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The influence of water vapour on the photocatalytic oxidation of cyclohexane in an internally illuminated monolith reactor

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ABSTRACT

This paper discusses effects of humidity on photocatalytic cyclohexane oxidation performed in an internally illuminated monolith reactor equipped with an immobilised layer of approximately 3 μm titania (Hombikat UV100). Using dry nitrogen containing 10–20% of oxygen, cyclohexanone is produced with high selectivity (>90%) over cyclohexanol. The photocatalytic monolith deactivates within 80 min of operation. Regeneration of activity of such deactivated monolith is possible by air treatment at 450 °C.

When the applied nitrogen/oxygen gas is humidified, stable ketone production rates are obtained around 5×10^{-6} mol h^{-1} at an optimised relative humidity of 65%. Ketone over alcohol selectivity is lower in humidified conditions, the ratio of the cyclohexanol/cyclohexanone production rates increases from 0.4 to 1.0 as a function of increasing humidity from 30% to 90%.

Rapid transients in water vapour content lead to relatively slow changes in concentration of *in situ* produced cyclohexanone and cyclohexanol. The observation of these changes is used to explain the effect of humidity on reactor performance.

1. Introduction

In photocatalysis, photons activate catalysts to highly energetic states, while no additional heat is needed to supply activation energy to convert reactants. Photocatalysis is employed for contaminant removal from gases and liquids such as air and water, self-cleaning of surfaces such as glass windows, transferring solar energy into chemical energy by for example water splitting and CO_2 activation. Photocatalysis has also been investigated for chemical synthesis [1–4]. In particular, photocatalysis has been shown to improve the selectivity of synthesis processes that are conventionally employed at elevated temperatures. Thermally activated consecutive and parallel reactions are suppressed at the near-ambient temperatures at which photocatalysis is carried out.

The industrial production of cyclohexanone is energy-intense. Cyclohexane is oxidised at 140–180 °C [5]. To minimise side product formation, the conversion is kept low. Unconverted cyclohexane is separated from the reaction mixture and is recycled. Cyclohexanol and other byproducts are converted into cyclohexanone, again after energy intensive separation processes.

Oxidation of liquid cyclohexane by using an UV-illuminated titania photocatalyst around room temperature promises improved selectivity and overall energy savings. The following aspects have been addressed in the literature:

- modification of the TiO_2 photocatalyst [6–15]
- optimisation of reactant/product adsorption/desorption on/from the photocatalyst [16,17,9], e.g. by addition of water [18,19] or solvents [20,21,19]
- regeneration of deactivated photocatalysts [22]
- optimisation of the operation temperature [23]
- optimisation of (the wavelength of) the irradiance [24,15]
- optimisation of the oxygen concentration [21]
- optimisation of the reactor design [25]
- mechanistic understanding [26,27] to allow rational design of improved catalyst materials

Most of the studies indicated above employed slurry reactors to evaluate catalytic performance. Immobilisation of the photocatalyst eliminates the need for filtration of the reactor effluent and principally enables continuous operation of the photocatalyst. Various photocatalytic reactor concepts using a monolith (channel diameter >2 mm) and/or fibres have been proposed to immobilise titania:

- an internally illuminated monolith reactor (IIMR) [28] that contains a monolith onto which the photocatalyst is immobilised

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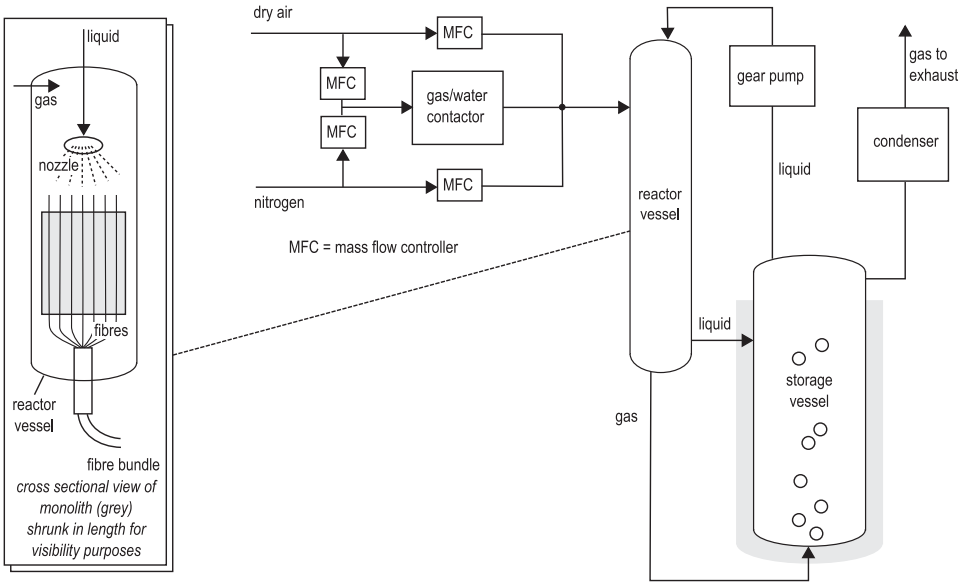

Fig. 1. Schematic diagram of the internally illuminated monolith reactor system (IIMR). The storage vessel is maintained at constant temperature by a water bath (grey-coloured area). A cross-sectional zoom of the reactor including monolith and fibres is displayed at the left side of the figure.

