Synergic interactions in a urania–titania catalyst for isobutene partial oxidation

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The partial oxidation of isobutene has been studied over titania-supported uranium oxide catalysts which exhibit a strong synergy between UO_x and support phases.

Keywords: uranium, isobutene oxidation, titania

1. Introduction

The partial oxidation of hydrocarbons by dioxygen remains one of the current major challenges facing heterogeneous catalysis [1], and, in particular, the bulk and fine chemicals industries. To date much attention has focused on d-block transition metal oxides for vapour phase partial oxidation chemistry, however the potential of actinides has rarely been explored. Uranium oxides (UO_x) exhibit diverse catalytic properties [2], and have been identified as candidates for the total oxidation of VOCs [3]. U–Sb [4] and U–Mo [5] mixed oxides have also shown some promise in propene and butene partial oxidation. We recently demonstrated the efficacy of supported UO_x for the selective reduction of NO_x and simultaneous combustion of methane [6]. Here we report the application of titania-supported UO_x for the partial oxidation of isobutene, a widely available C_4 feedstock commercially used for methacrolein/methacrylic acid production.

2. Experimental

Reactions were performed in a single-pass, fixed-bed microreactor. The reactor comprised a 4 mm i.d. silica tube located inside a Carbolite MTF furnace. Gas flow rates were independently regulated by three mass flow controllers (Brooks). An in-line filter (2 μm) was located downstream of the reactor to contain UO_x dust particles. On-line analysis of reactant and product gas streams was performed by use of a Shimadzu 14a GC equipped with a 2 m Poropack Q column and methanator. Quoted conversions are ±2% and selectivities are ±5%. A 100 and 200 mg catalyst charge (50–150 μm particle size) for supported and bulk UO_x catalysts, respectively, was placed inside the reactor on a silica frit. The catalyst temperature was read from an internal thermocouple located adjacent to the catalyst bed. The feed gases used in this study were C_4H_8 (99.9%, Linde), O_2 (99.99%, E&G) and He (99%, E&G). A total gas flow rate of 38 $\mathrm{ml\,min^{-1}}$ was employed in all experiments, using a $1:1$ $C_4H_8:O_2$ mixture with He balance of 30 $\mathrm{ml\,min^{-1}}$. Before reaction, samples were heated to temperature under He (30 $\mathrm{ml\,min^{-1}}$) before introducing reactants. *Ex situ* X-ray diffraction spectra were acquired by use of a Siemens D5000 diffractometer and Cu K_α radiation, and indexed using the JCPDS database. The scan range was from $2\theta = 5^\circ$ to 60° in increments of 0.05°. Surface areas were determined by standard N_2 adsorption for samples degassed at 200 °C and are quoted ±5% (single-point BET method).

Titania-supported catalysts were synthesised from solutions of uranium(VI) dinitrate oxide hexahydrate, $UO_2(NO_3)_2\cdot 6H_2O$ (Strem Chemicals, 99.8%) as follows. First, $UO_2(NO_3)_2\cdot 6H_2O$ (containing $\sim$0.2% ^{235}U) was dissolved in water to produce a 1.1 M solution (pH $= 2$). An appropriate quantity of the Euro-Titania support (Ti oxide) was dried and subsequently impregnated with the $UO_2(NO_3)_2\cdot 6H_2O$ solution by the incipient wetness method. Finally, samples were dried for 24 h at 100 °C before calcination under flowing air for 3 h at 800 °C. Uranium oxide loadings ranged between 3 and 29 wt% (0.5–9 mol%). Comparative experiments were also conducted with bulk UO_2, U_3O_8 and UO_3 (all 99%, Strem). Before reaction, samples were heated under He (30 $\mathrm{ml\,min^{-1}}$) to 150 °C for 1 h and then taken to reaction temperature. Steady state was achieved and the results reported herein obtained after >1 h reaction.

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3. Results and discussion

3.1. X-ray diffraction (XRD)

The structure of titania-supported urania catalysts was examined by XRD as a function of catalyst loading, figure 1. Urania addition induces a gradual phase transformation of TiO_2 from rutile to anatase in the as-prepared catalysts, with a concomitant rise in catalyst total surface area from 5 to 8 $m^2\,g^{-1}$. This change coincides with the emergence of UO_x reflections corresponding to a mix of phases, principally UO_2, U_3O_8 and UO_3. Even for the highest loading some titania remains present as rutile suggesting a localised UO_x–TiO_2 interaction which helps stabilise anatase domains. Volume-averaged particle sizes determined by linewidth broadening of the (111) reflections, indicate UO_x crystallites of ~300–700 Å for the highest loading 9 mol% catalyst.

