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Titanium silicate molecular sieves (TS-1 and TS-2) catalyzed Michael reaction of silyl enol ethers with α,β unsaturated carbonyl compounds

M. Sasidharan and R. Kumar [1]

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

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The Michael addition reaction has been carried out with silyl enol ether and Michael acceptors such as acrylates, and α,β-unsaturated ketones over aluminum-free titanium silicates (TS-1 and TS-2) in the absence of H_2O_2. The reaction was carried out slightly above room temperature (40°C) in the presence of dry solvents giving moderate to good yield. The effect of various modified zeolites like RE-Y, La-Y, steamed-Y, Na-Y, VS-1, SnS-1, Zn/ZSM-5 and different solvents has been studied. The catalytic activity is explained on the basis of "oxophilic Lewis acidity" of titanium silicate molecular sieves.

Keywords: titanium silicate molecular sieves; Michael addition; oxophilic Lewis acidity; low temperature reaction

1. Introduction

The titanium silicate molecular sieves, TS-1 (with MFI structure) [1,2] and TS-2 (with MEL structure) [3] catalyze oxidation reactions under liquid phase, heterogeneous conditions using dilute H_2O_2 [4,5]. However, not much information is available on the catalytic use of zeolites including the above mentioned titanium silicate molecular sieves in carbon–carbon bond formation under heterogeneous, liquid phase, mild reaction conditions. The Michael reaction between silyl enol ethers and α,β-carbonyl compounds is a well-known and important method for carbon–carbon bond formation in methodology as well as in total synthesis. This reaction is usually carried out with trialkyl silyl enol ethers with various α,β-carbonyl compounds using several homogeneous Lewis acids such as $TiCl_4$, $SnCl_4$, $Ti(O\text{-}i\mathrm{Pr})_4$, $Ti(OCEt)_4$ in stoichiometric amounts and at lower temperatures [6,7]. The utility of bifluorides such as $(Me_2N)_3S^+Me_3SiF_2^{4-}$ [8], $(Me_2N)_3S^+Me_3SiF_2^{6-}$ and the perchlorate Ph_3CClO_4 [9], has also been reported in the homogeneous medium for Michael reactions. However, only a few heterogeneous catalysts like CsF, $ZnCl_2$, and Al-clay montmorillonite [10,11] working in the temperature range of −20 to −78°C have been reported.

Recently, we have reported [12] the Mukaiyama aldol reaction over aluminum-free titanium silicates in the absence of H_2O_2 using silyl enol ethers and various aldehydes. This paper reports, for the first time, Michael reaction of silyl enol ether **1** with α,β-unsaturated carbonyl compounds **2a**–**2g** catalyzed by aluminum- and sodium-free titanium silicate molecular sieves (TS-1 and TS-2) (in the absence of H_2O_2) under mild reaction conditions (scheme 1). The products have been isolated through column chromatography using silica gel and characterized through NMR, IR and mass spectra.

2. Experimental

2.1. Synthesis and characterization of catalysts

Titanium silicate molecular sieves, TS-1 and TS-2, were synthesized according to the literature [2,3], and thoroughly characterized by XRD, IR, SEM, UV and adsorption measurements. The samples were carefully calcined in dry air for 16 h in order to remove the organic additives. VS-1 [13] and SnS-1 [14] were synthesized according to the published procedures. These samples were further characterized through XRD, IR and adsorption techniques. The physico-chemical properties of the samples are given in table 1.

2.2. Catalysis

The reaction was carried out using a batch reactor under N_2 atmosphere under dry conditions. In a typical reaction, 10 mmol of silyl enol ether in *dry* dichloromethane was added to the pre-activated catalyst (20%), then 10 mmol of methyl methacrylate was added to the reaction vessel. This reaction mixture was magnetically stirred at 40°C for 12 h under perfect dry conditions. The progress of the reaction was monitored by TLC using 10% ethyl acetate in pet ether as solvent system. Once the reaction was completed, the catalyst was separated, the product was extracted with dichloromethane (3 × 50 ml), then the combined extract was evaporated in vacuo and the products were separated by column chromatography using silica gel. The products were identified by NMR, IR and mass spectra.

