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Mesoporous titanium-aluminosilicate as an efficient catalyst for selective oxidation of cyclohexene at mild reaction conditions

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ABSTRACT

Mesoporous titanium containing alumino-silicate materials with various titanium/silicon (Ti/Si) ratio (AlSi-Ti(*n*); *n* = Ti/Si mole ratio) have been successfully synthesized by a novel single-step sodium (Na)-free method, for the first time. The obtained characterization results of the prepared materials reveal that *in-situ* addition of Ti into AlSi shows ordered mesoporous structure along with uniformly dispersed Ti species in +4 and +3 oxidation states suitable for selective oxidation of allylic C—H bond. The prepared mesoporouse Ti-AlSi(*n*) samples exhibited excellent activity in the oxidation of cyclohexene with 100% conversion and 100% selectivity to ketone-alcohol (KA) oil (cyclohex-2-en-1-ol and 2-cyclohexen-1-one) at low temperature and reaction time (35 °C and 30 min reaction time). This study suggests that AlSi-Ti(0.05) material can be a promising catalyst for the selective oxidation of cyclohexene under mild reaction conditions.

1. Introduction

Heterogeneous catalysis has been preferentially adopted from the last few decades, by the obvious reason of easy handling and simplicity involved in the process which does not require cumbersome steps otherwise common in homogenous catalyst systems, thus overall improving process economics in a greener way [1,2]. However, the diluted concentration of active sites on heterogeneous catalysts when compared to the equivalent homogeneous ones, and the limited stability of the active sites in the supported catalysts need to be addressed through proper designing of heterogeneous systems for a desired reaction [3,4]. Synthesis of catalyst systems that are active and highly selective towards chemical transformation are highly challenging and have been continuously attempted by researchers to improve the properties like high activity, selectivity, thermal stability, renewability *etc*., so as to make them suitable for industrial applications [5]. Porous materials are playing a vital role in the catalytic applications due to their high surface area and various surface functionalities [6–8]. Aluminosilicates (AlSi) are one of the important classes of catalyst materials that have attracted much attention due to the valency difference created by their combination that can act as a source of active sites within the materials. Further, such active sites created by the combination of Al and Si can be a source for functionalization by wide spectrum of metal ions selectable based on the desired type of reactions such as cracking, isomerization, aromatization and oxidation *etc*., of hydrocarbons [9–11]. Though zeolites, the crystalline AlSi of commonly microporous nature, have been successfully operating in various industrial processes, zeolites have some limitations for the reactions related to larger molecular transformations. Much larger pores are requisite for such reactions to accommodate the larger molecular transformations and to facilitate facile molecular diffusion, where mesoporous AlSi are much desired candidates [12–14].

Towards the development of such efficient functionalized mesoporous materials, here we are reporting a simple, one step, Na-free route for the synthesis of titanium containing aluminosilicate (AlSi-Ti) useful for selective oxidation reaction applications. Here, the direct Na-free synthesis of the material provides a greener way of catalyst preparation by having an advantage of obtaining the proton form the AlSi catalyst which does not require any additional NH_4^+ exchange and decomposition treatments to evolve ammonia gas [10]. Ti is known for its oxidation property of variety of molecules but it is always challenging to obtain higher product yields in the selective oxidation reactions such as those of olefins and cyclic olefins to drive the reaction towards allylic oxidation [15–19]. Serious attempts have been conducted in this direction especially for the development of catalysts that are active

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at the milder reaction condition for selective oxidation [20,21]. Cyclohexene is one of the low-price and easily available raw material obtained from fossil fuel fractions and refinery streams in the industries. Oxidation of cyclohexene is a value added process but the reaction produces a variety of oxygenated derivatives that needs special attention to be addressed by a catalytic process to produce desired products in economically feasible yields to work in the industry. Generally oxidation in the cyclohexene occurs at its two active groups namely C—H bond at allylic site and C═C bond (Fig. 1). In the case of epoxidation route (path 1), the C═C group is oxidized leading to the formation of epoxycyclohexane and cyclohexane-1,2-diol. In the allylic route (path 2), C—H group takes part in the oxidation reaction resulting in the formation of cyclohex-2-en-1-ol (III) and 2-cyclohexen-1-one (IV) products.

Both pathways (path 1 & 2) are industrially very important for the production of such oxygen-containing intermediates (I–IV) which are widely used for the medicine, pesticides, spices, surfactant and polymer production. Among them, cyclohex-2-en-1-ol and 2-cyclohexen-1-one show more attention due to their emerging application in pharmaceutical, chemical and material industries [20,22]. However, cyclohexene oxidation usually show poor selectivity to allylic oxidized products due to presence of multiple oxidation sites-unsaturated C═C double bond and α-H atoms, which results in undesirable oxidation products (I & II) and leads to difficulty in separation. The studies conducted earlier to find out the reaction pathway of cyclohexene oxidation revealed that transition metals present in the catalyst play the main role in allylic oxidation. The metals also exhibited advantages of high thermal stability, high catalytic activity further supportive for easy catalyst separation and recycling [23,24]. It was also reported that presence of Ti in catalyst systems plays an important role in oxidation reaction [25–27]. Due to the industrial importance of the reaction, several research studies have been reported even in recent years, but, the conversion of cyclohexene and selectivity towards I–IV products in most of the cases was reported to be less than 50% [28–31]. The reports indicate the importance of process improvement and huge scope in catalyst development for achieving improved conversion/ selectivity. Aim of the preset work is to synthesize an efficient mesoporous Ti containing AlSi catalyst through a simple method to produce allylic oxidized products with higher selectivities at higher cyclohexene conversion. Herein we report for the first time, a facile single-step Na-free method for the synthesis of AlSi-Ti with different Ti/Si ratio possessing high surface area, mesoporosity and Ti^{4+}/Ti^{3+}species suitable for allylic oxidation of cyclohexene.

