

Microporous Titanosilicates as Heterogeneous Catalysts for Basic Organic Synthesis

Eleonora Butenko, Alexey Kapustin

Department of Chemical Technology and Engineering, Priazovskiy State Technical University, Mariupol, Ukraine

Email address:

butenko_e_o@pstu.edu (E. Butenko)

To cite this article:

Eleonora Butenko, Alexey Kapustin. Microporous Titanosilicates as Heterogeneous Catalysts for Basic Organic Synthesis. *Modern Chemistry*. Vol. 10, No. 1, 2022, pp. 1-4. doi: 10.11648/j.mc.20221001.11

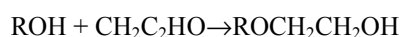
Received: November 25, 2021; **Accepted:** January 11, 2022; **Published:** January 21, 2022

Abstract: The products of the reactions of ethylene oxide with fatty alcohols, acids and amines are of great industrial importance. They include surfactants, plasticizers and insecticides. The reactions can be generally represented as oligomerization. Interaction between ethylene oxide and alcohols can proceed in the presence of acidic as well as basic catalysts; the main distinction being in the quantitative distribution of reaction products. In the presence of basic catalysts the rate of reaction increases with the molecular weight of the products and polyaddition reaction products have a wide distribution of molecular weights. Most of the information available comes from the well investigated uses of homogeneous bases as catalysts. Research on the use of solid catalysts in this area is comparatively recent. Heterogeneous catalysts, such as the synthetic zeolites, are better known as acid catalysts. Heterogeneous catalysts with well-defined sites able to display basic properties over a wide pH range, whilst retaining insolubility and thermal stability, are little known. This work described herein studies the basic properties of two microporous titanosilicates, known as ETS-4 and ETS-10. Determinations of surface basicity were also carried out by following the titration method. The titanosilicates were examined as catalysts for the ethoxylation of ethylene glycol. One-parameter experiments showed that the processes observed had a first-order dependence on the concentrations of ethylene oxide and catalyst. The excess of alcohol present was assumed to lead to a first-order dependence on alcohol concentration as confirmed by studies on basic. The interaction of the proton donor agent with ethylene oxide proceeds through a tri-molecular transition state. The activated C-O bond is opened by a nucleophilic attack; a similar mechanism to an SN₂ nucleophilic replacement. Titanosilicates are very effective catalysts with basic sites for organic synthesis processes.

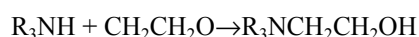
Keywords: Titanosilicates, Alcohol Ethoxylation, Basic Catalyst

1. Introduction

The products of the reactions between ethylene oxide and alcohols, acids and amines are of great industrial importance. They include surfactants, plasticizers and insecticides and the reactions can be generally represented as:



The most significant reaction is that between ethylene oxide and alcohols because ethoxylation of other substances produces alcohols as products, for example:



Interaction between ethylene oxide and alcohols can

proceed in the presence of acidic as well as basic catalysts; the main distinction being in the quantitative distribution of reaction products. In the presence of basic catalysts the rate of reaction increases with the molecular weight of the products and polyaddition reaction products have a wide distribution of molecular weights.

Most of the information available comes from the well investigated uses of homogeneous bases as catalysts. Research on the use of solid catalysts in this area is comparatively recent. Heterogeneous catalysts, such as the synthetic zeolites, are better known as acid catalysts. Heterogeneous catalysts with well-defined sites able to display basic properties over a wide pH range, whilst retaining insolubility and thermal stability, are little known.

Potential base catalysts that may fulfil these conditions are the titanosilicate family. They have been shown to be

microporous framework structures containing channels similar to the well-known zeolite catalysts [1-3]. In their alkaline form the presence of surface basic sites within a molecular sieve material can be anticipated.

The work described herein studies the basic properties of two microporous titanosilicates, known as ETS-4 and ETS-10 [4-6], having the general formulas $M^{n+}_{2/n}Ti_3Si_8O_{11}$ and $M^{n+}_{2/n}TiSi_5O_{13}$.

