



A temperature programmed desorption study of the interaction of ethyl cyanoacetate and benzaldehyde on metal oxide surfaces



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ABSTRACT

Reagents from a base catalysed condensation reaction (Knoevenagel condensation reaction between ethyl cyanoacetate and benzaldehyde), were adsorbed on ZnO and Al₂O₃ catalyst surfaces and subject to temperature programmed desorption experiments, monitored using mass spectrometry. Ethyl formate, ketenimine species, carbon dioxide and carbon monoxide were desorption products from ethyl cyanoacetate, while benzene, carbon dioxide and carbon monoxide were desorbed from the catalysts loaded with benzaldehyde. The formation of the ketenimine species was confirmed by *in situ* FTIR experiments. The observation of the decomposition species further substantiates a proposed reaction mechanism for the Knoevenagel condensation reaction on the catalyst surface of some oxide catalysts.

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1. Introduction

The Knoevenagel condensation is a well-known C–C bond formation reaction used in the synthesis of small molecules. Studies have been applied to a variety of solid catalysts exhibiting basic properties and showing activity in the Knoevenagel condensation, including catalysts derived from supported alkali metals, such as alkali exchanged zeolites [1], mesoporous molecular sieves [2], modified metallic oxides [3] and organic base modified Zeolite beta [4,5]. We have previously observed through *in situ* FTIR spectroscopy the Knoevenagel condensation reaction occurs on a ZnO surface, observing intermediate enolate species originating from ethyl cyanoacetate (ECA) and acetal type surface species from benzaldehyde (B), followed by reaction on the surface [6]. Beyond the influence of surface basicity [7], the nature of the surface and the desorption kinetics of the components involved in the reaction over metal oxides is not well established. In the investigation presented here, ECA and B were adsorbed on ZnO catalyst followed by temperature programmed desorption (TPD), observing any desorption products desorbed. This was compared with a similar experiment using γ -Al₂O₃.

2. Experimental

Using temperature programmed desorption-mass spectrometry (TPD-MS), ECA and B were adsorbed on the catalyst surface. To purify adsorbents, they were frozen with liquid nitrogen, the headspace pumped and then the reagents were thawed. The procedure was repeated three times, ECA and B vapours were adsorbed on the catalyst in separate experiments. The analysis allows for evaluation of the desorption temperatures of ECA and B, along with the amount and nature of products desorbed from Al₂O₃ and ZnO.

2.1. Materials

Zinc oxide (Ajax chemicals) with a specific surface area of 4 m²/g and γ -Al₂O₃ (Sigma–Aldrich) with a specific surface area of 200 m²/g, were used as the catalysts in the experiments. Ethyl cyanoacetate (Acros Organics, 98%) and benzaldehyde (Acros Organics, 98%) were used as the reagents of interest.

2.2. Temperature programmed desorption mass spectrometry (TPD-MS)

Desorption and decomposition of ethyl cyanoacetate and benzaldehyde over ZnO was investigated by TPD using a Pfeiffer Prisma quadrupole mass spectrometer as detector. The experiments were performed in a compact, purpose built, stainless steel apparatus equipped with a 60 l s⁻¹ turbo pump (see Fig. 1). The desorption cell was connected through a leak valve which was independently

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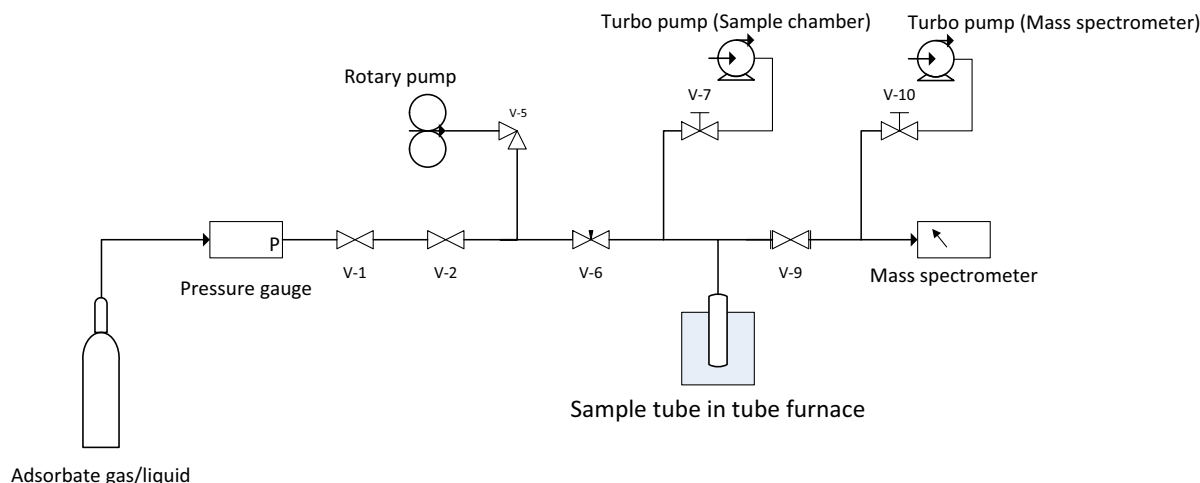