2. Experimental

2.1. Materials

For catalyst preparation, aluminum-*iso*-propoxide (AIP, SD Fine Chem-Limited) and *tert*-ethyl ortho-silicates (TEOS, Merck India Limited) were used as a precursor for Al and Si, respectively. For structure directing agent tetra-propyl ammonium hydroxide (TPAOH, Merck India Limited) and tetra-methyl ammonium hydroxide (TMAOH, ACROS) have been used, and titanium ethoxide used as a Ti precursor for metal functionalization. For the catalyst performance test, we have used cyclohexene (MERCK) as a reactant, hydrogen peroxide (H_2O_2 50% RANKEM) as an oxidant and for the solvent acetonitrile (HIMEDIA) was used.

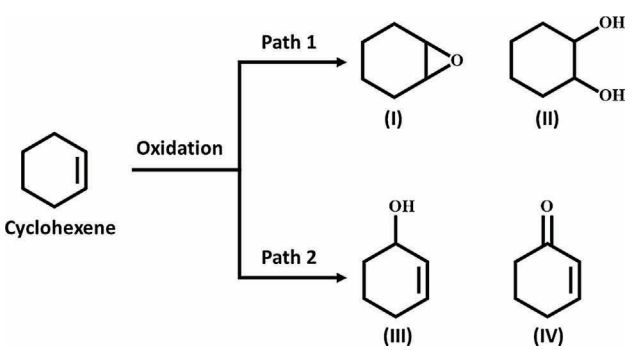

Fig. 1. Oxidation of cyclohexene.

2.2. Single-pot Na-free synthesis of AlSi-Ti(n) materials

Alumino-silicate (AlSi) was synthesized by using our previous method reported earlier [10]. In the typical synthesis of Ti-induced AlSi catalysts, solution A was prepared by mixing of 1.8 g aluminum-*iso*-propoxide, 24 g tetra-propyl ammonium hydroxide and desirable amount of titanium ethoxide (as per the Ti/Si ratio) in a 100 ml beaker. It was allowed to stir for 1 h at room temperature to get a homogeneous solution. Similarly, solution B was prepared by mixing of 24 g tetra-methyl ammonium hydroxide with 28.8 g of *tert*-ethyl ortho-silicates. The resultant solution B was slowly mixed with solution A in a drop-wise manner under constant stirring until get the wet gel, which was then transferred into a teflon lined autoclave for hydrothermal treatment at 140 °C for 48 h. The solid product obtained from the hydrothermal treatment was thoroughly washed with ample amount of distilled water and then filtered. The solid cake thus obtained was dried overnight at room temperature and then calcined at 500 °C for 5 h. The resultant materials were denoted by AlSi-Ti(n) where n stands for Ti/Si ratio such as 0.005, 0.01, 0.03, 0.05 and 0.07 (0 indicates Ti-free AlSi).

2.3. Characterizations

X-ray powder diffraction (XRD) patterns were measured on D8 advance, Bruker, Germany, equipped with rotating anode and CuK_α radiations. The measurements were carried out in continuous $\theta/2\theta$ scan refraction mode. Low angle XRD patterns are also measured (0.2°–1.4°, θ) to understand the mesopore nature of the materials. The Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were recorded adopting KBr pellet method on Perkin Elmer-spectrum, USA. Transmission electron microscopy (TEM) images were recorded for obtaining particle morphology on JEOL, JSM-2100F instrument, Japan. N_2-adsorption–desorption study was carried out using a standard adsorption equipment (ASAP 2010, Micromeritics Instruments Inc., Norcross, GA, USA). X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos AXIS Ultra DLD apparatus, United Kingdom, equipped with monochromated Al K_α radiation X-ray source, a charge neutralizer and a hemispherical electron energy analyzer. During data acquisition, the chamber pressure was kept below 10^{-9} mbar (1bar=0.1MPa). The spectra were analyzed using the CasaXPS software pack and corrected for charging using C 1s binding energy (BE) as the reference at 284.8 eV. The Ti/Si % (mass) ratio of the catalysts was carried out by atomic absorption spectroscopy (AAS) (DRE, PS-3000UV, Leeman Labs, INC, USA).

2.4. Catalyst performance on allylic oxidation of cyclohexene

For cyclohexene oxidation reaction, 1:2 (cyclohexene:H_2O_2) mole ratio of the reactant has been allowed to react in presence of catalyst in acetonitrile medium. In a typical procedure, the catalyst (0.5 g) was added to a mixture of 50% H_2O_2 and 1.26 ml of cyclohexene with 15 ml of acetonitrile (solvent) in a 50 ml round bottom flask equipped with stirrer and water condenser. Temperature of the reaction mixture was raised upto 35 °C using hot-plate and the reaction was performed at this temperature for 2 h under

constant starring. Reaction product was pipette out in every 30 min of interval, and the catalyst was separated by filtration. The reaction product was analysed by Agilant gas chromatography (GC) (7890B) equipped with the HP-1 column (30 m × 0.25 mm) and Agilant MS (5977A) detector.

3. Results and Discussion

3.1. Properties of AlSi-Ti(n) materials

In wide angle XRD (Fig. 2(a)), the AlSi-Ti(0) sample exhibited two diffraction peaks around 15° and 25° 2θ; the characteristic of amorphous nature of alumino-silicate [32,33]. Other AlSi-Ti(n) samples also showed these patterns with a shift towards low angle (around 13° and 22° 2θ), perhaps caused by the interaction of Ti with AlSi structure in these samples. It was also observed that no separate diffraction peak appeared related to Ti particles in XRD, which indicates the fine dispersion of Ti in the alumina-silicate structure. Both Ti-free and Ti-containing AlSi samples exhibited diffraction peaks in the region of 1° to 3° 2θ in low angle XRD (Fig. 2(b)), characteristic of mesoporous materials [34,35].

