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Water as a promoter of the complete oxidation of volatile organic compounds over uranium oxide catalysts

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The effect of water addition on the complete oxidation of benzene and propane VOCs by uranium oxide catalysts has been investigated. Benzene oxidation was studied using a silica supported U_3O_8 catalyst. Complete oxidation is promoted by the addition of 2.6% water compared with the reactivity when no water is added to the reactant feed. Increasing the water concentration to 12.1% resulted in a suppression of oxidation activity. Investigation of propane oxidation using U_3O_8 shows a dramatic promotion of activity. Propane conversion was *ca.* 50% at 600 °C without added water, whilst it increased to 100% at 400 °C with the addition of 2.6% water. A comparison of oxidation activity has been made with Mn_2O_3, an oxide recognised for complete oxidation. In contrast to the U_3O_8 catalysts the addition of 2.6% water suppresses the activity of Mn_2O_3. *In situ* powder X-ray diffraction studies showed that the bulk U_3O_8 structure was stable under all the reaction conditions. The origin of the increased activity is not clear but may be due to modification of the catalyst surface and the contribution from new reaction pathways such as steam reforming.

KEY WORDS: water as a promoter; catalytic oxidation; uranium oxide; hydrocarbon oxidation; VOC destruction

1. Introduction

A major class of common pollutants are Volatile Organic Compounds (VOCs). The range of these compounds is diverse, and many are involved in detrimental atmospheric chemical reactions resulting in the formation of photochemical smog and destruction of the ozone layer. The abatement of VOC discharge into the environment is, at the present time, of crucial importance. Recently, much attention has focused on the use of catalytic oxidation as an effective method for the oxidative destruction of harmful VOCs. This catalytic technology is applied as an *end of pipe* solution to remove these pollutants, which are often of low concentration in air. It is often the case that the effluent streams contain moisture, and that the moisture is known to be detrimental for the deep oxidation performance of the most widely used commercial precious metal catalysts. The presence of water in the effluent stream can have a dramatic effect and has been shown to inhibit activity over supported Pd [1,2] and Pt [3] catalysts. Attempts have been made to improve the tolerance of precious metal catalysts to water vapour, and supporting Pt on a hydrophobic support such as a fluorinated carbon reduces the inhibiting effect of water when compared to a conventional alumina support; however, inhibition is still observed [3]. We have previously shown that uranium oxide based catalysts exhibit high activity for the combustion of a range of VOCs at industrially relevant temperatures and space velocities [4]. We have now addressed this problem of water inhibition of catalyst performance; in this paper we present results that indicate the addition of low concentrations of water to the effluent stream further enhances the catalytic activity of uranium oxide catalysts. This is in contrast to many metal oxide based catalysts, and precious metal catalysts, which are less active when water is present.

2. Experimental

2.1. Catalyst preparation

The U_3O_8 catalyst was prepared by decomposition of $UO_2(NO_3)_2{\cdot}6H_2O$ (Strem 99.9%) by calcination in static air at 300 °C for 1 h and then at 800 °C for 3 h. A supported uranium catalyst was also prepared by impregnation of fumed silica (BDH, Cab-O-Sil M5) with $4.2\,\mathrm{ml\,g^{-1}}$ of uranyl nitrate solution ($0.397\,\mathrm{mol\,l^{-1}}$). The resulting material was dried at 100 °C and subsequently calcined using the same conditions as the unsupported catalyst. The uranium loading for this catalyst was 10 mol% (U/SiO_2), approximately representing theoretical monolayer coverage. For comparison of catalyst performance the oxidation catalyst Mn_2O_3 (Aldrich, 99.9%) was selected as it is known to have high complete oxidation activity [5].

2.2. Catalytic activity

The catalysts were tested for VOC destruction using a fixed-bed laboratory microreactor equipped with an

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on-line gas chromatograph analysis system using propane and benzene. Gas flow rates were regulated with electronic thermal mass flow controllers. Water was introduced by passing the air flow through a set of two saturators. The concentration of water was controlled by oversaturating the gas stream at room temperature in the first saturator and then reduced by passing through the second saturator maintained in a thermostatically controlled bath. The water concentration was calculated using water vapour pressure data. The reactant gases were pre-heated to 150 °C prior to entering the reactor. Catalysts were tested in powdered form using a $\frac{1}{4}''$ o.d. stainless steel reactor using a gas hourly space velocity of 35 000 h^{-1}. The VOC concentrations used were 1% propane and 600 ppm benzene in air. VOC conversion was calculated from the difference of concentration at reaction temperature and a lower temperature at which the catalyst was inactive. Carbon balances were in the range $100 \pm 10\%$.

