

A Catalysis, kinetic and mechanistical studies for the transformation of ethylene glycol by alumina and silica gel under autogenous pressure and solvent-free conditions

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Supporting Information

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EXPERIMENTAL

General

NMR spectra were recorded on a Bruker AC spectrometer (300 MHz ^1H and 75 MHz ^{13}C) in CDCl_3 solution. The chemical shift (δ) of the signals described is expressed in ppm relative to TMS taken as internal reference. The following abbreviations are used: s: singlet, d: doublet, t: triplet, m: multiplet, l: large. The coupling constants (J) are expressed in Hz. The reagents are from Aldrich. The silica gel is commercial type Merck 60 (70-230 mesh) and alumina is an Aldrich commercial product. In all experiments, ethylene glycol **1** present in the crude reaction product was removed by adding water to the crude reaction mixture. After the treatment, the mixture of carbonyl compounds **4** and dioxolane **5** was recovered. The yields of products **5** were estimated from the ^1H and ^{13}C NMR spectra of the crude reaction mixtures in order to avoid their decomposition during chromatographic purification, as reported in the other work [26]. Compounds **2**, **3** and **5** were identified by comparing their ^1H and ^{13}C NMR spectra with authentic samples marketed by Aldrich.

Synthesis of dioxolane **5** using sulfuric acid

Procedure at atmospheric pressure: ethylene glycol **1** (7.67 g, 124 mmol) and H_2SO_4 (4% by mass) were placed in a flask (50 mL) equipped with a reflux condenser and then heated at 196 °C for 3 h. After cooling, 20 mL of water was added to the crude mixture to remove residual ethylene glycol. The aqueous solution was extracted with ether (3×50 mL). The organic phases were combined and then dried over MgSO_4 . After filtration and evaporation of the ether in vacuo, the mixture of **2** and **3** was recovered. The yields of products **2** and **3** are displayed in Table 1.

Procedure under pressure: ethylene glycol **1** (7.67 g, 124 mmol) and H₂SO₄ (4% by mass) were placed in an autoclave (100 mL). The sealed reactor was heated at 150 °C for 3 hours or for 24 hours. After cooling, the residue was treated in the same manner as described above. The yields of products **2** and **3** are listed in Table 1.

Synthesis of 1,3-dioxolanes by silica gel

Procedure at atmospheric pressure: ethylene glycol **1** (7.67 g, 124 mmol) and 0.1 g of silica gel were placed in a flask (50 mL) equipped with a reflux condenser and the whole was heated at 196 °C for 120 h. After cooling and separating the silica gel by filtration, the residue was treated in the same manner as described above. Diethylene glycol **2** was obtained in a yield of 1% (Table 1).

Procedure under pressure: ethylene glycol **1** (7.67 g, 124 mmol) and 0.1 g of silica gel were placed in an autoclave (100 mL). The sealed reactor was heated to 150 °C for various amounts of time. After cooling and separating the silica gel by filtration, the residue was treated in the same manner as described above. The yields of products **2** and **5** are listed in Table 1.

Reaction under atmospheric pressure

In a single-layer ground-glass flask equipped with an ascending refrigerant and a magnetic stirrer, ethylene glycol **1** (6.9 mL, 7.68 g, 0.124 mmol) was introduced to which 0.307 g (1.3% by mass) of concentrated sulfuric acid was added. The mixture was heated under reflux at 150 °C for 1 hour and 3 hours and under atmospheric pressure. After cooling to room temperature, 20 mL of water was added to the reaction crude to remove ethylene glycol **1**. The aqueous phase was extracted by ether (3 ×20 mL) and then the organic phase was dried on MgSO₄. After filtration and evaporation of the solvent under a vacuum, the mixture of diethylene glycol **2** and dioxane **3** was recovered.

Autogenous pressure reaction

Ethylene glycol **1** (6.9 mL, 7.68 g, 0.124 mmol) and concentrated sulfuric acid (0.307 g, 1.3% by weight) were placed in a sealed autoclave and the mixture was heated to 150 °C under autogenous pressure for varying times. After cooling the reactor to room temperature, 20 mL of water was added to the filtrate to remove the remaining ethylene glycol **1** in the reaction mixture. The aqueous phase was extracted by ether (3 ×20 mL) and then the organic phase was dried on MgSO₄. After filtration and evaporation of the solvent under a vacuum, the mixture of diethylene glycol **2** and dioxane **3** was recovered.

