A layered titanosilicate AM-4 as a novel catalyst for the synthesis of 1-methoxy-2-propanone from propylene oxide and methanol

Maria N. Timofeeva, Julia V. Kurchenko, Galina O. Kalashnikova, Valentina N. Panchenko, Anatoliy I. Nikolaev, Antonio Gil

PII: S0926-860X(19)30395-3
DOI: https://doi.org/10.1016/j.apcata.2019.117240
Reference: APCATA 117240
To appear in: Applied Catalysis A: General

Received Date: 18 July 2019
Revised Date: 5 September 2019
Accepted Date: 6 September 2019

Please cite this article as: Timofeeva MN, Kurchenko JV, Kalashnikova GO, Panchenko VN, Nikolaev AI, Gil A, A layered titanosilicate AM-4 as a novel catalyst for the synthesis of 1-methoxy-2-propanone from propylene oxide and methanol, Applied Catalysis A, General (2019), doi: https://doi.org/10.1016/j.apcata.2019.117240

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.
A layered titanosilicate AM-4 as a novel catalyst for the synthesis of 1-methoxy-2-propanole from propylene oxide and methanol

Maria N. Timofeeva$^{1,2,*}$, Julia V. Kurchenko$^{1,2}$, Galina O. Kalashnikova$^3$, Valentina N. Panchenko$^{1,2}$, Anatoliy I. Nikolaev$^3$, Antonio Gil$^4$

$^1$ Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090, Novosibirsk, Russian Federation
$^2$ Novosibirsk State Technical University, Prospekt K. Marksa 20, 630092, Novosibirsk, Russian Federation
$^3$ Nanomaterials Research Center, Kola Science Center, the Russian Academy of Sciences, 14 Fersman Street, Apatity 184209, Russia
$^4$ INAMAT-Science Department, Public University of Navarra, 31006 Pamplona, Spain

Corresponding authors
M.N. Timofeeva
Tel.: +7-383-330-7284
Fax: +7-383-330-8056
E-mail: timofeeva@catalysis.ru
Address: Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090, Novosibirsk, Russian Federation

Graphical Abstract
Highlights

- Layered titanosilicate AM-4 of the synthetic analog of the natural Lintisite group was synthesized
- Dependence of basic properties on AM-4 treatment with HNO₃ was investigated
- Catalytic behavior of AM-4 materials in reaction of propylene oxide with methanol
- Basicity of AM-4 materials affects the reaction rate and selectivity towards 1-methoxy-2-propanol.
- 1-methoxy-2-propanol was the main product with 92-95% selectivity in the presence of AM-4

Abstract

In this paper we report for the first time the catalytic properties of the titanosilicate AM-4 in the synthesis of 1-methoxy-2-propanol (PGME) from methanol and propylene oxide (PO). PGME is widely used as a pollution-free solvent and intermediate in the synthesis of propylene glycol methyl ether acetate, the herbicide metolachlor and in other industrial applications. We found that the catalytic properties of AM-4 could be adjusted by treatment with 0.0625-0.25 M HNO₃. Increasing the concentration of HNO₃ led to a decrease in basicity, which played a critical role in the reaction rate and the selectivity towards PGME. The yield of PGME decreased with increased acid concentration. The maximum conversion of PO (88.4%) and the selectivity towards PGME (92.3%) were found to be in the presence of AM-4 at 110 °C and 8 mol/mol MeOH/PO. Our results suggest that titanosilicate AM-4 has great potential for application in basic catalysis.

Keywords: Layered Titanosilicate AM-4, Catalytic properties, Basic properties, Acid activation, 1-Methoxy-2-propanol, Propylene oxide.
Heterogeneous catalysis is now one of the fastest developing fields in chemistry and provokes the design of novel catalytic systems. A large variety of inorganic materials, such as zeolites, zeotype materials, clay materials, silicates, etc. have been suggested for use as catalysts. Among of these systems, titanosilicate molecular sieves (Tis), a relatively new class of silicates, should be emphasised. The first known mention of crystalline Tis with the empirical formula (M₂O):TiO₂: (SiO₂)ᵣ (M - a monovalent or divalent metal, NH₄⁺ or H⁺; x - 0.5-3.0; y - 1.0-3.5) is from the 1967 when Young has patented this material [1]. In 1983 Taramasso et al. [2] reported about synthesis of the titanosilicate TS-1. Isolated Ti⁴⁺ sites having tetrahedral coordination [TiO₄] are located into the silica framework having an MFI structure due to the isomorphous Si⁴⁺. Since then, a number of papers have demonstrated the synthesis of Tis having 3D structure with well-defined channels and cavities of molecular dimensions, such as TS-2, Ti-beta etc. [3-6]. Tis found application as adsorbents and catalysts due to their unique structural and physicochemical properties, [5, 6]. It was noteworthy that TS-1, Ti-Beta and Ti-MOR are used in industrial processes [5, 6].

Tis could have not only 3D structure, but also 2D structure. JDF-L1 (Jilin Davy Faraday-Layered solid 1, Na₄Ti₂Si₈O₂₂-4H₂O) was the first Tis with layered structure synthesized by Roberts et al. [3] and Du et al. [4]. The titanosilicate JDF-L1 (also known as AM-1, i.e. Aveiro-Manchester material number 1), has an unusual noncentrosymmetric tetragonal layered solid. The structure is unusual in that JDF-L1 contains 5-coordinated Ti(IV) in the form of TiO₅ square pyramids in which each of the vertices of the base is linked to SiO₄ tetrahedra to form continuous layers [9-11]. The five-coordinate Ti(IV) is also in the titanosilicate ETS-4 (ETS type, Engelhard titanosilicate) with the structure of the natural mineral zorite [12-13]. Recently, a great deal of attention is being focused on the creation of the layered Tis materials, because these materials could be important in practice as ion exchangers, gas sorbents and catalysts [5, 11,14-17].
In our investigation we wished to draw attention to the physicochemical and catalytic properties of AM-4 (Aveiro-Manchester material number 4, Na₃(Na,H)Ti₂O₇[Si₂O₆]₂ 2H₂O), which is analogous to the mineral lintisite [8,18-20]. This mineral was discovered in the hyperalkaline pegmatites of Mount Alluaiv (the north-western part of the Lovozero massif, Kola peninsula). This material has a unique layered structure. According to Dadachov et al. [19], the structure of AM-4 consists on interconnecting brookite-type TiO₆ octahedra and SiO₄ octahedra, forming layers perpendicular to the c axis (Fig. S1, Supporting Information (SI)) [19,21]. The coordination geometry of T(IV) can be envisaged as a highly distorted octahedron. The TiO₆ octahedra are linked to each other via edge-sharing, forming brookite-type zigzag chains, while the SiO₄ tetrahedra are linked via corner-sharing, forming pyroxene-type chains. Structure of AM-4 can be viewed as a five-tier sandwich of SiO₄:TiO₆:SiO₄:TiO₆:SiO₄. The charge on the Ti-Si layers is balanced by sodium cations located between the layers. Sodium cations are also in small cages within the layers.