2.3. Catalyst characterisation

Ex situ powder X-ray diffraction patterns were collected using an Enraf FR590 instrument with a Cu source operated at an X-ray power of 1.2 kW (30 mA and 40 kV). A Ge(111) monochromator was used to select Cu Kα_1 X-rays. The powdered samples were compressed into an aluminium sample holder, which was rotated during data collection to compensate for any crystallite ordering. The diffraction pattern was measured by means of a position sensitive detector (Inel PSD120), covering all 2θ values in the range 4.4–124.6°. Raw data were corrected against a silicon standard and phase identification was performed by matching the experimental pattern against standard entries in the JCPDS powder diffraction file.

In situ powder XRD studies were performed using a Phillips X-PERT diffractometer with a high temperature Parr XRK reaction chamber and a position sensitive detector. Copper Cu Kα X-rays (30 KeV, 40 mA) were used and data in the 2Θ range 18° to 60° were collected. The *in situ* reaction cell was designed so that gases flowed through the catalyst sample which was heated from ambient to 600 °C. Experiments were carried out with a flow of dry air and an air stream containing *ca.* 4% water. Typical analysis times at each temperature were in the region of 1.5 min.

3. Results and discussion

The powder X-ray diffraction patterns of the U_3O_8 and the SiO_2 supported uranium catalysts are shown in figure 1. The XRD confirms that the calcination procedure used produced orthorhombic U_3O_8 from the nitrate precursor. The diffraction peaks from the silica supported uranium oxide catalyst were centred at the same d spacings as U_3O_8 and confirm that the supported catalyst also contained U_3O_8. The diffraction peaks from U_3O_8/SiO_2 were significantly broader when compared to U_3O_8, indicating that the supported U_3O_8 crystallite size was considerably smaller.

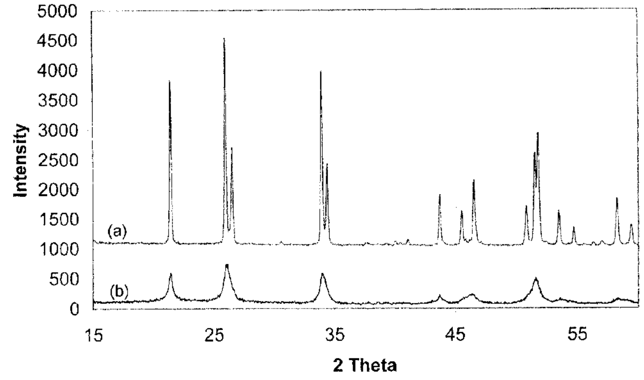

Figure 1. Powder X-ray diffraction patterns of the U_3O_8 and U_3O_8/SiO_2 catalysts: (a) U_3O_8; (b) U_3O_8/SiO2.

The oxidation of benzene over silica supported U_3O_8 showed no activity for hydrocarbon oxidation below 300 °C in the absence of water (figure 2). Conversion increased to 99.9% at 450 °C and was maintained at higher temperatures. On the addition of 2.6% water, the catalyst was active at 250 °C, 100 °C lower than the dry conditions, and 99.9% conversion was achieved at 400 °C, 50 °C lower than the dry conditions. Conversely, the addition of a greater concentration of water (12.1%) resulted in the temperature required for 99.9% conversion to be increased by 50 °C to 500 °C and the conversion was lower than the dry conditions throughout the active temperature range. The only products formed under all conditions tested were H_2O, CO_2 and CO. The CO_2/CO ratio was dependent on the concentration of water co-fed. The product selectivities for benzene oxidation using U_3O_8/SiO_2 in the absence of co-fed water and 2.6% water are shown in figure 3. Under dry conditions at 400 °C selectivity was 70% towards CO_2, whilst on the addition of 2.6% water, CO_2 selectivity

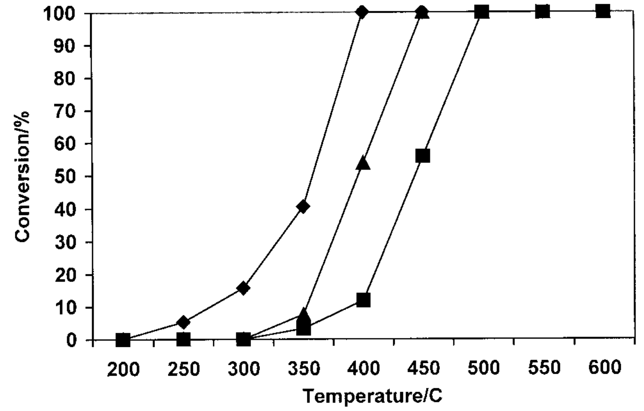

Figure 2. The effect of co-feeding water on the oxidation of 600 ppm benzene in air over U_3O_8/SiO_2: ▲ No water; ◆ 2.6% water; ■ 12.1% water.