2. Experimental

The titanosilicates were synthesised in a similar manner to the method of Liu and Thomas [3]. Gels of composition TiO_2 : 5 SiO_2 : 3 NaOH: 0.73KF: 4.1 H_2O and TiO_2 : 5 SiO_2 : 5NaOH: 0.48 NaF: 4.1 H_2O yielded Na/K ETS-10 and Na ETS-4 respectively after being held at 200°C for 64 hr. Degussa TitanOxid P25 and Luox HS-400 were the sources of TiO_2 and SiO_2 . The products were recovered by centrifugation, washed twice by dispersal in deionised water, and then dried at 50-60°C. Their XRD patterns showed them to be highly crystalline and in accord with data recorded by Liu and Thomas [3]. Spacings (d, Å) and intensities (in brackets) observed were as follows:

ETS-4- 11.977 (5.1) 11.547 (100.0) 6.940 (8.8) 6.833 (1.1) 5.788 (1.6) 5.244 (2.2) 4.458 (3.9) 3.381 (3.7) 3.069 (1.2) 3.047 (4.1) 2.985 (7.8) 2.902 (2.4) 2.764 (1.5) 2.627 (6.7) 2.583 (3.8) 2.429 (2.0) 1.936 (1.6).

ETS-10- 14.879 (58.0) 11.510 (12.4) 8.838 (4.2) 7.217 (17.2) 6.836 (5.7) 4.935 (4.7) 4.410 (38.9) 3.736 (2.1) 3.608 (100.0) 3.511 (8.3) 3.451 (30.0) 3.282 (20.8) 3.142 (5.9) 2.990 (10.7) 2.810 (3.5) 2.542 (8.1) 2.522 (17.2) 2.469 (9.1)

2.429 (4.41) 2.357 (8.3) 2.206 (2.8) 2.092 (3.1) 1.993 (1.2) 1.945 (6.9) 1.920 (1.6) 1.871 (6.9) 1.858 (5.7).

Thermal analysis showed that ETS-10 had one broad mass loss peak between 35-452°C ($T_{max}=108^\circ C$) equivalent to 11.79% mass loss. ETS-4 had a similar loss of 14.46% between 45-427°C ($T_{max}=255^\circ C$). Samples were calcined for 24 hr in a furnace under a dry nitrogen flow. Two temperatures were used (155, 265°C) and mass losses recorded. The calcined samples were introduced to a thermal balance in a nitrogen atmosphere. The atmosphere was changed to dry carbon dioxide and the increases in mass due to CO_2 sorption observed, over a period of 50 hr, at the temperatures of pre-calcination. From this, estimates of the expected concentration of anionic sites could be made. These are shown in Table 1.

These are estimates of the likely basic nature of the catalyst surface, and they suggest that the initial weight losses under nitrogen contain changes due to both water loss and dehydroxylation processes. Carbon dioxide uptake values may well be a function of both physi- and chemisorption. Determinations of surface basicity were also carried out by following the titration method as described by Kapustin *et al.* [3] The sample were first washed with decarbonated, deionised water followed by an alkaline solution to remove any acid sites present. Final water washes restored the samples to neutral pH. The samples were dried to constant weight at 120°C, and a residual pressure of 100 torr. A tared weight of catalyst close to 0.1g was placed in a closed measuring flask filled with nitrogen. Benzene and a suitable acid-base indicator were added immediately.

Table 1. Weight /mass changes for ETS-4,-10 and estimated anionic capacities.

Calcination temperature, °C	Wt./mass change, %	Anion capacity as HCO_3^- , meq/g	Anion capacity as $\frac{1}{2} CO_3^{2-}$, meq/g
ETS-4, Initial (N_2)			
155	-4,08	0,67	0,14
265	-13,65	2,23	4,55
ETS-4, CO_2 uptake			
155	+4,92	-	1,18
265	+2,81	-	0,63
ETS-10, Initial (N_2)			
155	-6,97	1,14	2,32
265	-10,52	1,72	3,50
ETS-10, CO_2 uptake			
155	+8,88	-	1,0
265	+12,33	-	2,80

Sufficient for equilibrium was allowed, with benzoic acid (0.1M) being added to those samples whose equilibration times were long (several days). The uptake of indicator onto basic sites for ETS-10 could be observed visually to reach apparent equilibrium after 1 minute, whilst that for ETS-4 was much longer. When bromothymol blue ($H_0 = 7.2$) or phenolphthalein ($H_0 = 9.3$) was the indicator the basicity of ETS-4 was 0.044 ± 0.005 meq/g and that of ETS-10 was 0.105 ± 0.01 meq/g.