The physicochemical properties of AM-4 are still under-researched. According to the literature [22], AM-4 possesses excellent cation-exchange properties, which give the opportunity of using AM-4 as adsorbent for Ag⁺, Zn²⁺, Cu²⁺ [18, 19], Cs and Sr [23, 24] and radionuclides ²⁴¹Am and ²³⁶Pu [23, 25]. Recently, Lima et al. [26] showed that AM-4 can be used as a solid base catalyst for the aqueous phase isomerisation of glucose and the condensation of benzaldehyde with ethyl acetoacetate (the Knoevenagel reaction). Unfortunately, the basic properties of AM-4 have not been investigated.

In this work we investigated the catalytic behaviour of AM-4 in the synthesis of propylene glycol methyl ether (PGME) from propylene oxide (PO) and methanol (Scheme 1). This reaction is of interest to industry, because PGME has important applications as a pollution-free solvent and intermediate in the synthesis of propylene glycol methyl ether acetate, the herbicide metolachlor and in other industrial applications [27, 28]. Moreover, this reaction is scientifically interesting because the reaction rate and the reaction selectivity are dictated by the nature of the active sites...
of the catalyst. The maximum yield of PGME with 80–92% selectivity was demonstrated in the presence of basic-type systems, such as NaOH [29], the ionic liquid 1,1,3,3-tetramethylguanidium lactate immobilised on bentonite and SBA-15 (IL/Support) [30], synthetic and natural layered double hydroxides (LDHs) [31,32], and $\text{M}_x\text{O}_y$ oxides ($\text{M} = \text{Cu, Fe, Zn, Sn, Ni and Mg}$) [33-35]. The primary alcohol 2-methoxy-1-propanol (MEPG) is formed mainly in the presence of acid-type catalysts (BF$_3$, H$_2$SO$_4$ [36]). Following on from the previous investigations of this reaction [31-33], it was clear that reaction rate and selectivity towards PGME were controlled by variations in the acid-base properties of the catalytic system. An increase in surface acidity leads to an increase in reaction rate, but an increased basicity of the system results in an enhancement of selectivity towards PGME. On that basis and considering the chemical composition of AM-4, it may be estimated that this material can be used as catalyst for the synthesis of PGME from PO and MeOH. We assume that treatment of AM-4 with HNO$_3$ will allow regulation of its catalytic behaviour, i.e., both rate and selectivity of the reaction. Our study focused on three main themes: (a) investigation of basic properties of AM-4 by IR spectroscopy using CDCl$_3$ as probe molecule, (b) the understanding of the role and effect of that basicity on the catalytic behaviour of AM-4 in the synthesis of PGME, and (c) assessment of the potential of AM-4 as basic-type catalyst for further applications in catalysis.

2. Experimental

2.1. Materials

Propylene oxide (99.5%) was purchased from Acros Organic. Commercial methanol was used without any further purification. Powder of ammonium sulfate oxytitanium ($\text{NH}_4\text{TiO(SO}_4\text{)}_2\cdot \text{H}_2\text{O}$ was the product of loparite concentrate reprocessing (PJSC PhosAgro, Russia). Na$_2$SiO$_3$·5H$_2$O and NaOH purchased from Neva Reactive and Merck, respectively. All chemicals were used as received without any further purification.

2.1.1. Synthesis of AM-4
Hydrothermal synthesis of layer titanosilicate was carried out in a Teflon-lined autoclave with an inner volume of 450 cm³. A typical synthesis started from the preparation of gel by the mixing of 52.61 g of (NH₄)₂TiO(SO₄)₂·H₂O, 85.48 g of Na₂SiO₃·5H₂O, 28.22 g of NaOH, and 317 g of distilled water. The molar ratio of Na₂O:SiO₂:TiO₂:H₂O was 5.6:3.1:1:130.4. This mixture was stirred at 25 °C for 3 h. Then, the resulting mixture was transferred to an autoclave for further reaction. The temperature and time of reaction were modified from time to time. First step: autoclave was kept motionless at 230 °C for 15 h, then was cooled down to 150 °C for 2 h and was kept under stirring for 4 h. Second step (all the following procedures were under stirring): autoclave was heated up to 230 °C and the mixture was aged in autoclave for 64 h. Then, autoclave was cooled down to 100 °C for 2 h and was kept for 3 h. Third step: the autoclave was heated up to 230 °C for 1 h and then quickly was cooled down to room temperature. The obtained compound was separated by filtration, followed by repeated washing with distilled water and subsequent dryness at 60-70 °C for 24 h. The yield of solid was 45 g. Chemical composition, XRD data, IR spectrum and textural properties of AM-4 are shown in Table 1, Tables S1-S1 (SI) and Fig. S2-S3 (SI).

2.1.2. Modification of AM-4 by HNO₃

1 g of solid was suspended in 10 cm³ of aqueous solutions of 0.0625-0.25 M of HNO₃ and the mixture was stirred at room temperature for 30 min. Then, the solid was separated, washed with water and dried at room temperature. The designation of the samples and the conditions of their synthesis are presented in Table 1. Chemical composition, XRD data, IR spectrum and textural properties of samples are shown in Table 1, Tables S1-S1 (SI) and Fig. S2-S3 (SI).