In FT-IR spectrum the AlSi-Ti(0) sample exhibited three intensive absorbance bands near 800 cm^{-1}, 1050 cm^{-1} and 1650 cm^{-1} respectively due to Si—OH bending vibration, Si—O—Al stretching vibration and hydration of water molecules (Fig. 3) [14]. In addition, a band around 470 cm^{-1} related to Si—O—T (where T = Si or Al) is also observed in this sample. The Ti-containing samples also exhibited similar bands as that of AlSi-Ti(0) sample, but the intensity of the band at 470 cm^{-1} is significantly increased with Ti amount in these samples. This may be due to the combined contribution of Si—O—Si, Si—O—Al and Si—O—Ti stretching vibrations that supports the chemical interaction of Ti with AlSi structure [36]. Overall, these results clearly indicate the involvement of Ti in the alumino-silicate structure.

The presence of Ti also caused visible changes in the morphology of the AlSi recorded by TEM (Fig. 4(a)). In this, the AlSi-Ti(0) sample appeared as a typical layered structure without any clear-cut particulate nature which is shifted to form clear-cut particulate morphology by the involvement of Ti in other Ti-containing samples. At very lower levels of Ti addition (AlSi-Ti (0.01)), the visibility of small particular structure (~3–5 nm) is observed, which is progressed to give a clear cut particle formation of ~10 nm in AlSi-Ti(0.03) sample, and the phenomenon further progressed with Ti to obtain ~20 nm sized distinct particles in case of AlSi-Ti(0.05) sample. Thus, the involvement of Ti in the structure of AlSi seems to be responsible for the formation of nanosize par-

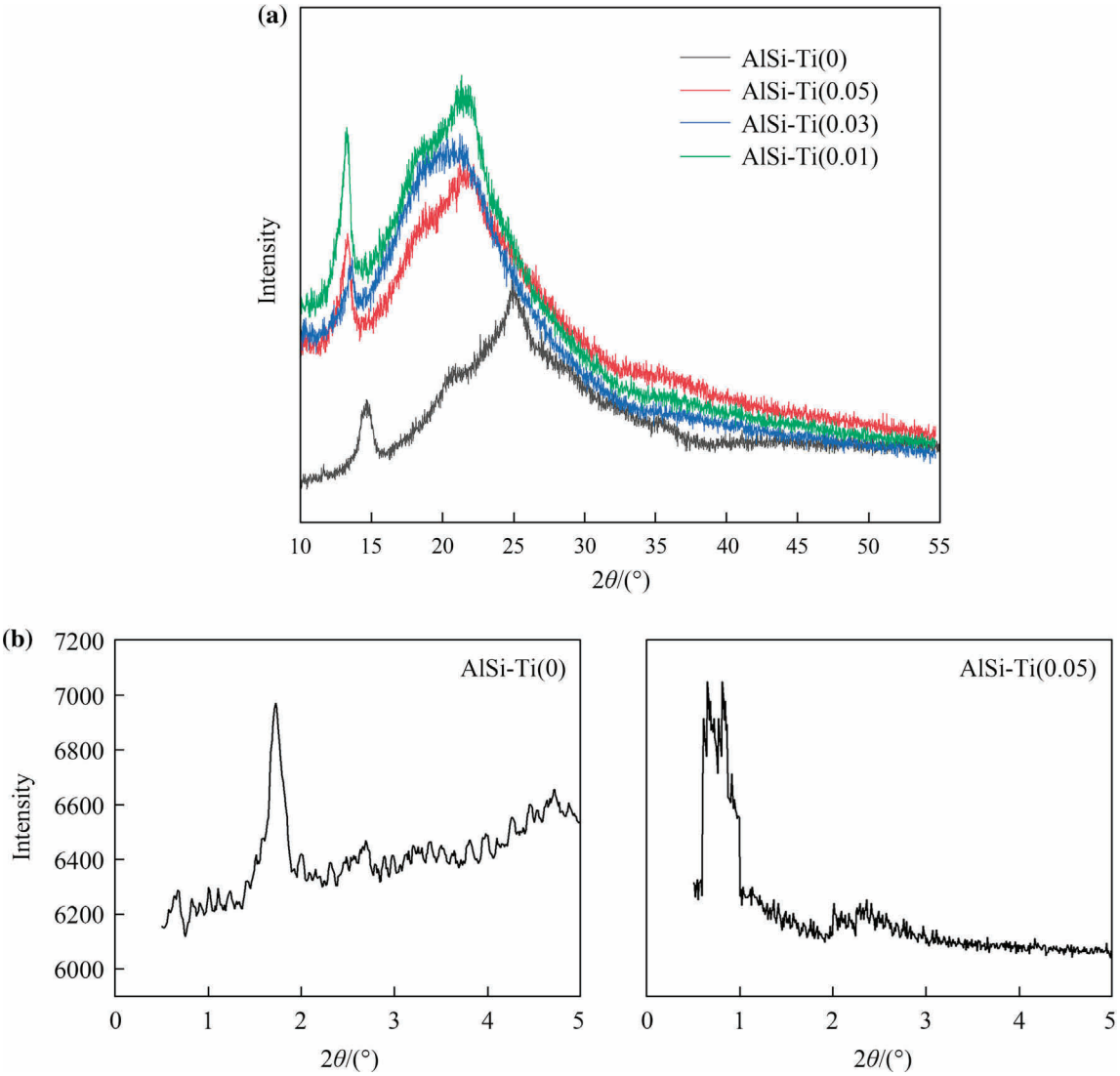

Fig. 2. (a) Wide angle and (b) low angle XRD patterns of AlSi-Ti(n) samples.

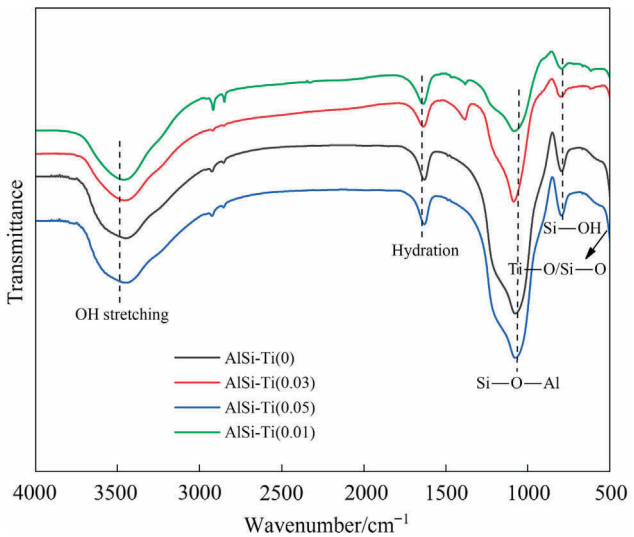

Fig. 3. FT-IR spectra of AlSi-Ti(n) samples.

ticulate (~20 nm) morphology with uniform size. Further, TEM-elemental mapping of synthesized samples clearly evidenced the presence of uniformly distributed Al, Si and Ti elements in the samples (Fig. 4(b)).

