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The Effect of nitric oxide on the photocatalytic oxidation of small hydrocarbons over titania

Stephen Poulston [a], Martyn V. Twigg [b,*], Andrew P. Walker [c]

[a] Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, UK
[b] Johnson Matthey Plc, Orchard Road, Royston, Hertfordshire SG8 5HE, UK
[c] Johnson Matthey ECT, 380 Lapp Road, Malvern, PA 19355, USA

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ABSTRACT

The catalytic UV photo-oxidation of NO in the absence and presence of ethane, ethene, propane, propene, and *n*-butane over TiO_2 in the presence of excess oxygen was studied in the temperature range 21–150 °C. It was confirmed in our system that in the absence of hydrocarbon NO was photocatalytically oxidised by oxygen to NO_2 over TiO_2 and was strongly absorbed. Both NO and hydrocarbon could be simultaneously photo-converted with the conversion varying considerably with both NO and hydrocarbon concentration and the nature of the hydrocarbon. In some instances the presence of NO in the feed gas enhanced hydrocarbon oxidation via reactions involving NO_2 that is a powerful oxidant. The extent of this effect depended on the relative strengths of adsorption on TiO_2 of the reactants and products. To reduce surface coverage of hydrocarbon most reactions were run at 150 °C, and it was shown that at this temperature NO*x* adsorbed on titania could be reduced by photogenerated hydrocarbon surface species to N_2O and N_2 under these conditions. The formation of N_2 was confirmed using ^{15}NO with helium as carrier gas. By contrast, at room temperature in the presence of propene NO was converted to NO_2.

1. Introduction

Previously we studied the catalytic photo-oxidation of ethane, ethene, propane and propene over titania, in excess oxygen and found under most conditions at room temperature the selectivity of hydrocarbon conversion to CO_2 was at least 95%. We also studied reactions with *n*-butane and *n*-hexane, and they had significantly lower conversion to CO_2. The reasons for this were not explored, but the formation of brown carbonaceous surface deposits on the titania were implicated [1]. There is a lot of interest in the photo-oxidation of NO to NO_2 in the presence of oxygen, and eventually to nitric acid if sufficient adsorbed water is present [2–12], and TiO_2 is being used on building materials for the removal of atmospheric pollutants in urban areas via these reactions. Although some suggest the oxidative cleansing action involves the formation of nitric acid, it seems equally likely the extremely powerful oxidant NO_2 is directly involved. A number of studies have also dealt with the photodecomposition and photoadsorption of NO with titania surfaces [13–17] in the absence of oxygen which seems to be a complex reaction since different workers reported widely varying products including NO_2, N_2O, and NO^{3-}.

NO_2 is a very powerful oxidant, and it has long been known it reacts rapidly with hydrocarbons in the gas phase [18], that it can oxidise soot from diesel engines at moderate temperatures [19] and that NO_2/hydrocarbon mixtures can form the basis of rocket propellant systems. We therefore thought it worthwhile to explore the effect of NO on the photo-oxidation of hydrocarbons over titania, since NO_2 should be generated *in situ* on the titania surface so keeping it free of carbonaceous deposits. A number of papers have been published on photoinduced reactions of NO and hydrocarbons over titania [20–22], in addition two recent studies dealt with the photoreaction of NO with CO [23] and NH_3 [24] over titania.

Here we report results for the catalytic oxidation of ethene, ethane, propene, propane, and *n*-butane in the presence of NO and excess oxygen, and surprising evidence was obtained showing photogenerated surface organic fragments can reduce nitrogen oxide species to dinitrogen. Outside the field of photocatalysis the hydrocarbon selective reduction of NO (HC-SCR) in the presence of excess oxygen has attracted great interest, and the subject has been extensively reviewed [25–30]. The most effective catalysts are Pt/alumina, Cu exchanged ZSM5 and Ag/alumina though a large

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* Corresponding author. Tel.: +44 1763 253141.
E-mail address: martyn.twigg@matthey.com (M.V. Twigg).

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variety of other Cu, zeolite and pgm based systems have also been studied. Interestingly the mechanism of NO reduction via HC-SCR often invokes the formation of NO_2 which subsequently reacts with an activated hydrocarbon species.

2. Experimental

The photo reactor comprised a stainless steel Plate 100 mm × 100 mm evenly coated with TiO_2 by spraying its upper surface with an emulsion of TiO_2 in water, followed by drying at room temperature. Reactant gas mixtures were passed over the TiO_2 through a 1 mm wide gap between a quartz window and the sample plate. A viton gasket made a gas tight seal between the quartz plate and a stainless steel block which contained a recess that retained the sample plate, as illustrated in Fig. 1. The whole assembly holder could be heated to temperatures up to 150 °C by a hotplate on which the stainless steel block was placed. An air-cooled housing containing a broad-spectrum 400 W lamp (Philips HPA 400 S) was placed 50 mm above the centre of the sample plate. The lamp reached full intensity within three minutes. The full output was 66.8 mW/m^2 with visible and UV accounting for 43.2% and 56.8% of the output respectively. The output in the UV region consisted of 49.3% in the UVA and 8.8% in the UVB and C regions [31]. With the sample at 150 °C there was an increase of ~3 °C when the light was switched on. After ~30 min the sample temperature returned to 150 °C as the feedback gas temperature controller reduced the input power to compensate for the heating effect of the lamp. Unless otherwise stated experiments were carried out at 150 °C and 250 ml/min total gas flow rate with varying concentrations of hydrocarbon and NO while maintaining an O_2 concentration of 12%. Gases were obtained from bottles (Air Products), and mass flow controllers were used to produce desired mixtures and flow rates.