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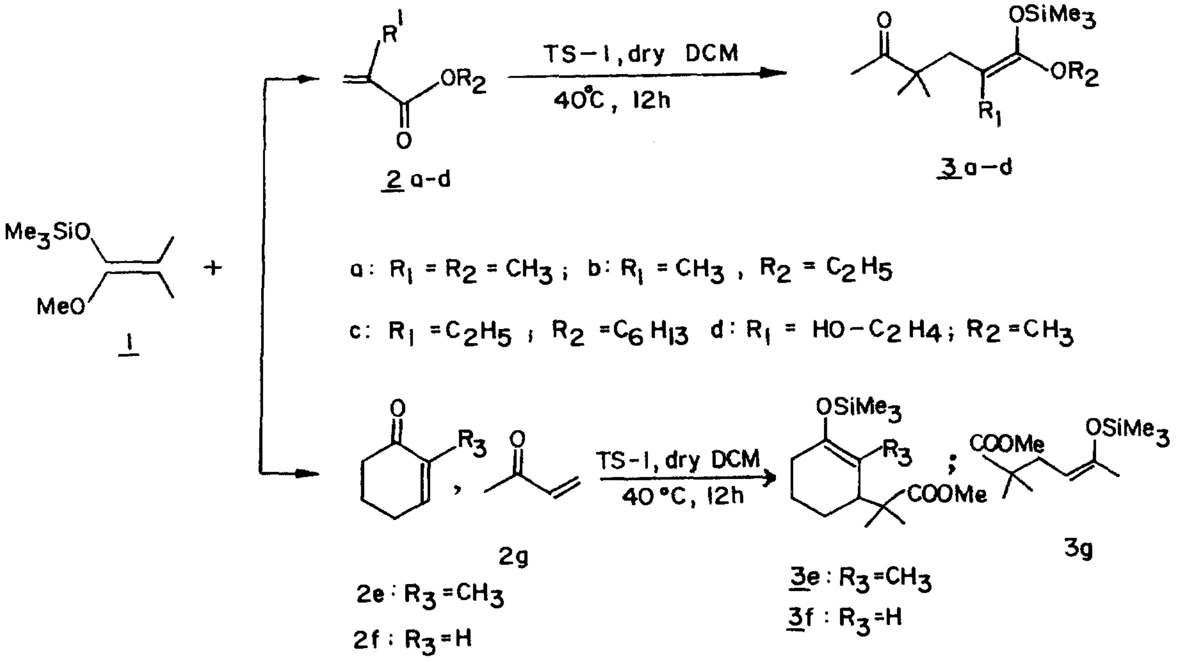
[1] To whom correspondence should be addressed.



Scheme 1.

3. Results and discussion

3.1. *Effect of various zeolites*

Table 1 shows the effect of various zeolites over the 1,4-addition of methylmethacrylate with silyl enol ether. Among various catalysts scanned for this reaction, TS-1 and TS-2 show better activity (yield = 62 and 45%, respectively) than that exhibited by other zeolites. For example, RE-Y and La-Y exhibit moderate yields (ca. 40%). However, in the case of isomorphously substituted Sn-ZSM-5, cation exchanged Zn/ZSM-5 and steamed zeolite-Y, the yields are very low (20%). Na-Y and VS-1 exhibit almost no activity in this reaction. Even though, RE-Y and La-Y, quite strong Lewis acids and efficient catalysts for electrophilic acylation and alkylation, are less reactive in this nucleophilic C–C bond formation.

3.2. *Substrate and solvent effect*

Table 2 shows 1,4-addition of various α,β-unsaturated compounds with silyl enol ether in moderate to good yield. Entries 2, 3 and 4 clearly indicate that, as the bulkiness of the carbonyl group increases, the reaction proceeds slowly resulting in less conversion. This may be partly due to electronic effects and diffusional limitation in the pores and channels as observed in other oxidation reactions. The Si/Ti ratio has no large effect on the conversion as shown in the entries 1 and 11. (The conversions are 62 and 55% for Si/Ti ratio of 33 and 52

Table 1
Physico-chemical properties of various zeolites and corresponding yields of the addition product, 3a, of 1 and 2a

Entry	Sample	Si/M ratio	Particle size (μm)	Surface area (m^2 g^{-1})	C_6H_{12} ads. (wt%)[a]	Yield (%)
1	TS-1	36	0.2–0.3	405	6.5	62
2	TS-1	52	0.2–0.3	398	6.1	55
3	TS-2	64	0.5–1.0	375	5.9	45
4	VS-1	86	0.4–0.6	460	8.60	nil
5	RE-Y[b]	2.5–3.0	0.5–0.7	712	21.75	45
6	La-Y[b]	2.5–3.0	0.5–0.7	725	21.45	40
7	Na-Y	2.5–3.0	0.5–0.7	720	21.80	nil
8	Sn-S-1	70	0.4–0.6	518	12.80	20
9	Zn/ZSM-5[c]	40	0.8–1.0	460	6.70	20
10	ZSM-5	40	0.8–1.0	474	6.85	nil

[a] Gravimetric adsorption of cyclohexane (Cahn balance), temperature = 298 K, $p/p_0 = 0.5$.

[b] Na-Y was obtained from United Catalyst India Ltd and converted into RE-Y and La-Y by ion exchange with the respective rare earth solutions.