N_2-adsorption–desorption isotherms of all the synthesized AlSi-Ti(n) samples exhibit type IV isotherm due to the presence of mesopore structure (Fig. 5). It was noticed that AlSi-Ti(0), AlSi-Ti (0.01) and AlSi-Ti(0.03) samples shows H2 hysteresis loops configuration, which is a characteristic of wormhole-like disordered mesopores, whereas AlSi-Ti(0.05) sample exhibits H1 loop configuration due to the presence of a well-ordered mesopores. The data compiled in Table S1 clearly elucidates considerable changes in pore structure of the samples with Ti-involvement (Ti-amount). The parent AlSi-Ti(0) sample shows surface area, pore volume and pore diameter of about 265.5 $m^2 \cdot g^{-1}$, 0.22 $cm^3 \cdot g^{-1}$ and 6.8 nm, respectively. While a slight decrease in surface area is occurred, there is a considerable improvement in the pore volume of the samples after Ti-involvement; the specific surface area of AlSi-Ti(0) sample has been gradually decreased from 265.5 $m^2 \cdot g^{-1}$ to 206.0 $m^2 \cdot g^{-1}$ with increase of Ti content. But, the pore volume of the samples has been linearly increased with Ti content (0.22–0.37 $cm^3 \cdot g^{-1}$), mainly contributed by the mesopore volume (increased from 0.18 $cm^3 \cdot g^{-1}$ to 0.36 $cm^3 \cdot g^{-1}$). The data reveals the Ti-involved structural changes in the porous system to almost double the mesopore volume, contributing to the enhancement in the total pore volume of the Ti-containing samples.

The elemental composition of synthesized samples analyzed by atomic absorption spectroscopy is given in Table S1. The data revealed that Ti/Si ratio of all the samples are comparable as per the concentrations of Ti used during the synthesis of these samples. This observation confirms the AlSi-Ti(n) materials have been successfully synthesized by a single pot Na-free route without loss of any constituent elements during the synthesis.

In XPS analysis, the survey spectrum of AlSi-Ti(0.05) sample shows various peaks at corresponding binding energy values related to presence of Ti, Al, Si and O atoms (Fig. 6(a)). The Ti 2p XPS spectrum of AlSi-Ti(0.05) sample exhibited two intense peaks around 458 eV (Ti $2p_{3/2}$) and 466 eV (Ti $2p_{1/2}$) (Fig. 6(b)) corresponding to Ti^{4+} present in the AlSi framework [37,38]. Further, a very small peak appeared ~465 eV indicates the presence of Ti^{3+} also in this sample [38,39]. Overall results suggest that most of the Ti species existed in +4 oxidation state in the sample, perhaps due to the involvement of Ti in the framework structure of the AlSi. The presence of both Ti^{4+} and Ti^{3+} species seems to be a suitable condition to create redox sites required for the selective allylic oxidation of cyclohexene.

3.2. Catalyst performance studies towards selective allylic oxidation of cyclohexene

Selective oxidation of cyclohexene is an industrially important reaction. The products of cyclohexene oxidation are used as potential intermediates in the synthesis of many organic molecules. In particular, the products obtained from allylic oxidation of cyclohexene *i.e.* cyclohex-2-en-1-ol and 2-cyclohexen-1-one are promising starting materials for important chemical industries like fragrance, pharmaceutical and agrochemicals industry. However,

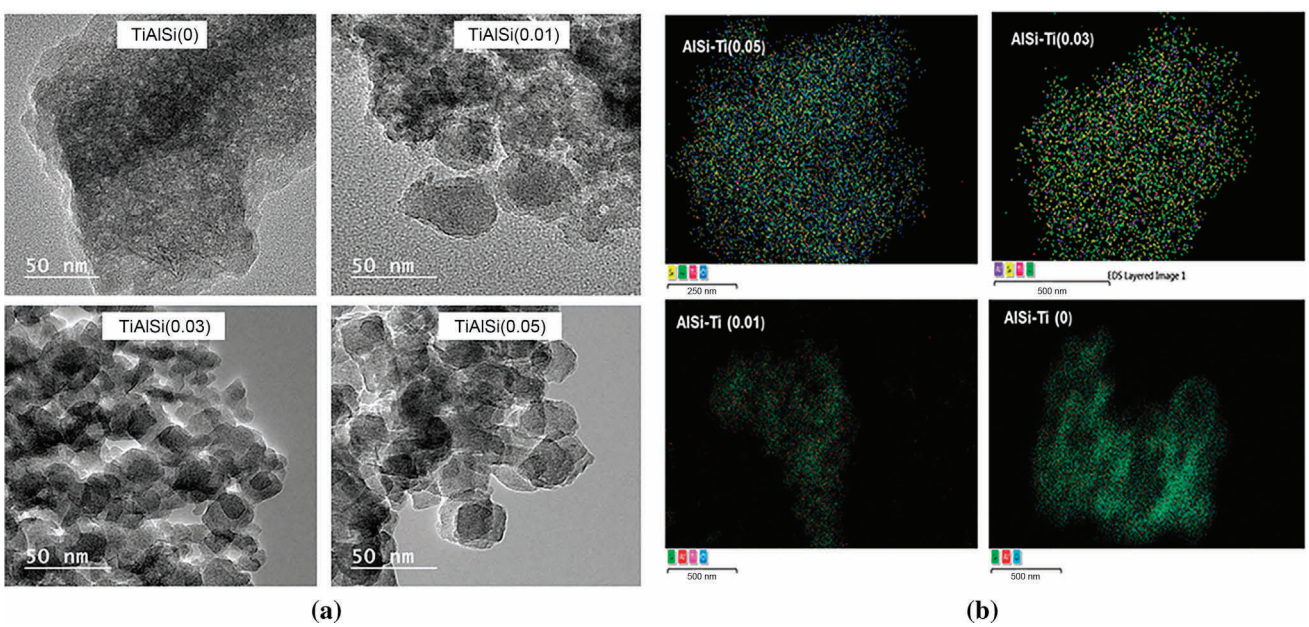

Fig. 4. (a) TEM images and (b) elemental mapping images of AlSi-Ti(n) samples.