Reactor outlet gas was analysed using a quadrupole mass spectrometer (VG Gaslab 300) and for N_2O and C_2H_6 a GC (PerkinElmer 8500) was used. When no NO was present in the gas feed the C_2H_6 conversion was determined from the change in the mass 30 signal monitored by the mass spectrometer. However, when NO (also mass 30) was present in the gas feed the C_2H_6 conversion was determined with the GC. Once the C_2H_6 conversion was known from the GC its contribution to the mass 30 signal could be calculated, and so the amount of NO from the mass 30 signal obtained. The C_2H_6 conversions in the absence of NO in the gas feed calculated using the GC and mass spectrometer data agreed to within ±5%. Contributions to the mass 30 signal (used to monitor NO) arise from the fragmentation of NO_2 which unambiguously also gives a mass 46 signal. This fragmentation was determined using a known NO_2 concentration and then used to compensate for NO_2 in the mass 30 signal.

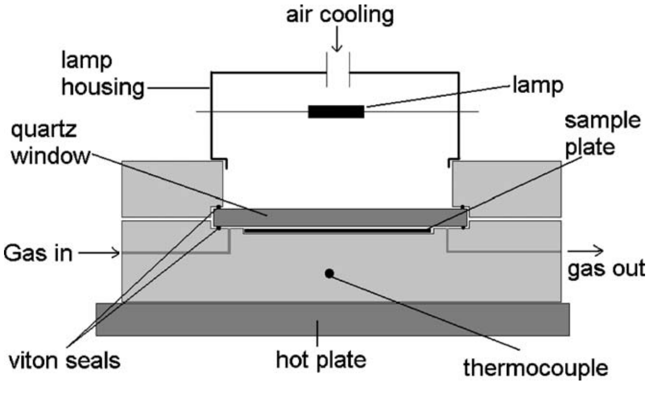

Fig. 1. Schematic of photoreactor.

In all of the experiments described here the TiO_2 used was "Hombifine N" obtained from Sachtleben Chemie GmbH, Germany. Anatase was the only crystalline phase identified by X-ray diffraction (Siemens D500 Diffractometer) with an estimated crystallite size of 6.8 nm from line broadening. The BET surface area was 357 $m^2\,g^{-1}$. Typical TiO_2 loadings on the sample plate were between 0.3 g and 0.4 g, and from this a TiO_2 film thickness of 7.5–10 μm was estimated assuming a density of 3.89 $g\,cm^{-3}$ (i.e, 100% packing efficiency). In practice the film was somewhat thicker than this due to inefficient packing. The typical penetration depth of UV light into powdered TiO_2 is about 2 μm, and twice this thickness of film would be required for saturation of the reaction rate. Consistent with this only small changes (± 5%) in propene conversion were observed when the TiO_2 loading was varied between 0.16 g and 1.28 g, corresponding to a film thickness of 4 μm and 32 μm respectively (assuming 100% packing efficiency).

3. Results and discussion

3.1. Hydrocarbon oxidation in the absence of NO

Previously we reported results for the UV-induced photo-oxidation of propene, propane, ethene, ethane, *n*-butane and *n*-hexane over a TiO_2 photocatalyst at 150 °C with hydrocarbon concentrations up to 4000 ppm and O_2 concentrations up to 20% [1]. In the absence of O_2, a small amount of reaction was observed for just a short period. Increasing the O_2 concentration led to increased hydrocarbon conversion. With hydrocarbon concentrations up to ~1000 ppm conversion to CO_2 was at least 95% for propene, propane, ethene and ethane though the CO_2 selectivity fell at higher concentrations and at all *n*-hexane concentrations down to 50 ppm there was little reaction.

For propene and propane, we previously showed the extent of photoconversion depended on the gas-phase hydrocarbon concentration, and had maxima at 500 ppm and 1000 ppm, respectively. The decrease at higher concentrations was attributed to hydrocarbon blocking oxygen adsorption sites, and thereby inhibiting the production of the photogenerated reactive oxygen species responsible for hydrocarbon oxidation. This effect also explains the increased conversion of hydrocarbon at 150 °C compared to that at room temperature observed for propene. The increased temperature reduces the amount of adsorbed propene and allows more reactive oxygen species to be generated. It was for this reason that most experiments reported (here and those done previously) were carried out at 150 °C, so higher NO and hydrocarbon conversions could be achieved. Increased photo-oxidation at slightly elevated temperature due to the lowering of a hydrocarbon blocking effect has also been reported for other related systems [32,33]. Durability of the photo-oxidation reaction without catalyst deactivation was demonstrated for propene, propane, ethene and ethane. In contrast with *n*-butane and to a greater extent *n*-hexane, the deposition of carbonaceous species on the TiO_2 surface led to rapid catalyst deactivation.

It was thought the presence of photogenerated NO_2 might keep the surface clean and so improve conversions by oxidizing them to CO_2 and H_2O, and re-forming NO. Therefore the current paper focuses on the effect of NO and hydrocarbon which is reported in the following sections.

3.2. Photo-oxidation of NO to NO_2

Initially experiments were made on the photo-oxidation of NO to NO_2 in the absence of hydrocarbon, and the results using varying NO concentrations in an excess of oxygen are given in