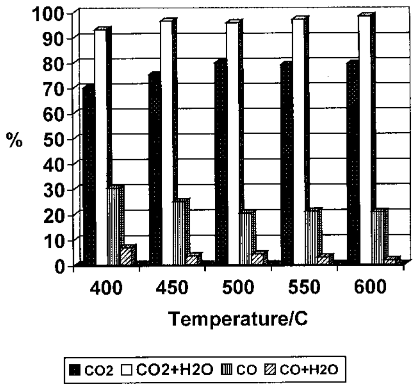

Figure 3. Product selectivities for benzene oxidation using U_3O_8/SiO_2 in the absence of co-fed water and 2.6% water.

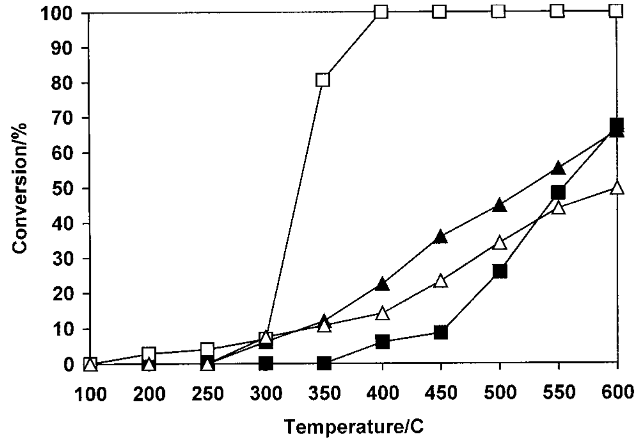

Figure 4. Comparison of catalytic activity for 1% propane oxidation in air: △ U_3O_8; □ U_3O_8 + 2.6% water; ▲ Mn_2O_3; ■ Mn_2O_3 + 2.6% water.

was increased to 93%. At 500 °C in the absence of co-fed water and with the addition of 2.6% water the CO_2 selectivity increased to 75% and 96% respectively. Similar results were also observed when the reaction temperature was increased to 600 °C. The increase in the CO_2 selectivity with co-fed water is consistent with the water gas shift reaction.

To establish whether the effect of water was specific for benzene oxidation, and to probe further the effect of water, propane oxidation experiments were performed with the U_3O_8 catalyst (figure 4). Results show that in the presence of 2.6% water, 99.9% propane was converted at 450 °C over U_3O_8; however, in the absence of co-fed water U_3O_8 only produced 70% conversion at 600 °C. To establish whether this type of behaviour was limited to uranium oxide catalysts the propane experiments were repeated using Mn_2O_3, which is known to be an active catalyst for complete oxidation [6]. The Mn_2O_3 catalyst produced 65% conversion at 600 °C in the absence of water, whilst this was suppressed to 49% when water was present at 2.6%. Indeed over Mn_2O_3 the conversion of propane was lower at all temperatures when water was co-fed. Determination of the BET surface areas showed that the surface area of Mn_2O_3 was $1.8\,m^2\,g^{-1}$, whilst U_3O_8 was $0.8\,m^2\,g^{-1}$. These data may account, in part, for the higher activity of Mn_2O_3 under dry reaction conditions, but it is clear that the effect of co-feeding water has an opposing effect for the two catalysts.

In situ powder X-ray diffraction studies have investigated the catalyst structure under reactions conditions; the diffraction patterns of the U_3O_8/SiO_2 catalyst in flowing 4% water/air over the temperature range 100–600 °C is shown in figure 5. The results indicated that even at 600 °C no change in the initial U_3O_8 phase occurred. Some thermal broadening and loss of peak resolution were observed but even after approximately 7 h at elevated temperature patterns were comparable