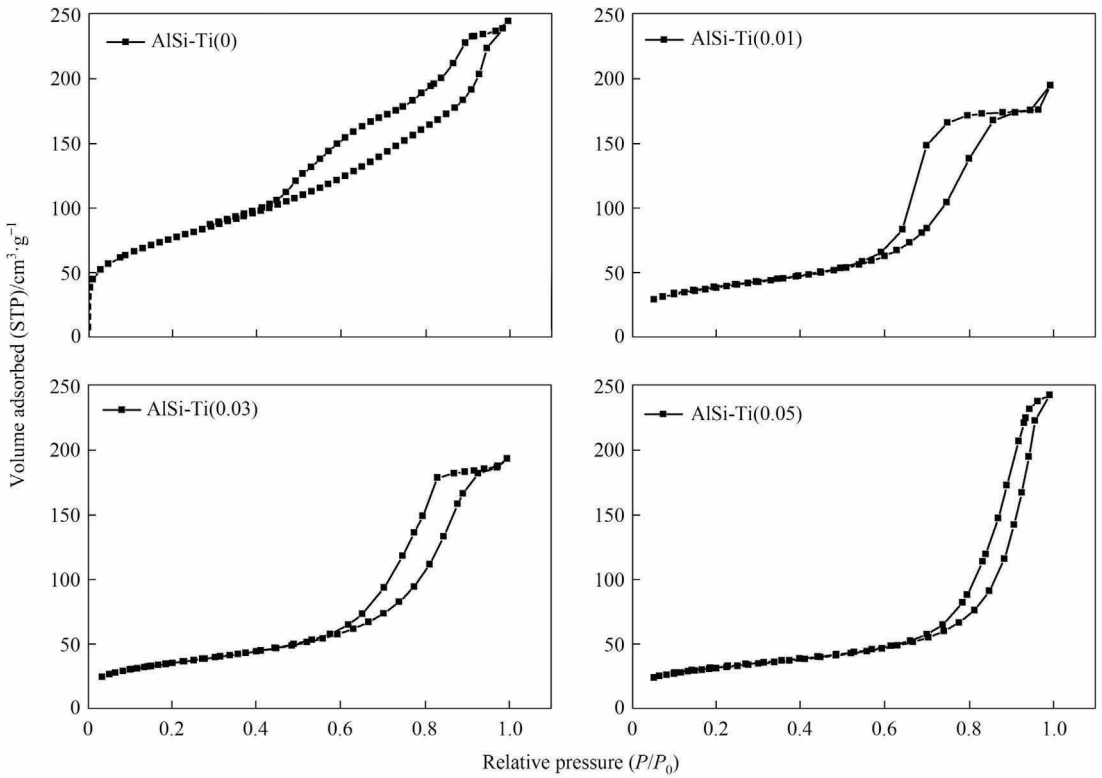

Fig. 5. N_2-adsorption–desorption isotherms of AlSi-Ti(n) samples.

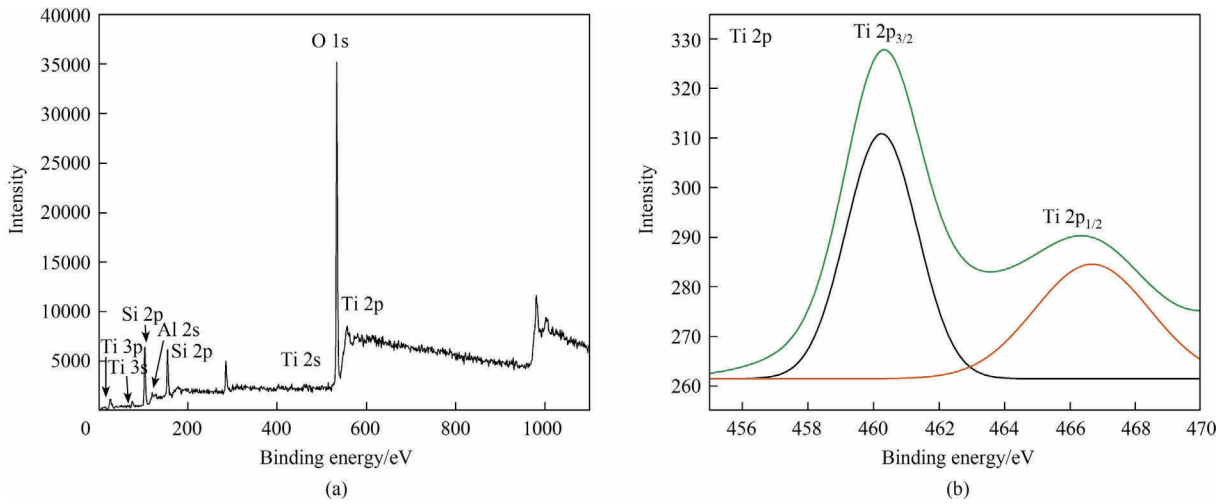

Fig. 6. (a) XPS survey spectrum of AlSi-Ti(n) and (b) Ti 2p spectra.

such an oxidation process requires harsh reaction conditions and it may also produce many side products making separation of the desired oxidation product by complex procedure and affects process economics. So facilitating the selective allylic oxidation of cyclohexene especially at mild reaction conditions is still desirable and challenging. The AlSi-Ti materials with variable oxidation state of Ti synthesized in the present study have been explored for the selective oxidation of cyclohexene to produce industrially important KA oil (cyclohex-2-en-1-ol and 2-cyclohexen-1-one) using H_2O_2 as an oxidant under mild reaction conditions.