2.2. Instrumental measurements

The chemical analyses of the solids were carried out by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES). The diffraction images were obtained with the use of a Thermo ARL X’tra device, with a non-monochromated Cu Kα radiation (λ = 1.5418
Å), focusing geometry θ-θ in the scanning mode within the range of angles from 3 to 75°, with a step of 0.05°. Morphology of samples was studied by SEM analysis using a JSM-6460LV (JEOL) field-emission scanning electron microscope.

The porous structures of samples were determined from the adsorption of N\textsubscript{2} at 77 K using an ASAP 2020 Plus Instrument from Micromeritics. The specific surface area \(S_{\text{BET}}\) was calculated from the adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume \(V_{\Sigma}\) was evaluated at a \(p/p_0\) of 0.99.

The basicity of the samples was determined by DRIFT spectroscopy using CDCl\textsubscript{3} as probe molecule. The analysis method was described previously [37]. The sample (0.15-0.2 g) was transferred to a cuvette (cell) suitable for DRIFTS measurements for FTIR characterization. The sample was heated under vacuum at 150°C for 1 h. The strength of the base sites was estimated using the following equation:

\[
\log \nu_{C\cdot D} = 0.0066 \text{PA} - 4.36
\]

(Eq. 1)

where \(\nu_{C\cdot D}\) is the shift, in cm\textsuperscript{-1}, of C-D vibration and PA is the proton affinity. DRIFT spectra were recorded on a Shimadzu FTIR-8300S spectrometer with a DRS-8000 diffusion reflectance cell in the 400-6000 cm\textsuperscript{-1} range with a resolution of 4 cm\textsuperscript{-1}.

### 2.3. Catalytic tests

The catalytic properties of the samples were tested in the synthesis of 1-methoxy-2-propanol from methanol and propylene oxide (PO) at 50-130 °C. The reaction was carried out in a stainless steel autoclave reactor with an inner volume of 25 cm\textsuperscript{3}. Before the reaction, all catalysts were activated at 60 °C for 2 h in air. The standard procedure was as follows: 7.4 mmol PO, MeOH (MeOH/PO = 8 mol/mol) and catalyst (1.8 wt.%) were introduced into the autoclave. After 5 or 7.5 h of reaction, the reactor was cooled down to room temperature. The products were analyzed by a gas chromatograph (Agilent 7820) equipped with a flame ionization detector and using a HP-5 capillary column, after separation by centrifugation of the catalysts.

### 3. Results and discussion
3.1. Synthesis and characterisation of AM-4 modified with HNO₃

A pure crystalline phase of AM-4 was obtained from (NH₄)₂TiO(SO₄)₂·H₂O, Na₂SiO₃·5H₂O and NaOH. The crystal morphology, elemental analysis and textural properties of the sample are shown in Table 1, Tables S1-S2 and Fig. S2-S3 (SI). The chemical analysis of AM-4 indicated that sodium ions were leached from the framework of AM-4 after its modification with 0.0625–25 M HNO₃ (Table 1). The application of 0.25 M HNO₃ led to the leaching of 97.9 wt.% of sodium ions. Moreover, the modification of AM-4 with acid led to a decrease in the unit cell parameter c from 29.22 to 5.21 Å (Table S1, SI), which points to the contraction of the unit cell due to the leaching of Na⁺ and the incorporation of protons into the framework.

The morphology and particle sizes of AM-4 and 0.25M AM-4 was investigated by Scanning electron microscope (SEM). SEM images of samples are shown in Fig. 1. These data point that AM-4 consists of the relatively uniform aggregates of rosette-like crystalline aggregates with 7-8 µm of the width and 15-17 µm of the length (Fig. 1A). These aggregates are formed by the titanosilicate platelets. The thickness of individual titanosilicate platelets is 0.15-0.25 µm (Fig. 1B). After AM-4 modification with 0.25M HNO₃ the particles became inhomogeneous with size from 3 to 5 and 5-17 µm of the width and the length, respectively (Fig. 1C). The thickness of titanosilicate platelets decreases and is in the range of 0.05-0.20 µm (Fig. 1D). This phenomenon agrees with the decreasing the unit cell parameters (Table S1, SI). Note that the space between the titanosilicate platelets increases slightly that is consistent with the increasing specific surface area from 20 to 30 m²/g and total pore volume from 0.070 to 0.095 cm³/g (Table S2, SI)

The change of the chemical composition should affect the acid-base properties. These changes in the course of the acid modification were estimated by two approaches. The first was based on the estimation of the optical basicity concept suggested by Duffy [38]. The basicity of oxides [39] is compared in terms of optical basicity (Λ), which is concerned with the electron-donor power of lattice oxygen atoms and depends on the oxidation number and coordination of the cations. This parameter is also successfully used for the characterisation of inorganic oxyacids,
molten salts, and glasses, etc. [38, 40]. We estimated the values of optical basicity of pristine AM-4 and after modification with acid using Eq. 2 [38]:

\[ \Lambda = X_{Na} \Lambda_{Na} + X_{Si} \Lambda_{Si} + X_{Ti} \Lambda_{Ti} \]  

(Eq. 2)

where \(X_{Na}, X_{Si},\) and \(X_{Ti}\) are the equivalent fractions of metals; and \(\Lambda_{Na} (1.15)\) [38], \(\Lambda_{Si} (0.48)\) [38] and \(\Lambda_{Ti} (0.75)\) [38] are the optical basicities of Na, Si and Ti, respectively. The main results are shown in Fig. 2 and Fig. S4 (SI). These results indicate that optical basicity decreases with increasing acid concentration. The change in optical basicity relates to the change in surface acidity determined as the point of zero charge (pH\text{PZC}) (Fig. 2 and Fig. S4 (SI)). This result is not surprising, because the acid treatment should lead to the simultaneous decrease in surface basicity and increase in surface acidity.