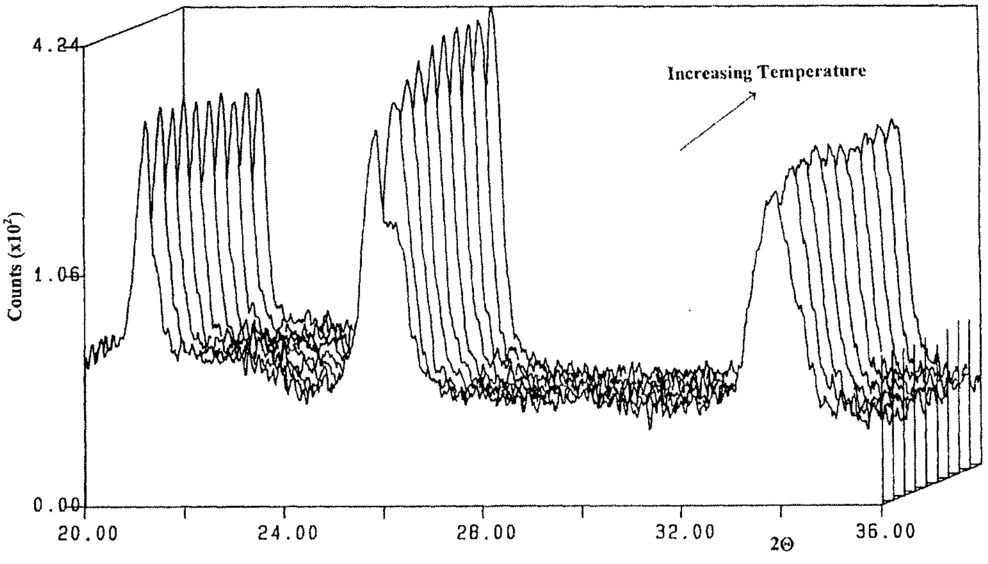

Figure 5. *In situ* powder X-ray diffraction patterns of the U_3O_8/SiO_2 catalyst in flowing 4% water/air over the temperature range 100–600 °C.

with those obtained under ambient conditions. Similar studies in a dry flow of air over the same temperature range also showed that the structure of U_3O_8 was unchanged during the reaction.

It is interesting to comment on the mechanism of the promotional effect of water over U_3O_8. It has been shown previously that the complete oxidation of VOCs by uranium oxide catalysts takes place by a redox mechanism with lattice oxygen, probably at defect sites, as oxidant [7]. The rate determining step over uranium oxide catalysts has not been unequivocally determined. However, it is feasible that the rate determining step may be reoxidation of the reduced catalyst, and this has also been proposed for other redox oxidation catalysts [8]. The presence of water vapour is known to promote the oxidation of uranium oxides when compared to oxidation rates under dry conditions [9]. It is therefore possible that the oxidation rate for VOCs is promoted by water as the catalyst reoxidation rate is enhanced. The reoxidation of the catalysts may also aid the desorption of adsorbed CO_2, although the higher rates of benzene oxidation compared to propane indicates that desorption of CO_2 may not be rate limiting. The role of water may also have an effect on the initial activation of the hydrocarbons, indeed co-feeding 2.6% water reduced the light off temperature for propane oxidation by 100 °C. This effect may be due to modification of the uranium oxide surface by hydroxylation which effectively aids hydrocarbon activation. Finally, the contribution from steam reforming reactions cannot be discounted when the water is co-fed. Uranium oxide catalysts have been identified as highly active steam reforming catalysts [10]; however, at the active temperatures used in this study steam reforming activity is expected to be negligible.

At this stage no attempt has been made to optimise the concentration of water required for maximum effect since this can be expected to vary with the nature of the VOC, but it is feasible that further activity enhancement could be observed at lower concentrations (<1%). However it is clear that the addition of water is beneficial for the activity of uranium oxide catalysts for the oxidative destruction of VOCs. Since effluent streams often contain water, this is an additional advantage for this very active heterogeneous catalyst.

4. Conclusions

Uranium oxide based catalysts are active for the oxidation of benzene and propane to carbon oxide in the absence of co-fed water. However, the addition of low levels of water (2.6%) has a marked effect on oxidation activity, promoting the rate of complete oxidation. The addition of higher concentrations of water (12.1%) has a detrimental effect on oxidation activity. The addition of water also increases selectivity towards CO_2 and this may be due to the water gas shift reaction. A comparison of catalytic activity has been made with Mn_2O_3, an oxide recognised for its high complete oxidation activity. In contrast to the U_3O_8 catalysts the addition of 2.6% water suppresses the Mn_2O_3 oxidation activity. *In situ* powder XRD shows that the bulk U_3O_8 structure is stable under the reaction conditions used for this study. The origin of the increased activity is not clear but may be due to modification of the U_3O_8 catalyst surface by hydroxylation, and the contribution from new reaction pathways, such as steam reforming, cannot be discounted.

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