Preparation of synthetic silica

Synthetic silica Si syn was obtained by precipitating the silica from a sodium silicate solution of concentration $[\text{Si}] = 1.667 \text{ mol} \cdot \text{L}^{-1}$ by adding, drop by drop and with agitation, 2M HCl until a pH of 4 was reached. Si syn silica was recovered after successive washing to remove sodium chloride and drying at a temperature of 100 °C for a few hours. Sodium silicate was obtained by alkaline fusion of extra-silica sand, originating from the Safi region in Morocco, with sodium carbonate with a SiO₂/Na₂O ratio of 1.

Preparation of synthetic silica

The procedure followed is similar to the method described by Noor Abdulateef Ghulam [27].

Reaction of catalysts on ethylene glycol **1**

Ethylene glycol **1** (7.68 g, 124 mmol) and the catalyst (0.1 g, 1.3% by weight) were placed in a sealed autoclave and heated to 150 °C under autogenous pressure for varying times. After cooling the reactor to room temperature, the catalyst was separated by filtration. 20 mL of water was added to the filtrate to remove the remaining ethylene glycol **1** in the reaction mixture. The aqueous phase was extracted by ether (3 ×20 mL) and then the organic phase was dried on

MgSO₄. After filtration and evaporation of the solvent under a vacuum, a mixture of diethylene glycol **2**, dioxane **3** and dioxolane **5** was recovered.

Figures

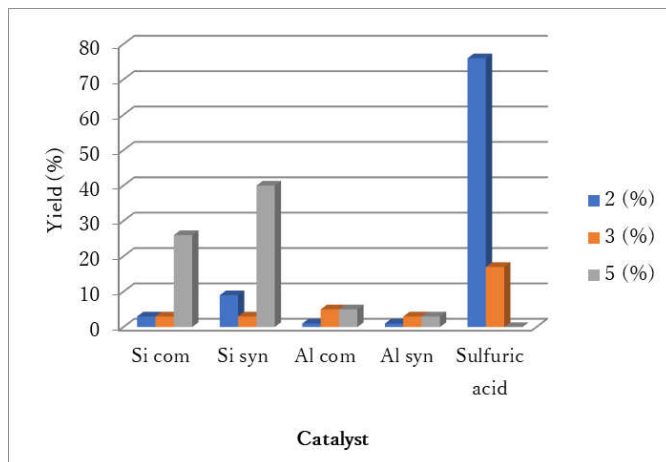


Fig.1 Evaluation of the yield of products **2**, **3** and **5** in the presence of H₂SO₄ (4% wt.) and of catalysts based on silica gel and alumina (1.3% wt.)

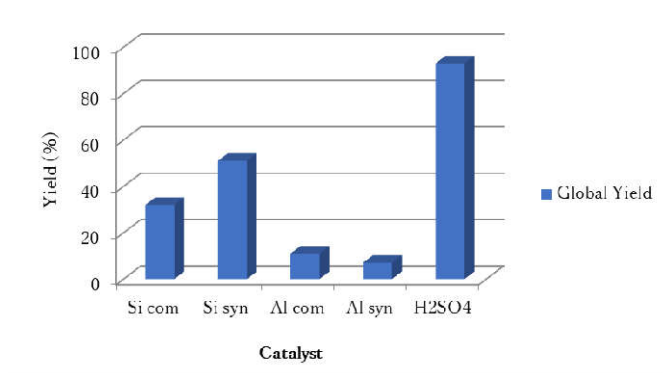


Fig.2 Evaluation of the overall yield in the presence of H₂SO₄ (4% wt.) and catalysts based on silica gel and alumina (1.3% wt.)

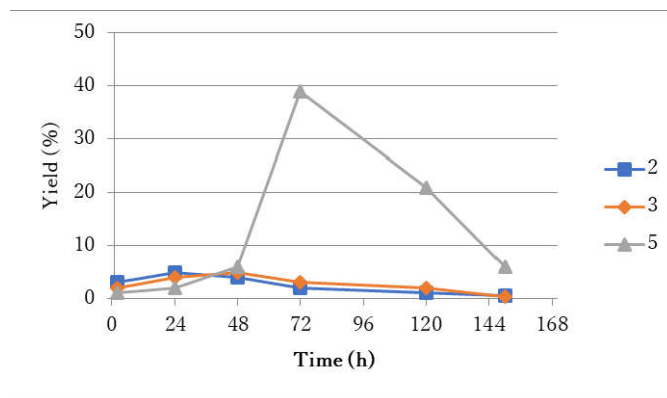


Fig.3 Evaluation of products **2**, **3** and **5** formed in the presence of commercial alumina Al com