The basicity of AM-4, both pristine and modified with 0.25 M HNO\textsubscript{3}, was also analysed by deuterated chloroform (CDCl\textsubscript{3}) as a C-H acid probe using IR spectroscopy. In 1979 Paukshtis et al. [37] suggested the use of CDCl\textsubscript{3} for analysis of the basic properties of oxide catalysts prepared by calcination of the respective hydroxides. A band at 2265 cm\textsuperscript{-1} in the spectrum of CDCl\textsubscript{3} adsorbed on SiO\textsubscript{2} was demonstrated to be close to the position of the \(\nu_{C-D}\) of physisorbed deuterated chloroform at 2264 cm\textsuperscript{-1} (Scheme S1 (SI), structure A). Investigations of other oxides (CaO, BaO, MgO) allowed the authors to propose ways of CDCl\textsubscript{3} adsorption on basic sites due to their different spectroscopic bands. Thus, CDCl\textsubscript{3} can interact with strong basic sites via one of the lone pairs of the oxygen atoms on the catalyst surface (Scheme S1 (SI), structure B\textsubscript{1}). Recently, in the spectrum of CDCl\textsubscript{3} adsorbed on silica–magnesia catalysts, the presence of bands at 2139 and 2086 cm\textsuperscript{-1} indicated the presence of strongly basic sites [41]. It was proposed that a basic site interacts with the deuterium and an additional closely located second basic site interacts with the electropositive carbon atom of the chloroform (Scheme S1 (SI), structures B\textsubscript{2}, C\textsubscript{1} and C\textsubscript{2}). Note that \(\nu_{C-H}\) of complexes B and C are different. Thus, for Al\textsubscript{2}O\textsubscript{3} the spectroscopic regions of \(\nu_{C-H}\) for B\textsubscript{1} and C\textsubscript{1} complexes are 2150-2190 and 2190-2220 cm\textsuperscript{-1}, respectively [42]. CDCl\textsubscript{3} has been applied in basicity studies
on oxides [43, 44], zeolites [43-45], and hydrotalcites (MgO-Al₂O₃ systems) [41, 46, 47], among others.

The spectra of CDCl₃ adsorbed on AM-4, both pristine and modified with 0.25 M HNO₃, are summarised in Fig. 3. The four bands observed can be related to the interaction of CDCl₃ with basic sites. Only one band, at 2260 cm⁻¹, is observed in the spectrum of CDCl₃ adsorbed on 0.25 M AM-4. The nature of these basic sites is not clear, but some assumptions can be considered. The band at 2253 cm⁻¹ can be assigned to C-D stretching of CDCl₃ chemisorbed on weakly basic sites, whereas other bands at 2055, 2130 and 2200 cm⁻¹ can be attributed to CDCl₃ chemisorbed on strongly basic sites [37, 44]. Taking into account the structure of AM-4, we can suggest that the three latter bands are result from the interaction of CDCl₃ with basic sites formed by oxygen anions which adjacent to sodium ions in the AM-4 framework (Fig. S1, SI). Structural investigations and DFT calculations [18,19,48] point that the charge balancing Na⁺ cations are found either in small cages formed by TiO₆ and SiO₄ within the layers (Na (1) or associated with water molecules in the interlayer space (Na(2) and Na(3)). Sodium cations located in the interlayer space (Na(2) and Na(3)) can be easily replaced by protons in the course of acid modification. As result, in 0.25M AM-4 sample basic sites is likely to be formed by oxygen ions which adjacent to sodium ions Na(1) located in small cages (Fig. S1, SI). This suggestion is in accordance with the changes in the spectrum after AM-4 treatment with 0.25 M HNO₃.

It was interesting to compare the basicity of AM-4 with other systems having basic sites [37, 41, 44]. The spectral characteristics (νC-D) for various catalytic systems determined by CDCl₃-IR spectroscopy are shown in Table 2. We also estimated the strength of basic sites (the proton affinity, PA) from the shift of νC-D using Eq. (1). The main results are also shown in Table 2. As is evident from the table, AM-4 has strong basic sites, although their strength are slightly lower than estimated for NaOH (Table 2, runs 2-3) [49]. In other respects, AM-4 has the strongest basic sites of all studied systems. Even the basicities of SiO₂, γ-Al₂O₃ and NaY systems impregnated
with caesium hydroxide (Table 2, runs 9-14) are lower than that of AM-4. Their maximum values of \( \Delta v_{\text{CD}} \) do not exceed 108-179 cm\(^{-1} \). Note that the band at 2213 cm\(^{-1} \) is dominant in the spectrum of Cs/\( \gamma \)-Al\(_2\)O\(_3\), whereas the band at 2200 cm\(^{-1} \) has a maximum intensity in the spectra of Cs/SiO\(_2\) and Cs/MCM-41. Noteworthy that basicity of AM-4 is higher 1019 kJ/mol) in compared with 0.25M AM-4 (797 kJ/mol). This is not surprising, since some of the sodium ions are replaced by protons that lead to the increasing surface acidity (Fig. 2).

3.2. Catalytic properties of AM-4 materials

The catalytic properties of AM-4 materials were investigated by considering the reaction between PO and MeOH (Scheme 1). First of all, in the presence of these materials the reaction was found to be heterogeneous; this was confirmed by several experimental results. Thus, the AM-4 sample was filtered off after 2 h of reaction at 110 °C, an 8:1 molar ratio of MeOH/PO and 1.8 wt.% of catalyst, when the conversion of PO was 35.5%. Then, the filtrate without catalyst was further stirred at 110 °C for 2 h in an autoclave. After removing the catalyst, the change in the conversion of PO (36.1%) was negligible. The main results are shown in Table 3 and Table S3 (SI). According to the experimental results, the main products were PGME and MEPG. Note that increasing the reaction temperature from 50 to 110 °C led to a slightly decreased selectivity, from 95.1 to 91.5%, whereas the conversion of PO increased (Table 3).

The reaction selectivity depends strongly on the concentration of HNO\(_3\) used for the AM-4 modification (Fig. 4). Selectivity towards PGME is reduced with increasing acid concentration. Thus, after the AM-4 treatment with 0.25 M HNO\(_3\) the selectivity towards PGME decreased from 95.0 to 53.3%. This result can be related to changes in the nature of the active sites. This is consistent with the linear relation between selectivity and optical basicity (\( \Lambda \)) (Fig. 5).