Both catalysts showed colour changes when the indicator was 2,4,6 trinitroaniline ($pK_a = 12.3$) but estimates of basic strengths were close to the limits of detection.

3. Results and Discussion

The titanosilicates were examined as catalysts for the ethoxylation of ethylene glycol. This was carried out in the presence of excess alcohol [7-9].

One-parameter experiments showed that the processes observed had a first -order dependence on the concentrations of ethylene oxide and catalyst. The excess of alcohol present was assumed to lead to a first-order dependence on alcohol concentration as confirmed by studies on basic homogeneous catalysts [3]. Results are summarized in Tables 2 and 3.

Proposed reaction schemes are assumed to have the first order dependencies discussed above and linked via:

$$r = -dC_{(eo)} / dt = k C_{(eo)} C_{(alc)} C_{(cat)}$$

where $C_{(eo)}$ – concentration of ethylene oxide (mol/kg), $C_{(alc)}$ – concentration of alcohol (mol/kg), $C_{(cat)}$ – concentration of basic sites in the reaction mixture (mol/kg), r – rate of reaction (mol/kg min), k – rate constant ($\text{kg}^2/\text{mol}^2 \text{ min}$).

If the catalysts are converted to their carbonate form after washing off physically sorbed products unused reactants, gas-liquid chromatography confirms that the catalysts are in the alcoholate form [10, 11].

Table 2. Ethylene glycol ethoxylation in the presence of ETS-4 at 94°C.

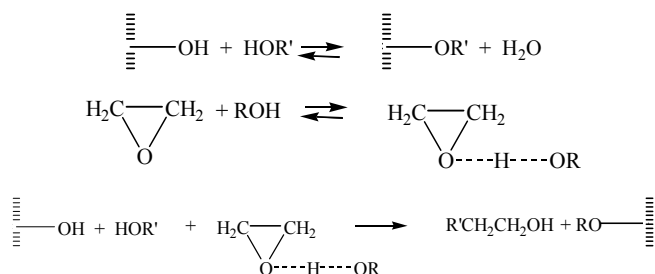
Experiment	1	2	3
$C_{(eo)}$, mol/kg	0,49	0,44	0,43
$C_{(alc)}$, mol/kg	15,78	15,81	15,83
$C_{(cat)}$, g/kg	129,5	85,52	50,10
Capacity, meg/g	5,69	3,72	2,20
k , 10^3 l/min	25,58	22,82	15,17

Table 3. Ethylene glycol ethoxylation in the presence of ETS-10.

Experiment	1*	2**	3**
$C_{(eo)}$, mol/kg	0,42	0,43	0,38
$C_{(alc)}$, mol/kg	15,83	15,82	15,85
$C_{(cat)}$, g/kg	115,69	161,49	84,17
Capacity, meg/g	12,15	16,96	8,84
k , 10^3 l/min	9,06	16,55	10,87

*86,5°C, **94°C.

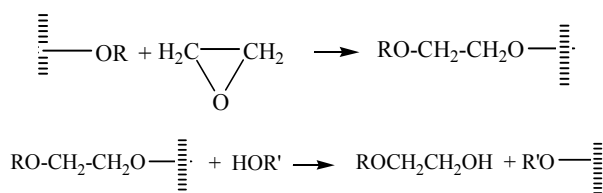
From this the following schemes of reaction are possible:



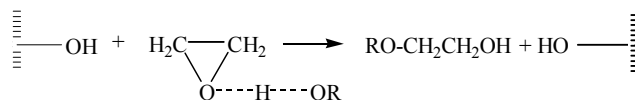
where R and R' are the same alcohol radicals.

The interaction of the proton donor agent (alcohol) with ethylene oxide proceeds through a tri-molecular transition state. Initially the ethylene oxide ring is activated by the formation of an O...H bond [12-17]. The activated C--O bond is opened by a nucleophilic attack; a similar mechanism to an $\text{S}_{\text{N}}2$ nucleophilic replacement.

An analogous tri-molecular mechanism can be envisaged in the ethoxylation reaction via:



The equilibrium in reaction depends upon alcohol concentration and alcohol acidity. Because all alcohols, apart from methanol, have an acidity less than that of water anion-exchange of the anion on the catalyst surface occurs according to the following route;



4. Conclusion

Solid base microporous titanasilicates represent one of the most technologically promising materials as a consequence of their low cost, relative ease of preparation, and the large number of composition variables that may be adopted.