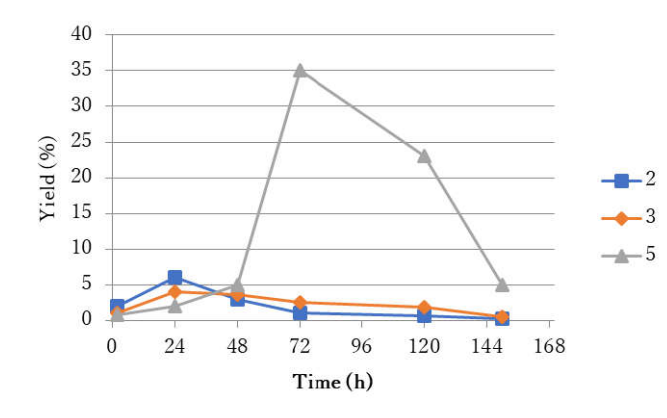


Fig.4 Evaluation of products **2**, **3** and **5** formed in the presence of synthetic alumina Al syn

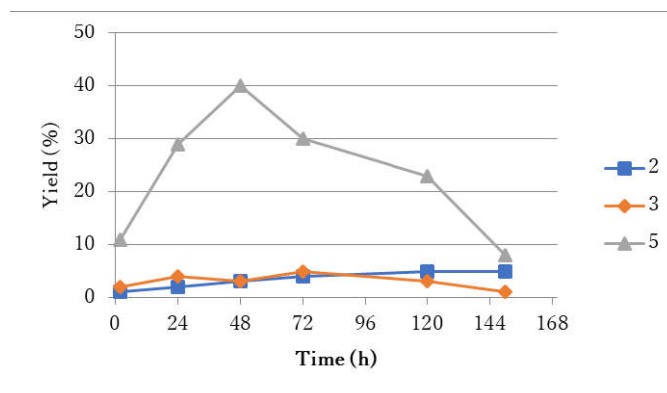


Fig. 5 Evaluation of products **2**, **3** and **5** formed in the presence of commercial silica Si com

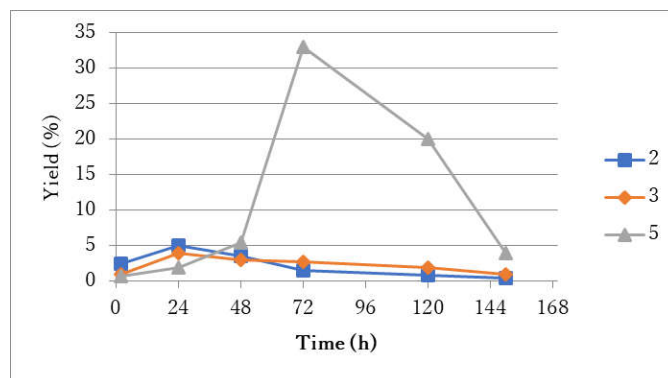


Fig. 6 Evaluation of products **2**, **3** and **5** formed in the presence of synthetic silica Si syn

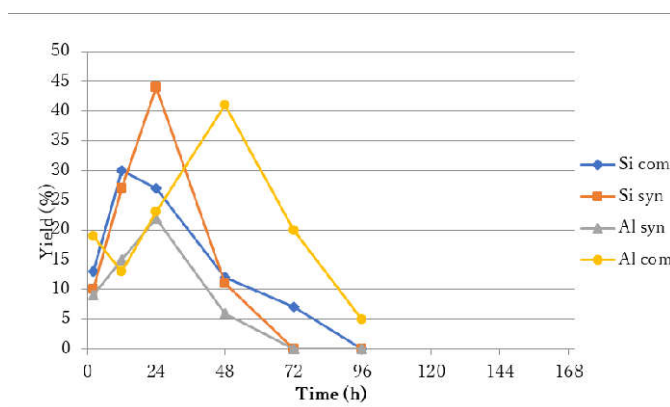


Fig.7 Evaluation of dioxolane **5** according to the nature of the catalyst and the reaction time

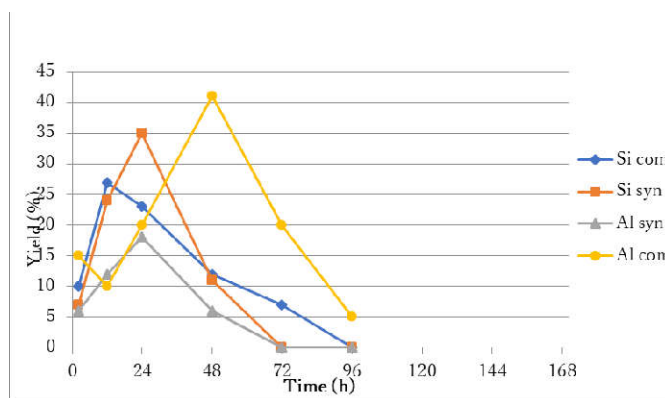


Fig.8 Evaluation of the overall efficiency according to the nature of the catalyst used