The concentration of acid has an unusual effect on the conversion of PO (Fig. 4). At the start, the conversion of PO is reduced rapidly at concentrations up to 0.0625 M, and then it rises. The U-shape trend can indicate the dependence of the reaction rate on various parameters. Several possibilities can be proposed: (a) the number of active sites drops dramatically due to the sodium
ions leaching from the framework of AM-4, and (b) the accessibility of the active sites reduces due to the changes in the structure, i.e., the sharp decrease in unit cell parameters. The consequent increase in the concentration of HNO₃ has a positive effect on the reaction rate. The conversion of PO rises linearly with increasing of HNO₃, which can be related to the change in surface acidity (Fig. 4).

It is interesting to compare the effect of HNO₃ activation on the catalytic behaviour of AM-4 and a montmorillonite (Mt). Both titanosilicate AM-4 and aluminosilicate Mt are layer materials and have sodium ions in the interlayer spaces. According to experimental data, in the presence of AM-4 the conversion of PO and yield of PGME decrease with increasing HNO₃ concentration up to 0.0625 M and then trend upward with a further increase in acid concentration. At the same time, the opposite effect of acid concentration on the conversion of PO and yield of PGME is observed in presence of Mt (Fig. 4 and Fig. S5 (SI)). These results indicate that the changes in the nature of the acid–base sites in AM-4 and Mt are affected differently by HNO₃. Thus, the change in Si/Al molar ratio in the course of the treatment of Mt with HNO₃ indicates that active acid sites are formed mainly via the leaching of the exchangeable cations (Table S4 (SI)) when concentration of acid is less than 0.25 M. In the region of 0.25-0.5 M HNO₃, the appearance of acid sites is caused by the leaching of the exchangeable cations and Al ions from the tetrahedral layers of Mt. However, increasing the acid concentration over 0.5 M leads to decreasing acid sites, i.e., a reduction in surface acidity due to the decreasing Al content in the layered clay. At the same time, active acid sites in AM-4 are formed due to the monotonic leaching of the sodium ions from framework.

3.3. Reaction mechanism in the presence of AM-4
The reaction mechanism was investigated by IR spectroscopy. Propylene oxide and MeOH were adsorbed on AM-4 in order to understand the nature of their interactions with surface functional groups.

First of all, we investigated the adsorption of PO on AM-4. The mid-infrared absorption spectra (400-1400 cm\(^{-1}\)) of AM-4, both pristine and after PO adsorption, are shown in Fig. 6. The spectrum of AM-4 reveals broad bands in the regions 400-700 cm\(^{-1}\) and 700-1200 cm\(^{-1}\), which can be attributed to the Ti-O and Si-O bending vibration modes and the asymmetric and symmetric stretching vibrations of the framework SiO\(_4\) polyhedra [50]. Note that in IR spectrum of the flower-like brookite TiO\(_2\) the bending vibrations of Ti-O and O-Ti-O bonds in TiO\(_6\) octahedron were observed at 420, 488, 564 and 710 cm\(^{-1}\) [51].

Adsorption of PO on the surface of AM-4 does not change significantly the shape of the spectrum (Fig. 6). However, it is possible to see some bands of PO. Thus, bands at 899 and 1254 cm\(^{-1}\), assigned to the stretching and bending vibrations of –CH\(_2\)- bonds in the epoxy ring, are seen (–CH\(_2\)- rocking/ring deformation) [52, 53]. Moreover, bands at 1436 and 1504 cm\(^{-1}\), assigned to deformation vibrations of the –CH\(_3\) group [52, 53] are observed. All these bands point to the physical adsorption of PO on AM-4.

In the second step of the investigation we considered the interaction of MeOH with surface functional groups of AM-4. The IR spectrum of MeOH adsorbed on AM-4 is shown in Fig. 6. The spectrum reveals weak bands at 1165 and 1436 cm\(^{-1}\) assigned to the \(\rho_{\text{CH}_3}\) rocking mode [54] and the \(\delta(\text{CH}_3)\) methyl deformation modes [55]. It is well known that adsorption of MeOH on the surface of oxides leads to the formation of both undissociated adsorbed forms (\(\text{CH}_3\text{OH}_{\text{ads}}\), species (I)) (mainly on acidic sites) and dissociatively adsorbed surface methoxy species (–OCH\(_3\), species (II)) (on less acidic or basic sites [54-56]). According to Busca et al. [57, 58] and Lavalley et al. [59], dissociated species (II) are characterised by bands at 2930 and 2830 cm\(^{-1}\) that arise from Fermi resonance between the symmetric stretch (\(\nu_s\)) and first overtone of the symmetric bend (2\(\delta_s\)) of CH\(_3\) units in adsorbed –OCH\(_3\) species, respectively. At the same time, the bands at 2950 and
2850 cm$^{-1}$ are assigned to the same modes occurring in the undissociated species (I). Burcham et al. [54] demonstrated that MeOH on the surface of TiO$_2$ can form species (I) and (II) characterised by bands at 2948/2843 and 2924/2822 cm$^{-1}$, respectively. It can be seen from Fig. 56 (SI) that adsorption of MeOH onto AM-4 leads to the formation of surface methoxy species, following from the appearance of the bands at 2860 and 2945 cm$^{-1}$.

It is interesting to analyse the bands in the region of 500-950 cm$^{-1}$ that characterise the Ti,Si-lattice of AM-4 (Fig. 6). First of all, in the spectrum of MeOH adsorbed onto AM-4 we can observe the appearance a new strong band at 747 cm$^{-1}$ that can be assigned to the Ti-O stretch of the ···Ti-O-Ti-O-Ti··· chains [60-62]. Intensities of bands at 892 and 924 cm$^{-1}$, assigned to the normal modes including the v(Si-O)/v(Ti-O) and the v(Ti-O-Si) vibrations [60, 61], respectively, increase significantly. In general, the increasing intensities and appearance of new bands assigned to the vibrations of the Si-O (where T = Si or Ti) bending modes are observed in the region of 450-600 cm$^{-1}$ [63-65]. Adsorption of MeOH onto AM-4 also leads to a shift of bands assigned to the -Si-O-T- (where T = Si or Ti) stretching modes from 679 to 672 cm$^{-1}$ [62, 64]. All these changes suggest that the adsorption of MeOH takes place on the -Ti-O-Si- or -Ti-O-Ti- sites.