The parent AlSi and three Ti-containing AlSi catalysts have been tested for the cyclohexene oxidation reaction at very mild reaction conditions of 35 °C in acetonitrile solvent medium using H_2O_2 as oxidizing agent for 30 min reaction time (Table 1). The Ti-free AlSi catalyst shows a very low cyclohexene conversion (14%) to form two selective allylic oxidation products namely, 2-cyclohexen-1-one and cyclohex-2-en-1-ol with selectivities of 33.47% and 66.53%, respectively. All three Ti-containing catalysts exhibited very high conversion (100%) irrespective of the concentration of Ti present in the catalysts. This observation suggests that the presence of Ti is playing a vital role in achieving higher molecular conversions, perhaps by creating the active sites (Ti^{4+}/Ti^{3+}) responsible for the effective conversion of cyclohexene. However, other than allylic oxidation products are also observed to form on Ti-containing catalysts. The selectivity to such other oxidation products is again decreased with Ti content. With this trend, the AlSi-

Table 1
Effect of Ti content on the allylic oxidation reaction

Catalyst	Conversion of cyclohexene/%	Selectivity/%			Efficiency of H_2O_2 utilization/%
		Cyclohex-2-en-1-ol	2-Cyclohexen-1-one	Other	
AlSi-Ti(0)	14	33.47	66.53	–	47
AlSi-Ti(0.01)	100	38.56	12.50	51.94	88
AlSi-Ti(0.03)	100	40.48	37.29	19.63	92
AlSi-Ti(0.05)	100	55.58	44.42	–	98

Reaction conditions: catalyst amount–0.5 g, time–30 min, temperature–35 °C, cyclohexene: H_2O_2 (mole ratio) –1:2, catalyst: cyclohexene (mass ratio)–1:2, solvent–acetonitrile, efficiency of H_2O_2 utilization = (mol of converted cyclohexene /mol of converted H_2O_2) × 100%.

Ti(0.05) exhibited complete selectivity to the allylic oxidation products. The catalyst characterization results also indicated some structural changes in the materials and improvement in the mesoporosity by the involvement of Ti in the AlSi structure. Noticeably, AlSi-Ti(0.05) exhibits 100% conversion with 100% total selectivity to allylic oxidation products, namely, 2-cyclohexen-1-one (55.58%) and cyclohex-2-en-1-ol (44.42%) without forming any side products. The higher activity of AlSi-Ti(0.05) catalyst may be due to its well-ordered mesopores as well as the presence of sufficient amount of suitable Ti^{4+}/Ti^{3+} species as evident from N_2 adsorption–desorption and Ti2p XPS results. Thus, Ti-incorporated AlSi of the present study is considered as an effective catalyst for the selective allylic oxidation of cyclohexene (100% conversion and 100% total selectivity). To understand the effect of support on the cyclohexene oxidation, the reaction was also conducted with Ti loaded conventional SBA-15 support (entry 2 in Table S2), it showed only 84% cyclohexene conversion with 35% 2-cyclohexen-1-one and 42% cyclohex-2-en-1-ol selectivities, indi-