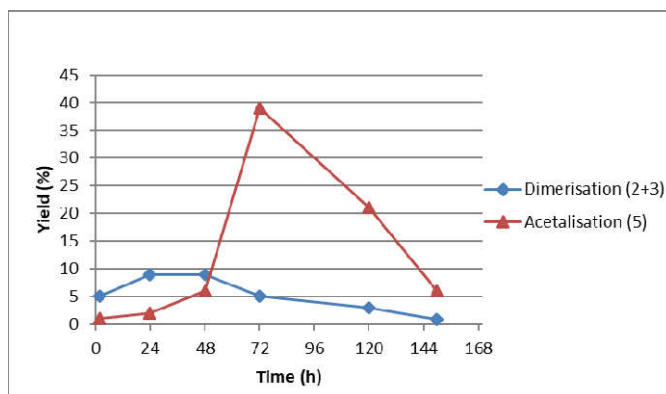


Fig. 9 Evaluation of dimerisation and cyclisation products in function of time and in the presence of commercial alumina Al com

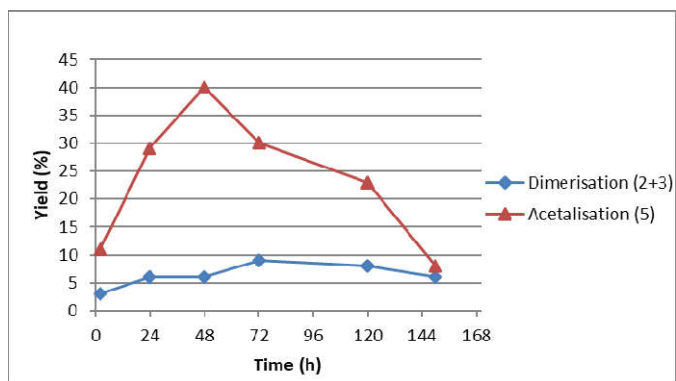


Fig. 10 Evaluation of dimerisation and cyclisation products formed in presence of commercial silica Si com

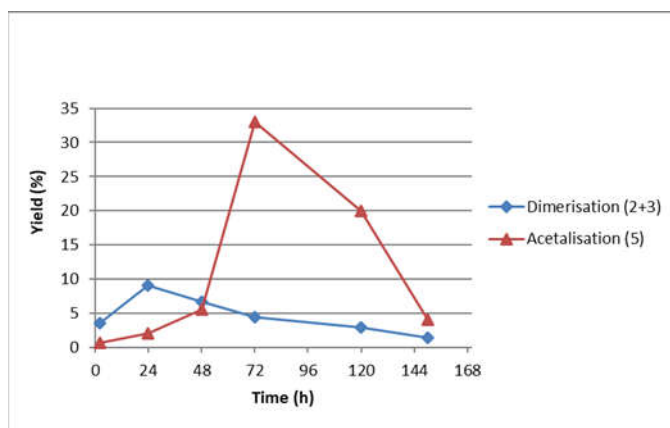


Fig. 11 Evaluation of dimerisation and cyclisation products formed in presence of synthetic silica Si syn

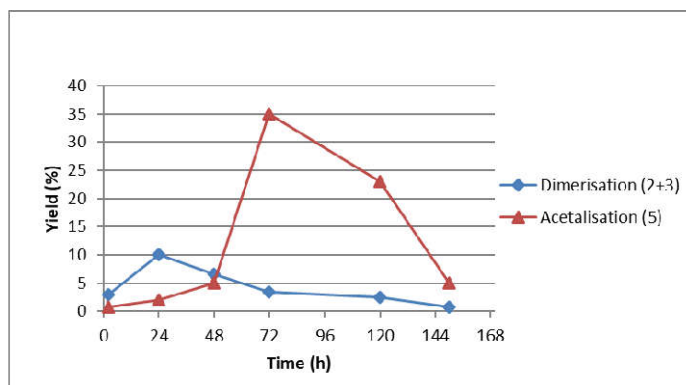


Fig. 12 Evaluation of dimerisation and cyclisation products formed in presence of synthetic alumina Al syn

^1H and ^{13}C NMR spectra: See (T. Rohand, J. Savary, I. E. Markó, *Monat. fur Chem.* **2018**, 149, 1429-1436).