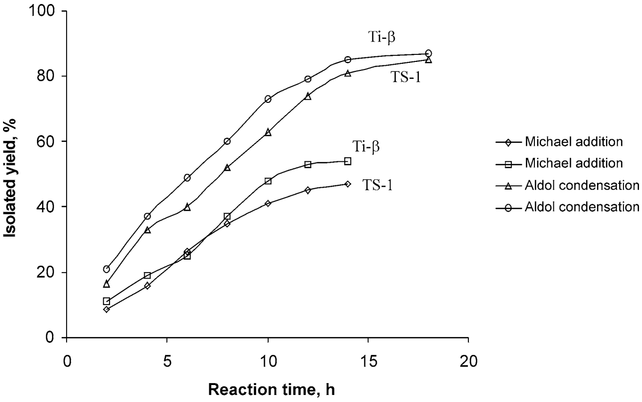
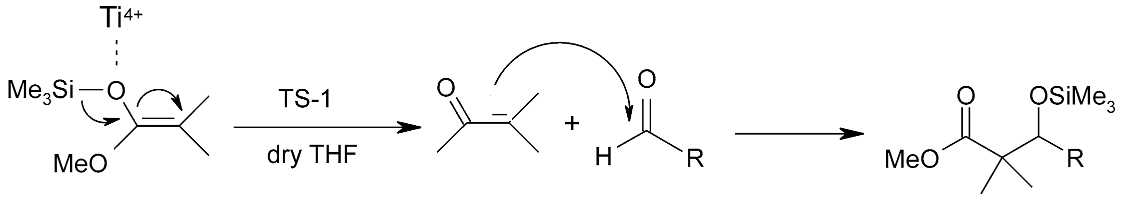


Fig. 2. Effect of reaction time on conversion or yield over Ti-β and TS-1.

slightly lower than that observed for open-chain carbonyl compounds. Unlike aldol condensation, the open-chain α,β-unsaturated carbonyl compounds exhibits better activity for the addition reaction than the cyclic analogues.

3.4. Effect of reaction time

Fig. 2 exhibits the reaction progress with time for the condensation of benzaldehyde and silyl enol ether over Ti-β and TS-1; separate experimental runs were carried out since the aldol products were quantified at each point by extraction and column chromatography. In the case of aldol condensation, the reaction progressed steadily up to the period of 12 h and reached a maximum after 18 h. Furthermore, in aldol condensation, the conversion over Ti-β is always higher than that of TS-1 at any given point on the graph. Similar to other nucleophilic reactions, aldol condensation also leads to 100% selectivity, regardless of the conversion level and the rest is essentially unconverted starting material. In the case of addition of methyl methacrylate with silyl enol ether (Michael addition) over TS-1 and Ti-β, the conversion reaches a maximum in about 12 h, and thereafter only slightly increased for an extended period of time. Also, the titanosilicates TS-1 and Ti-β were successfully reused for three times after the catalyst was reactivated at 623 K for 5 h in air in order to remove the occluded solvent and other organic molecules. Further, we emphasize that the activation of catalysts was carried out mainly to remove the occluded organics from the pores and absolutely no carbonous or polymeric products were detected by CHN (≈ 0.1 wt% carbon may be from the occluded organics) and HPLC analysis. For the aldol condensation reaction, after three successive uses the activity of TS-1 and Ti-β was found to be 95.0 and 92.0%, respectively. Similarly, in the case of Michael addition of methyl methacrylate, TS-1 exhibits 91% activity after three reuses. Furthermore, the analysis of reaction mixture after evaporation of solvents by AAS indicates a negligible amount of leaching and confirms that the titanium active sites are quite stable under the experimental conditions.



Scheme 3.

3.5. Reaction pathway

In the complete absence of water TS-1 exhibits "oxophilic Lewis acid" sites [26,27] while the possibility of Brönsted acid sites has been suggested [28–30] in the presence of H_2O_2 and H_2O. Since all the reactions were carried out under dry conditions, Lewis acidity can play an important role in the formation of nucleophiles as observed in the case of homogeneous catalysis. 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 leading to the condensation or addition (Scheme 3) in either the channels or the bulk reaction medium. Also, the observed activity of Ti-β with large-pore size is only marginally higher than that of TS-1 (Table 1, entries 1 and 5), indicating that a concerted mechanism involving delocalized charges on the silyl enol ether and carbonyl groups induced by Ti sites would be less operative, although such a process cannot be ruled out completely. Furthermore, the addition of a small amount of water to the reaction medium (Table 2, entry 11) decreased the activity probably by poisoning the Lewis acid sites but the observed activity is still appreciably high. Apparently, the Ti^{4+} in TS-1 with its d^0 configuration behaves as "oxophilic" to activate the O–Si bond in the silyl enol ethers even though some Lewis acid sites are poisoned by the presence of water. Thus, the Lewis acidity of TS-1 or Ti-β in the complete absence of H_2O_2 and H_2O would promote carbon–carbon bond formation reactions. Like aldol condensation, the addition reaction would also follow similar reaction pathways.

4. Conclusions

The titanium silicates such as TS-1 and Ti-β can be used as efficient heterogeneous catalysts for carbon–carbon bond formation reactions such as Mukaiyama-type aldol condensation and Michael addition under liquid-phase conditions. Titanium silicates showed better activity than the other isomorphously substituted Sn-, V-, and Al-silicates for the condensation of benzaldehyde and silyl enol ether, whereas modified zeolites such as RE-Y, LaY, and Zn-ZSM-5 resulted in poor activity under similar experimental conditions. THF as the reaction medium led to increased conversion compared to dichloromethane or nitromethane. Among the various aldehydes investigated for the aldol condensation, the reactivity of aromatic aldehydes is increased when it is attached to an electron-withdrawing group. Aliphatic aldehydes are less reactive than the aromatic aldehydes due to an electron-releasing effect of the alkyl groups attached to –C=O groups. In the case of Michael addition, open-chain acrylic and α,β-unsaturated carbonyl compounds showed comparatively better activity than the cyclic ketones with silyl enol ether to give 1,4-addition products. The titanium silicates with "oxophilic Lewis acidity" promote the successive nucleophile and carbon–carbon bond formation.

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