*Step-by-step adsorption of MeOH and PO.* Once these studies were completed, we investigated the step-by-step adsorption of MeOH and PO on AM-4. The IR spectra of AM-4 after step-by-step addition of reactants are shown in Fig. 7A. It can clearly be seen that the addition of PO to AM-4 with adsorption of MeOH leads to disappearance of the bands at 747 and 1165 cm$^{-1}$. Analysis of the different spectra indicates that the integral intensity of the band at 1436 cm$^{-1}$ assigned to -CH$_3$ bending vibrations ($\delta_3$) in MeOH [54] decreases sharply after the addition of MeOH to PO/AM-4 and then tends to increase with time (Fig. 7B). In general, after 30 min the shape of the spectrum and the position of the bands in the region of 500-850 cm$^{-1}$ became similar to that of pristine AM-4 (Fig. 7A). These changes can be related to the interaction of MeOH with PO. This suggestion is confirmed by the appearance of broad bands in the regions of 900-1000 cm$^{-1}$ and 1400-1500 cm$^{-1}$, indicating the formation of PGME and MEPG.
Spectral data obtained may suggest that active sites are formed by –Ti–O–Si– or –Ti–O–Ti– fragments. The following criteria were used in order to specify of structure of active site:

1. The observed changes in IR spectrum of AM-4 in the course of step-by-step adsorption of MeOH and PO on its also point to the important role of the "Lewis acid site - basic site" pair in reaction mechanism.

2. According to the calculation by Decaillon et al. [66], the formal charges of an oxygen in the AM-4 framework for –Ti-O-Ti-, -Si-O-Ti- and –Si-O-Si- fragments are -0.67, -0.33 and 0, respectively.

3. The two crystallographic Si sites are in AM-4 structure. The first site Si(1) has three neighboring Ti\(^{4+}\) and two neighboring Na\(^{+}\) centres, while second site Si(2) has only one neighboring Ti\(^{4+}\) and the six Na\(^{+}\) sites [18,19, 48].

4. Structural investigations pointed that Ti resides off-center within the TiO\(_6\) octahedra due to Ti\(^{4+}\) ... Ti\(^{4+}\) cationic repulsion within the titanate chains [18,19, 48].

These factors can indicate that active sites are formed by –Ti–O–Ti– fragments of the ‘zigzag’ fashion of edge-sharing TiO\(_6\) octahedra (Scheme 2). Therefore, taking into account the reaction mechanisms in the presence of several catalysts reported in literature [28, 33, 36] (Scheme 2) it consists of the following steps:

(1) Physical adsorption of PO on –Ti– ions;

(2) Dissociative adsorption of MeOH on the –O–Ti– fragment active site, i.e., formation of CH\(_3\)O\(^-\) and H\(^+\);

(3) Due to the favourable space configuration, the CH\(_3\)O\(^-\) ion attacks the C(1) atom of the epoxide ring with breakage of the C(1)–O bond; then addition of a proton to the intermediate leads to the formation of PGME.

3.4. Catalytic efficiency of AM-4

It was also interesting to compare the efficiency of the AM-4 materials with those of samples reported in the literature. First of all, we compared the efficiency of AM-4 in the synthesis
of PGME from PO and MeOH (Scheme 1) with that of Brucite and Mg,Al-LDHs [27, 32], metal oxides [67], amino-functionalised SiO₂ [68], and zeolitic imidazolate frameworks ZIF-8, and MAF-5 (ZIFs) [69]. It is possible to see from Table 3 that almost all systems have high catalytic performance at 120-140 °C, whereas AM-4, ZIF-8 and MAF-5 are active at 110 °C. However, a study of the ZIFs and AM-4 reveals that the high efficiency of the materials depends on many parameters. The selectivity towards PGME in the presence of AM-4 is similar to that in the presence of MAF-5 and ZIF-8. At the same time, in spite of the lower basicity (PA 884 kJ/mol, Table 2) MAF-5 possesses higher activity than AM-4 (PA 1019 kJ/mol). There are several reasons for the efficiency of the ZIFs. First of all, ZIFs possess (a) low adsorption capacity for water, and (b) an exceptional hydrophobicity on both the internal pore and external surfaces of their crystals [70, 71]. Both factors favour the easy adsorption of large numbers of organic molecules, including MeOH, that can affect positively the adsorption–desorption of reactants and (a) increase the reaction rate and (b) improve the selectivity towards PGME. The second reason for the high activity of MAF-5 could be related to the higher specific surface area (468 m²/g) in comparison to AM-4 (20 m²/g, Table S2, SI), which can affect the accessibility of reactants.

4. Summary and conclusions

In this work we synthesised the titanosilicate AM-4, a synthetic analogue of the natural lintisite group, from (NH₄)₂TiO(SO₄)₂, Na₂SiO₃ and NaOH in a Na₂O/SiO₂/TiO₂/H₂O molar ratio of 5.6:3.1:1:130.4. The effect of acid activation of AM-4 with HNO₃ on the physicochemical and catalytic properties of the resulting solids in the reaction between methanol and propylene oxide (PO) was investigated. The chemical analysis indicates that modification of AM-4 with 0.0625–25 M HNO₃ leads to the leaching of sodium ions from the framework of the solid that depends on the acid concentration. According to XRD, unit cell parameter c decreases from 29.22 to 5.21 Å after acid modification of AM-4. The effect of the acid treatment on the basicity of AM-4 was analysed by deuterated chloroform (CDCl₃) as a C–H acid probe using IR spectroscopy. It was
found that AM-4 possesses several types of basic sites with strong basicity (969–1019 kJ/mol). After acid modification, only the basic site with low basicity (797 kJ/mol) was monitored.

