

Microporous Titanosilicates as Heterogeneous Catalysts for Basic Organic Synthesis

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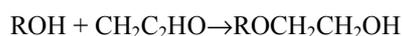
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Abstract: The products of the reactions of ethylene oxide with fatty alcohols, acids and amines are of great industrial importance. They include surfactants, plasticizers and insecticides. The reactions can be generally represented as oligomerization.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

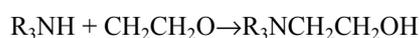
Keywords: Titanosilicates, Alcohol Ethoxylation, Basic Catalyst

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.

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