Fig. 1. Experimental setup of the TPD-MS apparatus.

pumped with the sample placed inside a quartz tube. In a typical experiment, the samples are heated at rate of $5^{\circ}\text{C}/\text{min}$ in vacuum up to 500°C and held for 1 h in vacuum then left to cool to the adsorption temperature of 80°C . Ethyl cyanoacetate and benzaldehyde were further purified by freeze/thaw pumping cycles and exposed to the ZnO sample at 80°C and 1 mbar of pressure. After pumping excess reagents, the samples are heated at rate of $5^{\circ}\text{C}/\text{min}$ in vacuum up to 900°C , then left to cool to room temperature, recording the desorption spectra during the heating process. Masses $m/z = 1-200$ were recorded and masses $m/z = 28, 31, 41, 44,$ and 113 were monitored to determine the evolution of carbon monoxide, ethyl formate (Liu et al. [8]), ketenimine (Mair et al. [9]), carbon dioxide, and ethyl cyanoacetate (Bowie et al. [10]). Using the same assessment as Peralta et al., masses $m/z = 28, 44, 77, 92$ and 106 were monitored to determine carbon monoxide, carbon dioxide, benzene, toluene, and benzaldehyde respectively [11].

Amounts desorbed were normalised to take into account the surface area of material under study. Blank experiments were performed where the empty TPD apparatus was exposed to benzaldehyde and ethyl cyanoacetate, followed by pumping and temperature ramping. The experiments showed that there was negligible adsorption on the apparatus walls.

2.3. *In situ* Fourier transform infrared spectroscopy (FTIR)

In situ Fourier transform infrared spectroscopy (FTIR) was performed in a specially designed stainless steel chamber installed in an ATI Research Series 1 FTIR spectrometer (see Fig. 2). The catalyst was compressed into a disc, activated at 550°C then left to cool to 80°C under ultrahigh vacuum (UHV) conditions. Adsorption experiments were performed by introducing benzaldehyde or ethyl cyanoacetate vapour (purified by freezing/thawing cycles, as described above) over the catalyst. Desorption experiments were performed by heating from 80 to 550°C and then leaving to cool to 30°C .

3. Results

3.1. Ethyl cyanoacetate desorption

For the ZnO sample, the key desorption peaks were observed at temperatures of 269°C , with two shoulders either side of the main peak at 155 and 369°C . The TPD profile is shown in Fig. 3. Desorption of molecular ethyl cyanoacetate ($m/z = 113$) was not detected in the system during the course of the experiment. It is likely that

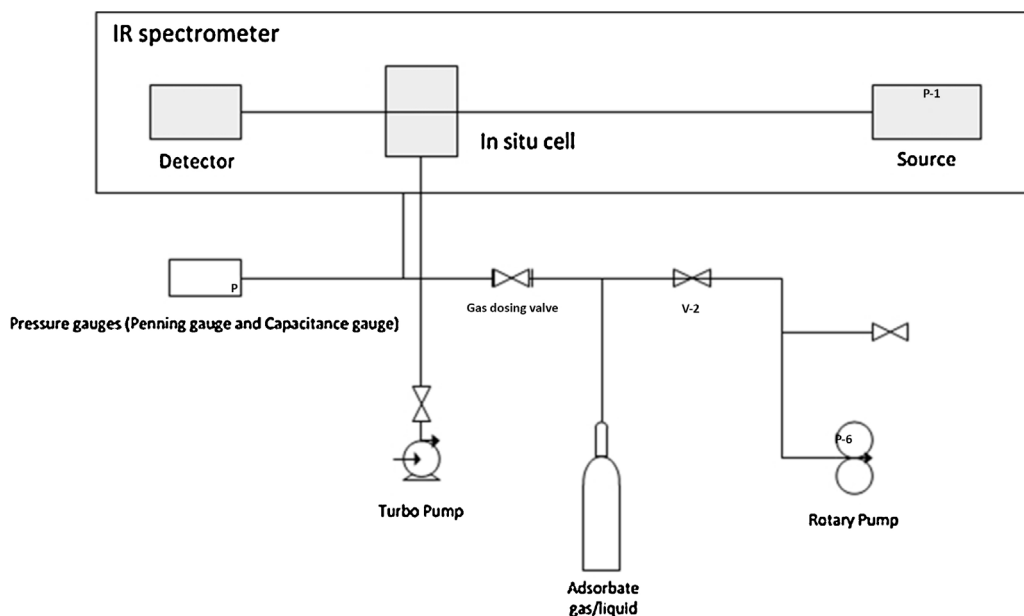


Fig. 2. Experimental setup of the *in situ* FTIR apparatus.

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