

Hydrothermal synthesis of catalytic zeolites from waste container glass

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1. Introduction – Soda-lime-silica glass containers constitute a significant proportion of the municipal waste-stream in every developed nation. Their full recycling potential is restricted by regional colour mismatch which limits the demand for green and amber waste container glass that can be effectively recycled as new bottles and jars [1]. Various projects have been carried out to upcycle surplus soda-lime-silica glass into value-added materials such as ion-exchangers, aggregates and ceramics [1,2]. In this study, waste green container glass was evaluated as a feedstock for the hydrothermal synthesis of a mixture of low-silica zeolites (sodalite (SOD) and cancrinite (CAN)) that have the potential to catalyse the industrially significant Knoevenagel condensation reaction [1].

2. Experimental - To prepare the zeolite mixture, 3.0 g of ground green glass (< 125 µm), 0.45 g of aluminium foil and 15 cm³ of 4M NaOH_(aq) were heated at 125 °C for 14 days in a sealed PTFE autoclave. The products were recovered by filtration, washed with deionised water to pH ~8, dried in air at 60 °C and analysed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). A mixture of benzaldehyde (20 mmol) with equimolar quantities of ethyl cyanoacetate (ECA) or malononitrile (MLN) in 50 cm³ of ethanol was heated under stirring at 40 °C in the presence and absence of 0.25 g of zeolitic product. At 15 and 60 min the composition of the reaction mixture was analysed by gas chromatography [1]. The ethyl trans- α -cyanocinnamate and benzylidenemalononitrile condensation products were confirmed by GC-MS. The ratio of the gradients of the condensation product versus time plots in the presence and absence of the catalyst was used as a measure of catalytic activity. All reactions and analyses were carried out in triplicate.

3. Results and Discussion - The principal hydrothermal reaction products were confirmed by XRD as the low-silica zeolites SOD and CAN (common formula Na₆[Al₆Si₆O₂₄].2NaX.6H₂O, X = anion) with minor proportions of tobermorite (Ca₅(Si)₆O₁₈H₂.4H₂O) and katoite (Ca₃Al₂SiO₁₂H₈). SOD and CAN form by successive transformation and typically occur together during hydrothermal reactions containing equimolar quantities of Si and Al [3]. In this case, tobermorite and katoite arise from an excess of calcium in the glass feedstock. SEM analysis (Image 1) confirmed the presence of wool-ball SOD and blocky CAN phases distributed across the surfaces of the granular product (particle size range 50 - 500 µm). The zeolitic product successfully catalysed the selected Knoevenagel reactions (as indicated by the enhanced reaction rates listed in Table I). The Knoevenagel reaction is widely utilised in the synthesis of new C-C bonds and is generally carried out in solution under basic homogeneous catalysis which presents problems associated with the separation of the product and disposal of the caustic waste liquor [1]. In this respect, solid heterogeneous catalysts are a superior alternative.

Table I. Relative reaction rates

Reagent	Relative reaction rate with catalyst
ECA	42.8 ± 0.7
MLN	4.1 ± 0.3

4. Conclusions - A waste glass-derived zeolitic mixture of SOD and CAN was found to successfully catalyse the Knoevenagel synthesis of ethyl trans- α -cyanocinnamate and benzylidenemalononitrile. These findings indicate that this material is a promising basic heterogeneous catalyst for organic synthesis.

5. References

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