Titanosilicates are very effective catalysts with basic sites for organic synthesis processes.

We believe that such studies will ensure that the application of titanosilicates in heterogeneous catalysis will continue to expand rapidly for the foreseeable future.

References

- [1] X. Lui, J. K. Thomas (1996) JCS, Chem. Comm, 196, 1435.
- [2] A. E. Kapustin, N. N. Grekova and O. V. Lebedeva. (1997) J. Ukr. Chem., 63, 25.
- [3] N. N. Lebedev and V. F. Shvets. (1980) Trans. Mendeleev Univ., 115, 87.
- [4] M. N. Timofeeva, A. E. Kapustin and E. O. Butenko. *Synthetic and natural materials with the brucite-like layers as high active catalyst for synthesis of 1-methoxy-2-propanol from methanol and propylene oxide* (2016) J. Mol. Cat. A: Chem., 423, 22. doi: 10.1016/j.molcata.2016.06.006.
- [5] E. O. Butenko, A. E. Kapustin (2020) Mercarbide catalyst for alcohol ethoxylation. Journal. of Siberian Federal University. Chemistry, 13, 3. doi: 10.17516/1998-2836-0186.
- [6] Tapio Salmi (2012) Ethylene oxide – kinetics and mechanism. Current Opinion in Chemical Engineering, V. 1-3. doi: 10.1016/j.coche.2012.06.002.
- [7] Georges, A. M.; Arturo, G.; Marc, E. L. (2001) Kinetics of the reactions of ethylene oxide with water and ethylene glycols. *Process Safety Progress*, V. 20. doi: 10.1002/prs.680200405.
- [8] Butenko E., Kapustin A., Dan, O. (2018) Propylene oxide polymerization in the presence of layered double hydroxides. *Chemistry-Didactics-Ecology-Metrology*, V. 23, N. 1-2. doi: 10.1515/cdem-2018-0009.
- [9] Butenko, E.; Kapustin, A. (2019) Catalysis by Pillared Layered Double Hydroxides. *Biomedical Journal of Scientific & Technical Research (BJSTR)*, V. 22, N1. doi: 10.26717/BJSTR.2019.22.003681.
- [10] David P. Penalzoa. (2019) Modified clay for the synthesis of clay-based nanocomposites. *Epitoanyag*, V. 71, N 1. doi: 10.14382/epitoanyag-jsbcm.2019.2.

- [11] Butenko, E.; Kapustin, A. (2019) Sorption reseaches on the removal of the bond ammonia from the wastewater. *Epitoanyag*, V. 71, N 3, doi: 10.14382/epitoanyag-jsbcm.2019.15.
- [12] Jinchang, Z.; Tiechun, L. (2019) Facile synthesis of a highly effective layered double hydroxide catalyst and its application in the one-step ethoxylation of butyl acetate to oligo-ethylene glycol butyl ether acetates. *Ind. Eng. Chem. Res.* doi: 10.1021/acs.iecr.9b01892.
- [13] Rupp M., Klemm E., Ruback W. (2013) Alcohol ethoxylation kinetics: Proton transfer influence on product distribution in microchannels. *Chemical Engineering and Processing*, V. 74 doi: 10.1016/j.cep.2013.09.006.
- [14] Kozlovskiy R., Makarov M. G., Shvets V. F. (2011) Oxyethylation kinetics of acetic acid and acetic anhydride during catalysis by polymer anion exchangers. *Chemical industry today*. № 6.
- [15] Wadhmode S., Thakur V. (2001) Efficient liquid phase acylation of alcohols over basic ETS-10 molecular sieves. *Tetrahedron Letters*. 2001. V. 42. N. 17. doi: 10.1016/S0040-4039(01)00389-6.
- [16] Bialowas E., Scymanowski (2004) J. Catalysts for Oxyethylation of Alcohols and Fatty Acid Methyl Esters. *Ind. Eng. Chem. Res.* V. 43. doi: 10.3389/iecr.2021.617701.
- [17] Di Serio M., Tesser R., Russo V. (2015) Catalysts for the Ethoxylation of Esters. *Journal of Surfactants and Detergents*. V. 18. doi: 10.1007/s11743-015-1719-1.