The catalytic properties of AM-4 materials were investigated in the synthesis of 1-methoxy-2-propanol (PGME) from PO and MeOH. It was found that acid treatment affected the effectiveness of AM-4. Thus, the selectivity with respect to PGME decreased with increasing acid concentration, while the reaction rate decreased significantly after AM-4 treatment with 0.0625 M HNO₃; a subsequent increase in acid concentration led to a rise in reaction rate. A comparison was undertaken of the effect of acid activation on the physicochemical and catalytic properties of AM-4 and a montmorillonite (Mt). It was found that their activity depended on the type of active sites, which is controlled by acid concentration.

The catalytic efficiencies of AM-4 materials were compared with those of zeolites, zeotype materials, layered materials and oxides reported in the literature. Except for MAF-5, the efficiency of AM-4 was higher than all materials compared in the reaction between PO and MeOH. We can assume that the advantage of MAF-5 over AM-4 is related to the differences in hydrophobicity and textural properties. Therefore, the results suggest that layered titanosilicate AM-4 is a material with a great potential for application in catalysis. From our point of view, base catalysis will be the most important and promising area where the availability of solid basic catalysts is limited. Our work opens the possibility of the use of AM-4 materials as solid base catalysts, thereby extending the number of basic-type catalytic systems.

**Acknowledgments**

This work was conducted within the framework of the budget projects AAAA-A17-117041710082-8 for Boreskov Institute of Catalysis and AAAA-A17-117020110075-1 for Nanomaterials Research Centre of the Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences” (NMRC KSC RAS), respectively. AG thanks Santander Bank for funding through the Research Intensification Program.
References


[59] J. C. Lavalley, N. Sheppard, Anharmonicity of CH$_3$ deformation vibrations and Fermi resonance between the symmetrical CH$_3$ stretching mode and overtones of CH$_3$ deformation


Figure caption

Figure 1. Scanning electron microscope micrographs of rosettelike crystalline aggregates of AM-4 and 0.25M AM-4.

Figure 2. Correlations between HNO₃ concentration, optical basicity (A) and surface acidity (pH₇₅°C) of AM-4 samples modified with HNO₃.

Figure 3. DRIFT spectra of adsorbed CDCl₃ on AM-4 and 0.25M AM-4.

Figure 4. Effect of HNO₃ concentration on the conversion of PO, selectivity towards PGME and yield of PGME in the reaction between PO and methanol in the presence of AM-4 (90°C) and a Mt modified with HNO₃ (60°C).

Figure 5. Effects of the optical basicity (A) and surface acidity (pH₇₅°C) on the selectivity towards PGME in the reaction between PO and methanol in the presence of AM-4 modified with HNO₃.

Figure 6. DRIFT spectra of AM-4 pristine and after adsorption of PO and MeOH.

Figure 7. (A) DRIFT spectra of AM-4 after successive additions of MeOH and PO, (B) IR difference spectra of AM-4 after adsorption of MeOH and then PO in the region of 1300-1600 cm⁻¹ and change of integral intensity of the band at 1436 cm⁻¹ for 26 min after PO adsorption onto MeOH/AM-4 sample.

Scheme 1. Reaction between propylene oxide and methanol.

Scheme 2. Structure of active sites in AM-4.
Figure 1. Scanning electron microscope micrographs of rosettelike crystalline aggregates of AM-4 and 0.25M AM-4
Figure 2. Correlations between HNO₃ concentration, optical basicity (Λ) and surface acidity (pH_{PZC}) of AM-4 samples modified with HNO₃.

Figure 3. DRIFT spectra of adsorbed CDCl₃ on AM-4 and 0.25M AM-4
Figure 4. Effect of HNO$_3$ concentration on the conversion of PO, selectivity towards PGME and yield of PGME in the reaction between PO and methanol in the presence of AM-4 (90°C) and a Mt modified with HNO$_3$ (60°C).

Figure 5. Effects of the optical basicity (Λ) and surface acidity (pH$_{PZC}$) on the selectivity towards PGME in the reaction between PO and methanol in the presence of AM-4 modified with HNO$_3$. 
Figure 6. DRIFT spectra of AM-4 pristine and after adsorption of PO and MeOH
Figure 7. (A) DRIFT spectra of AM-4 after successive additions of MeOH and PO, (B) IR difference spectra of AM-4 after adsorption of MeOH and then PO in the region of 1300-1600 cm\(^{-1}\) and change of integral intensity of the band at 1436 cm\(^{-1}\) for 26 min after PO adsorption onto MeOH/AM-4 sample.
**Scheme 1.** Reaction between propylene oxide and methanol.

\[
\text{CH}_3\text{-CH} = \text{CH}_2 + \text{CH}_3\text{OH} \xrightarrow{\text{O}} \text{CH}_3\text{-CH-CH}_2\text{-OH (MEPG)}
\]

\[
\xrightarrow{\text{OH}} \text{CH}_3\text{-CH-CH}_2\text{-OCH}_3 (\text{PGME})
\]

**Scheme 2.** Structure of active sites in AM-4.
Table 1. Chemical composition of AM-4 and AM-4 modified with HNO₃.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Chemical composition, (wt.%)</th>
<th>Na/Ti (mol/mol)</th>
<th>Si/Ti (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HNO₃ (mol/ml)</td>
<td>HNO₃/solid (mmol/g)</td>
<td>Na</td>
</tr>
<tr>
<td>AM-4</td>
<td>-</td>
<td>-</td>
<td>32.3±0.2</td>
</tr>
<tr>
<td>0.0625M AM-4</td>
<td>0.0625</td>
<td>3.125</td>
<td>8.8±0.1</td>
</tr>
<tr>
<td>0.125M AM-4</td>
<td>0.125</td>
<td>6.25</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>0.25M AM-4</td>
<td>0.25</td>
<td>12.5</td>
<td>0.7±0.1</td>
</tr>
</tbody>
</table>
Table 2. Spectral characteristics (ν_C-D) for several catalytic systems according to the adsorption of CDCl₃.