[c] Na-ZSM-5 was treated with $Zn(CH_3COO)_2$ (1 M solution) at 80°C. This process was repeated thrice in order to obtain 70% exchange.

Table 2
Addition of various α,β-unsaturated carbonyl compounds to silyl enol ether 1 over TS-1. Conditions: 10 mmol silyl enol ether; 10 mmol α,β-unsaturated carbonyl compounds; 10 ml dry solvent; 20 wt% activated TS-1; temperature = 40°C; time = 12 h

Sample No.	α,β-unsaturated carbonyl compounds	Solvent	Product	Yield[a] (%)
1	methylmethacrylate, 2a	DCM[b]	3a	62
2	methylethacrylate, 2b	DCM	3b	35
3	2-ethylhexylacrylate, 2c	DCM	3c	30
4	2-hydroxyethylmethacrylate, 2d	DCM	3d	20
5	2-methylcyclohexenone, 2e	DCM	3e	40
6	cyclohexenones, 2f	DCM	3f	40
7	methylvinylketone, 2g	DCM	3g	55
8	methylmethacrylate, 2a	THF[c]	3a	40
9	methylmethacrylate, 2a	CH_3NO_2	3a	35
10	methylmethacrylate, 2a	CH_3CN[d]	3a	40
11	methylmethacrylate[f], 2a	DCM	3a	55

[a] Isolated yield by column chromatography, the rest was unconverted starting material.
[b] Dry dichloromethane.
[c] Dry tetrahydrofuran.
[d] The reaction was carried out using dry acetonitrile at 70°C.
[f] TS-1; Si/Ti = 52.

respectively.) Fig. 1 shows the reaction progress with time exhibiting that the conversion reaches maximum in 12 h; after that no further increase in the conversion was observed. However, the use of different solvents (entries 1, 8–10) reveals that dichloromethane is a good solvent for this carbon–carbon bond formation reaction.

3.3. Mechanistic aspect

The representative scheme 1 depicts the reaction between methylmethacrylate **2a** and silyl enol ether **1** forming 1,4-addition product **3a**. Lewis acid interacts with the silyl enol ether causing the cleavage of the (–O–Si) bond and leading to the nucleophilic attack on the α,β-unsaturated compounds as observed in the case of "group transfer polymerization" [11] in homogeneous catalytic reactions. Recently, it has been reported that while in the absence of water TS-1 exhibits *oxophilic Lewis acidity* [15–17], in the presence of aq. H_2O_2, it behaves as a Brønsted acid [15]. Since, in our studies neither water nor H_2O_2 are used, the role of Brønsted acidity in catalyzing this Michael reaction under the present conditions can safely be ruled out. However, in the complete absence of water (as the reaction was carried out under dry conditions), TS-1 having Ti^{4+} with d_0 configuration behaving as an "oxophilic Lewis acid" may activate the O–Si bond in the silyl enol ether, a key step in the Michael reaction, leading to the formation of the 1,4-adduct with α,β-unsaturated compounds, as shown in scheme 1.

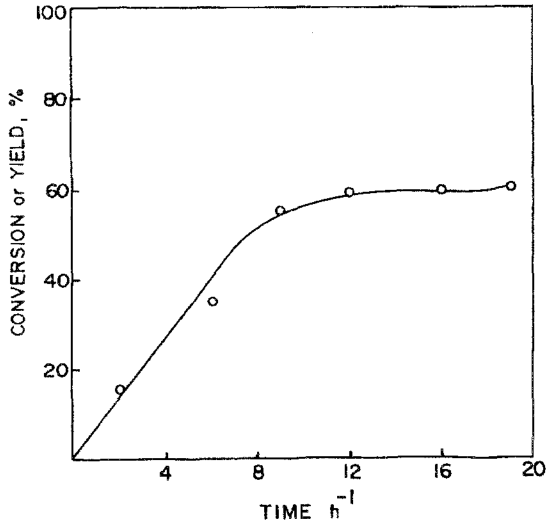


Fig. 1. Effect of reaction time in the conversion of silyl enol ether 1 and methylmethacrylate 2a into 1,4 adduct 3a.

4. Conclusions

TS-1 and TS-2 catalyze 1,4-Michael addition with α,β-unsaturated compounds and silyl enol ether in the absence of H_2O_2 under dry conditions. Dichloromethane was found to be a good solvent for this reaction. The various zeolites such as RE-Y, La-Y, steamed zeolite-Y, SnS-1, VS-1 and cation exchanged Zn-ZSM-5 exhibit less or no activity. TS-1 and TS-2, being "oxophilic Lewis acids", show good activity in the nucleophilic carbon–carbon bond forming reaction.

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