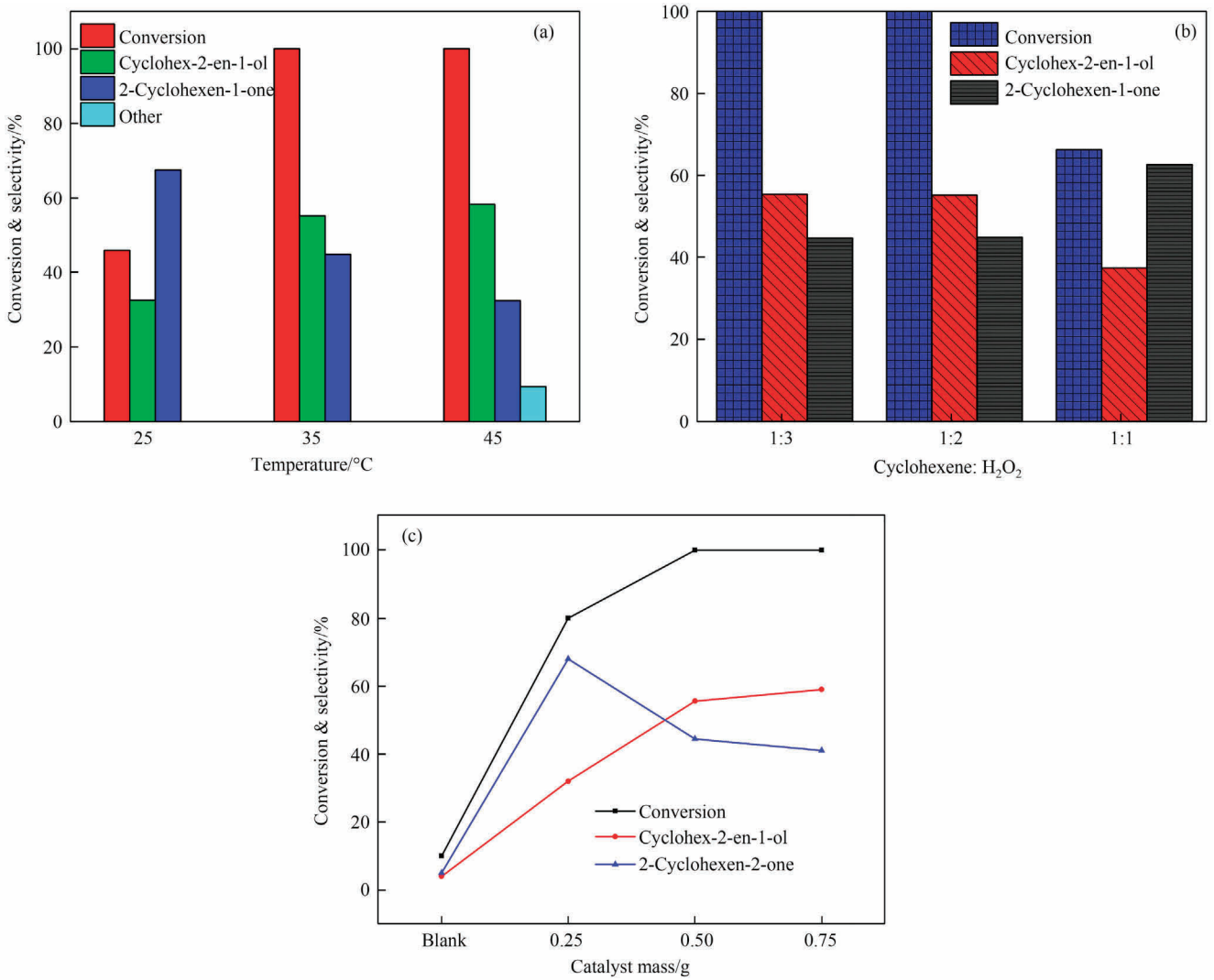

Fig. 7. Effects of (a) reaction temperature, (b) cyclohexene-to-H_2O_2 molar ratio and (c) catalyst amount. (Reaction conditions (a): catalyst–AlSi-Ti(0.05), catalyst amount–0.5 g, time–30 min, cyclohexene: H_2O_2–1:2, catalyst: cyclohexene–1:2, solvent–acetonitrile; Reaction conditions (b): temperature–35 °C, catalyst–AlSi-Ti(0.05), catalyst amount–0.5 g, time–30 min, catalyst: cyclohexene–1:2, solvent–acetonitrile; Reaction conditions (c): catalyst–TiAlSi(0.05), temperature–35 °C, time –30 min, cyclohexene: H_2O_2–1:2, catalyst: cyclohexene–1:2, solvent– acetonitrile.)

cating the catalytic activity of Ti-SBA-15 on the cyclohexene oxidation was significantly less compared to that of AlSi of the present study.

In order to explore the effect of temperature on the cyclohexene conversion for the formation of selective oxidation products the reaction temperature has been varied from 25 °C to 45 °C using the best performing AlSi-Ti(0.05) catalyst of the present study. Fig. 7(a) illustrates the conversion of cyclohexene and selectivity of products (2-cyclohex-2-en-1-ol and 2-cyclohexen-1-one) has been linearly increased with reaction temperature. At 35 °C, the catalyst shows 100% conversion and 100% total selectivity to said products. However, further increase of reaction temperature from 35 °C to 45 °C caused a slight drop in the selectivity due to formation of side products such as epoxide and di-ol. The decrease in the desired product selectivity at 45 °C was probably caused by the self-decomposition of H_2O_2 at higher temperature on AlSi-Ti (0.05) catalyst.

The effect of oxidant amount on the allylic oxidation of cyclohexene was determined by conducting the reaction with various amounts of H_2O_2, while cyclohexene amount was kept constant. Fig. 7(b) apparently indicates that the conversion of cyclohexene towards allylic oxidized products was significantly affected by the H_2O_2 amount. The absence of H_2O_2 has not shown any oxidation in the cyclohexene (not shown in Fig. 6(b)). It was observed that the use of H_2O_2:cyclohexene mole ratio of about 1:1 resulted in 66% conversion of cyclohexene with product selectivities towards 2-cyclohexen-1-one and cyclohex-2-en-1-ol. The conversion is increased with increase of this reactant ratio, where 100% conversion towards above products is obtained at 1:2 mole ratio of H_2O_2:cyclohexene. Further increase of H_2O_2:cyclohexene ratio from 1:2 to 1:3 caused constant conversion of 100%, but it was not shown any significant change in the product patterns. The studies indicate the need of 1:2 molar ratios for effective allylic oxidation cyclohexene towards KA oil. This ratio can be justified by understanding the below empirical equation of the H_2O_2 decomposition reaction.

$$H_2O_2 \rightarrow OH\cdot + OH\cdot.$$

As per empirical equations, one H_2O_2 molecule is sufficient to provide 2 OH· radicals, but this is not the situation observed at practical conditions. As observed from many literature findings, one molecule of H_2O_2 gives two OH· radical species, from which one OH· is participating in the oxidation of cyclohexene and another OH· radical gets converted to H_2O molecule [40]. Thus, for obtaining two OH· radicals, there is a requirement of two H_2O_2 molecules available in the reactant mixture. Based on this, 1:2 mole ratio of cyclohexene:H_2O_2 seems to be an ideal conditions which is in agreement with the results obtained in the present study, where, 100% conversion of cyclohexene is achieved.

The utilizing efficiency of H_2O_2 in the present study is given in Table 1, which demonstrates H_2O_2 had a significant influence on the cyclohexene oxidation reaction. AlSi-Ti(0) catalyst showed less conversion than other AlSi-Ti(n) perhaps due to the less utilizing efficiency of H_2O_2. It was well-known that self-decomposition of H_2O_2 could decrease its utilizing efficiency resulting in the low oxidizing ability. Whereas, AlSi-Ti(0.05) catalyst has shown 100% oxidation in cyclohexene towards allylic oxidized product ascribed due to the high utilizing efficiency of H_2O_2.