(coated). A favourable surface/volume ratio is achieved this way while eliminating the need for photocatalyst recovery. Side-light emitting fibres continuously illuminate the photocatalyst that is coated onto the walls of the monolith channels.

- UV-transparent monoliths [29,30] to allow external illumination by for example the sun, thus reaching a large surface of immobilised catalyst without suffering from shadow effects
- reticulated foam monoliths [31] in order to enhance mass transfer (compared to honeycomb monoliths) by the random, tortuous nature of the foam
- optical fibre reactors [32–36] to increase the illuminated surface area of immobilised catalyst
- photonic band-gap (inverse opal) TiO_2, i.e. "photonic crystals", coated onto fibres [37] showing an increased photonic efficiency

Here, we further discuss the internally illuminated monolith reactor (IIMR). Experimental data on monoliths for purification of water [31,32] and air [38–41] are available, but a detailed systematic evaluation of parameters affecting the performance in selective oxidation has not been reported so far. Du et al. [28] have published the results of only one experiment using the IIMR, in combination with the photocatalyst anatase titania Hombikat UV100 for production of cyclohexanone from cyclohexane. A significant initial rate was reported, which rapidly decreased. An explanation for this trend was not provided. Carneiro et al. [22] have also published a result on the performance of a Solaronix TiO_2 photocatalyst coated onto a silica-coated cordierite monolith. The silica was used to prevent accumulation of (inactive) TiO_2 in the macropores of the cordierite. This study does not provide information on the effects of process parameters, such as humidity, on the reaction efficiency in the monolith and neither on deactivation aspects.

Water vapour has been reported to affect the performance of photocatalytic cyclohexane oxidation in slurry reactors [18,19], by altering adsorption/desorption behaviour and/or by forming hydroxyl radicals.

The herein presented study provides novel detailed information on the performance of the IIMR in photocatalytic cyclohexane oxidation using titania Hombikat UV100, and specifically addresses the influence of water vapour on the performance.

2. Experimental

All chemicals used in this work were obtained from Sigma–Aldrich and used as received (unless otherwise stated). Anatase titania Hombikat UV100 was kindly provided by Sachtleben, and also used as received.

2.1. Internally illuminated monolith reactor system

The internally illuminated monolith reactor (IIMR) developed by Du et al. [28] was used in this work, see Fig. 1 for a schematic diagram. This reactor consists of a glass reactor vessel containing a titania-coated monolith of about 23 cm long and 4.2 cm in diameter. For illumination of the photocatalyst that was coated onto the monolith walls, side-light emitting fibres were inserted into the monolith channels from the bottom of the reactor vessel, see Fig. 2 for a photograph. Liquid cyclohexane (0.8–1.0 L, dried overnight by addition of 100 g 4 Å molecular sieve [4–8 mesh] to 5 L of cyclohexane) was recirculated from a 1 L storage tank over the reactor using a gear pump. A nozzle sprayed cyclohexane on top of the monolith channels. Liquid samples were taken from the storage vessel using a tube connected to a 10 mL plastic syringe. A water bath kept the storage vessel at a constant temperature of around 25 °C.

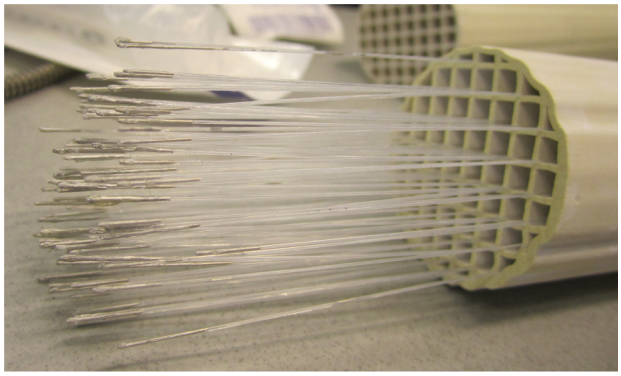

Fig. 2. Photograph of side-light emitting fibres inserted into the monolith. The aluminium coating of the end of the fibres is visible at the left side (Section 2.2).