<table>
<thead>
<tr>
<th>№</th>
<th>System</th>
<th>ν_C-D  (cm⁻¹)</th>
<th>Δν_C-D (cm⁻¹)</th>
<th>PA (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CDCl₃</td>
<td>2265</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>NaOH [49]</td>
<td>-</td>
<td>-</td>
<td>1071.8</td>
</tr>
<tr>
<td>3</td>
<td>AM-4</td>
<td>2253, 2200, 2130, 2055</td>
<td>12, 65, 135, 235</td>
<td>1019</td>
</tr>
<tr>
<td>4</td>
<td>0.25M AM-4</td>
<td>2260</td>
<td>5</td>
<td>797</td>
</tr>
<tr>
<td>5</td>
<td>SiO₂-MgO [31]</td>
<td>2248, 2139, 2086</td>
<td>23, 126, 179</td>
<td>1002</td>
</tr>
<tr>
<td>6</td>
<td>CaOᵇ [37]</td>
<td>2250, 2235, 2210, 2160</td>
<td>15, 30, 55, 105</td>
<td>967</td>
</tr>
<tr>
<td>7</td>
<td>MgOᵇ [37]</td>
<td>2245-2250, 2210-2220</td>
<td>20-15, 55-45</td>
<td>924-911</td>
</tr>
<tr>
<td>8</td>
<td>CsOH [49]</td>
<td></td>
<td></td>
<td>1117.9</td>
</tr>
<tr>
<td>9</td>
<td>γ-Al₂O₃ᵇ [37]</td>
<td>2250, 2220</td>
<td>15, 45</td>
<td>911</td>
</tr>
<tr>
<td>10</td>
<td>Cs/γ-Al₂O₃ [50]</td>
<td>2254, 2213, 2157</td>
<td>11, 42, 108</td>
<td>969</td>
</tr>
<tr>
<td>11</td>
<td>SiO₂ᵇ [37]</td>
<td>2265</td>
<td>3</td>
<td>733</td>
</tr>
<tr>
<td>12</td>
<td>Cs/SiO₂ [44]</td>
<td>2254, 2213, 2157</td>
<td>11, 42, 108</td>
<td>969</td>
</tr>
<tr>
<td>13</td>
<td>Cs/MCM-41 [44][44Error! Bookmark not defined.]</td>
<td>2254, 2213, 2157</td>
<td>11, 42, 108</td>
<td>969</td>
</tr>
<tr>
<td>14</td>
<td>Cs/NaY [44]</td>
<td>2239, 2212, 2166</td>
<td>26, 43, 99</td>
<td>963</td>
</tr>
<tr>
<td>15</td>
<td>Bruciteᵇ [32]</td>
<td>2245, 2231, 2212</td>
<td>20, 34, 53</td>
<td>922</td>
</tr>
<tr>
<td>16</td>
<td>Mg₂Al-LDH(3.89)ᵇ [32]</td>
<td>2247, 2220, 2210</td>
<td>18, 45, 55</td>
<td>924</td>
</tr>
</tbody>
</table>

[a] The maximum value of PA; [b] Samples were activated at 400°C; [c] Mg/Al – 3.89 mmol/mol
Table 3. Reaction between propylene oxide and methanol in the presence of several catalytic systems

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MeOH/PO (mol/mol)</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Conversion of PO (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM-4</td>
<td>1.8</td>
<td>8</td>
<td>50</td>
<td>4</td>
<td>15.6</td>
</tr>
<tr>
<td>AM-4</td>
<td>1.8</td>
<td>8</td>
<td>90</td>
<td>4</td>
<td>43.7</td>
</tr>
<tr>
<td>AM-4</td>
<td>1.8</td>
<td>8</td>
<td>110</td>
<td>4</td>
<td>79.0</td>
</tr>
<tr>
<td>AM-4</td>
<td>1.8</td>
<td>8</td>
<td>110</td>
<td>7.5</td>
<td>88.4</td>
</tr>
<tr>
<td>MgO-Al₂O₃ [67]</td>
<td>-</td>
<td>5</td>
<td>120</td>
<td>5</td>
<td>31.4</td>
</tr>
<tr>
<td>CaO [67]</td>
<td>-</td>
<td>5</td>
<td>120</td>
<td>5</td>
<td>37.3</td>
</tr>
<tr>
<td>MgO [67]</td>
<td>-</td>
<td>5</td>
<td>120</td>
<td>5</td>
<td>71.1</td>
</tr>
<tr>
<td>Brucite(150)ᵃ [32]</td>
<td>2.2</td>
<td>12</td>
<td>120</td>
<td>7.5</td>
<td>36</td>
</tr>
<tr>
<td>Brucite(150)ᵃ [32]</td>
<td>2.2</td>
<td>12</td>
<td>140</td>
<td>7.5</td>
<td>42</td>
</tr>
<tr>
<td>Mg,Al-LDH(Mg/Al 3.89/1)ᵇ [32]</td>
<td>2.2</td>
<td>12</td>
<td>140</td>
<td>7.5</td>
<td>28</td>
</tr>
<tr>
<td>Mg,Al-LDH (Mg/Al 3/1) [27]</td>
<td>1.8</td>
<td>5</td>
<td>120</td>
<td>3</td>
<td>88.7</td>
</tr>
<tr>
<td>Mg,Al-LDH (Mg/Al 5/1) [27]</td>
<td>1.8</td>
<td>5</td>
<td>120</td>
<td>3</td>
<td>81.2</td>
</tr>
<tr>
<td>ZnMgAl-LDH (Zn/Mg/Al 0.8/3/1) [27]</td>
<td>1.8</td>
<td>5</td>
<td>130</td>
<td>3</td>
<td>95.9</td>
</tr>
<tr>
<td>NH(CH₂)₂NH₂/SiO₂ [67]</td>
<td>-</td>
<td>5</td>
<td>130</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>NH₂-SiO₂ [67]</td>
<td>-</td>
<td>5</td>
<td>130</td>
<td>10</td>
<td>94.1</td>
</tr>
<tr>
<td>ZIF-8 [69]</td>
<td>1.8</td>
<td>8</td>
<td>110</td>
<td>5</td>
<td>54.4</td>
</tr>
<tr>
<td>MAF-5 [69]</td>
<td>1.8</td>
<td>8</td>
<td>110</td>
<td>5</td>
<td>90.3</td>
</tr>
</tbody>
</table>

[a] Brucite was activated at 150°C. [b] Mg/Al = 3.89 mol/mol