The effect of catalyst weight on catalyst performance of AlSi-Ti (0.05) sample has been conducted in the range of 0.25–0.75 g. It can be seen from Fig. 6(c) that conversion and selectivity of 2-cyclohex-2-en-1-ol and 2-cyclohexen-1-one were linearly increased with catalyst amount from 0.25 to 0.5 g indicating the activity of catalyst is directly related to Ti moieties that can be promoted the allylic oxidation reaction. It also observed that further increase of catalyst amount (0.75 g) has not shown any significant change in the selectivity of 2-cyclohex-2-en-1-ol and 2-cyclohexen-1-one, which indicates that 0.5 g catalyst is sufficient to show enough amount of Ti moieties to convert entire cyclohexene molecule into above allylic oxidized products. In order to establish the influence of catalyst on the present study, a blank reaction (absence of catalyst) has been conducted in presence of H_2O_2, it shows a very low conversion with undesirable products

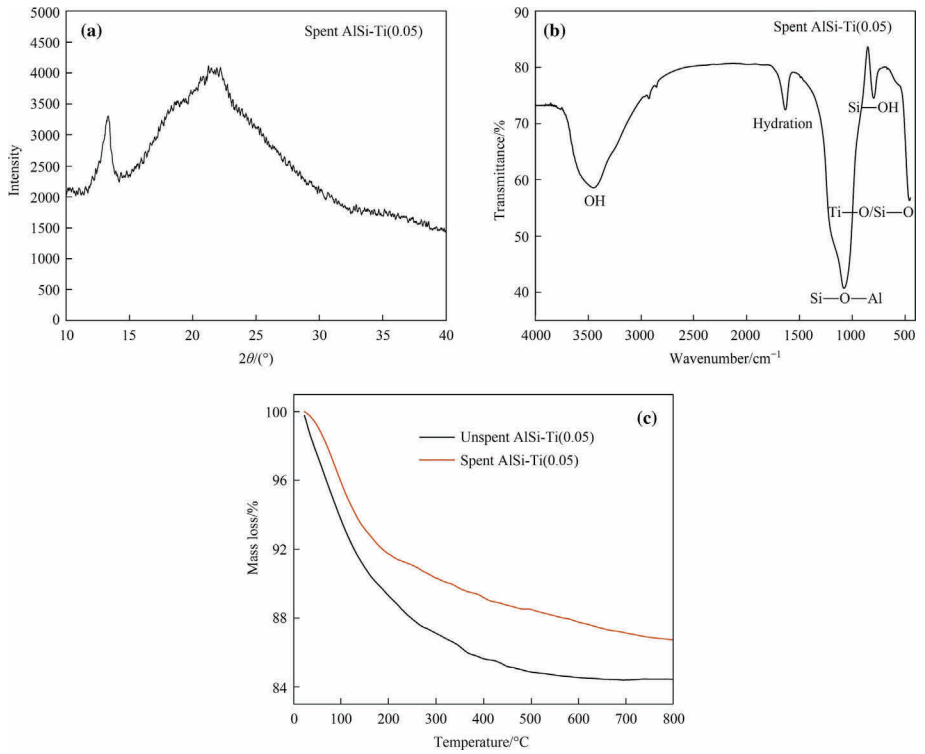

Fig. 8. Spent catalyst results (a) XRD, (b) FT-IR and (c) TGA.

which possibly ascribed due to direct oxidation of cyclohexene molecules by H_2O_2.

The performance of AlSi-Ti(0.05) catalyst in terms of conversions and products selectivities has been studied to understand the optimum reaction time (Table 2). At 25 min time, about 76% of cyclohexene has been converted into cyclohex-2-en-1-ol (48.87%) and 2-cyclohexen-1-one (14.02%) along with considerable amount of side products (37.11%). It was noteworthy that continuation of this reaction for another five minutes (at 30 min) could enhance the conversion levels to reach 100%, where the total selectivity to 2-cyclohexen-1-one and cyclohex-2-en-1-ol is also reached to 100%, without any side product formation. Further increase of reaction time from 30 to 120 min does not show any significant change in the catalytic activity in terms of conversion and product selectivity, which indicate the 30 min reaction time is enough for effective selective oxidation reaction of cyclohexene on the present catalyst system. To explore the stability of the catalyst, the spent AlSi-Ti(0.05) catalyst has been segregated from the reaction medium by simple filtration method and which was characterized by XRD, FT-IR and TGA techniques (Fig. 8). The results of the spent catalyst are comparable with those of fresh catalyst, indicating the catalyst properties were not changed even after conducting the reaction for 120 min. Moreover all the above catalyst performance results revealed that the conversion of cyclohexene and selectivity of the products were mainly dependent on the three important factors *i.e.* (i) Ti content especially Ti^{4+}/Ti^{3+} species, (ii) ordered-mesoporosity of AlSi-Ti and (iii) the amount of H_2O_2.

Overall, the AlSi-Ti(*n*) synthesized in the present study exhibited excellent performance towards selective oxidations of cyclohexene at very mild reaction temperature of 35 °C within 30 min reaction time. Performances of such catalysts reported in the literature have been compiled in Table S2 (Supplementary Material). These reports demonstrate the oxidation of cyclohexene had several disadvantages *i.e.* (i) low conversion, (ii) low selectivities to allylic oxidised products or formation of undesirable products and (iii) required high cost catalyst systems as well as oxidising components. The data also clearly reveals that so far there is no suitable catalyst system available for 100% cyclohexene conversion and 100% selectivity towards 2-cyclohex-2-en-1-ol and 2-cyclohexen-1-one at such a low temperature (35 °C) in 30 min of reaction time. In most of the report, the reaction has been conducted either at high temperature or longer reaction times, for achieving 100% conversion and 100% selectivity. Therefore, the mesoporous AlSi-Ti(0.05) material of the present study can be considered to be a promising catalyst for the selective oxidation of cyclohexene in terms of energy saving and fast conversions.

4. Conclusions

The present study demonstrates the successful synthesis of mesoporous Ti containing alumino-silicate by a novel single step Na-free method. XRD and N_2-adsorption–desorption results of the synthesized materials confirm the presence of high surface area and mesoporosity. XPS and FT-IR results clearly evidence the framework arrangement of Ti in the alumino-silicate structure. The synthesized mesoporous AlSi-Ti(*n*) materials of the present study are effective for selective allylic oxidation reaction of cyclohexene (100% conversion) at very low reaction temperature, 35 °C, within short reaction time of 30 min using H_2O_2 as a green oxidant to exhibit 100% selectivity for KA oil (2-cyclohexen-1-one and cyclohex-2-en-1-ol). The AlSi-Ti(*n*) of the present study may also be applied for other selective oxidation reactions especially for those where thermodynamics favours the low temperature operation to obtain the desired product in higher yields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

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