Post-reaction XRD on a 9 mol% catalyst reveals additional catalyst phase transformations occur under (the net reducing) reaction conditions. Following catalyst light-off and cooling under He, essentially all diffraction features due to U_3O_8 and UO_3 phases disappear irrespective of UO_x loading. The UO_2 reflections however remain, though greatly broadened, their peakwidths consistent with a *decrease* in urania domain size from ~300 down to ~20 Å. This change is clearest for the 9 mol% sample (figure 1). Bulk U_3O_8 and UO_3 do not undergo this reduction and restructuring under identical reaction conditions, indicating UO_2 is stabilised by titania (anatase). Isobutene oxidation thus both favours UO_2 formation with respect to high-stoichiometry urania phases and increases urania dispersion over the restructured TiO_2 surface. This is again consistent with a strong localised UO_x–TiO_2 interaction and may be driven by surface energetics, since UO_2 possesses the lowest coordination of the three bulk urania phases.

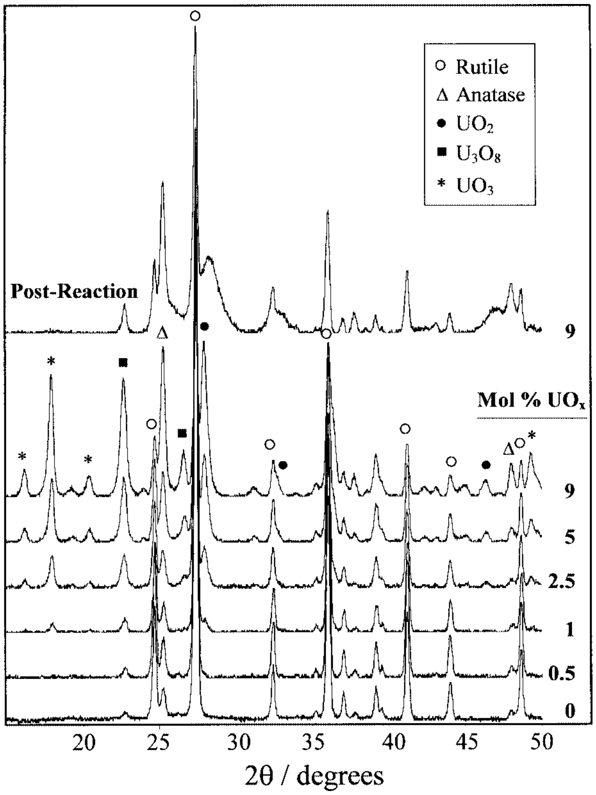

Figure 1. X-ray diffractograms of UO_x/TiO_2 catalysts calcined at 800 °C as a function of UO_x loading. A post-reaction diffractogram is also shown for the 9 mol% catalyst.

3.2. Scanning electron microscopy (SEM)

Pre- and post-reaction SEM chemical maps of the 9 mol% UO_x/TiO_2 catalyst show that urania is both uniformly distributed between individual titania particles and across the surface of each particle, figure 2(a). The absence of large urania crystallites is consistent with a layered coating of titania, suggesting an anatase to rutile phase change initiated at and confined to the titania selvedge. Topographic maps (figure 2(b)) reveal high-temperature isobutene oxidation promotes sintering of the titania support phase. Overall catalyst particle sizes increase from ~5 to ~75 μm with a concomitant change in morphology from cubic/tetragonal to spherical particles. These changes do not accompany simple high-temperature reduction or calcination, and must reflect reaction-induced surface restructuring. The increase in urania dispersion during reaction presumably results in greater wetting of the titania support, and may well be responsible for driving titania particle growth.

3.3. Reactor testing

The homogeneous gas phase reaction was first examined in an empty reactor, with negligible conversion (<3%) being observed below 650 °C (the highest temperature investigated for catalysts in this study). Above 900 °C isobutene combustion occurs depositing coke on the walls of the silica reactor.

Pure TiO_2, which XRD show is present as rutile following high-temperature calcination, shows poor activity towards isobutene oxidation peaking around 10% at 650 °C, figure 3, but with poor selectivity towards partial oxidation products, figure 4. For all catalysts the principal products of partial oxidation were formaldehyde and methacrolein, with trace levels of acetone and light alkanes/alkenes occasionally detected. Selectivity is defined as

$$S(\%) = \frac{\sum \mathrm{HCHO} + \mathrm{CH_2CCH_3CHO}}{\sum \mathrm{HCHO} + \mathrm{CH_2CCH_3CHO} + \mathrm{CO} + \mathrm{CO_2}} \times 100.$$

The prototypical bulk UO_2, U_3O_8 and UO_3 phases likewise showed isobutene conversions between 20 and 25% with even poorer partial oxidation performance.

Supporting urania on TiO_2 yields a material with only slightly improved light-off performance, and an overall catalytic activity that appears a simple superposition of the constituent phases, peaking at ~33%. However, the addition of even low (0.5 mol%) UO_x loadings to TiO_2 has

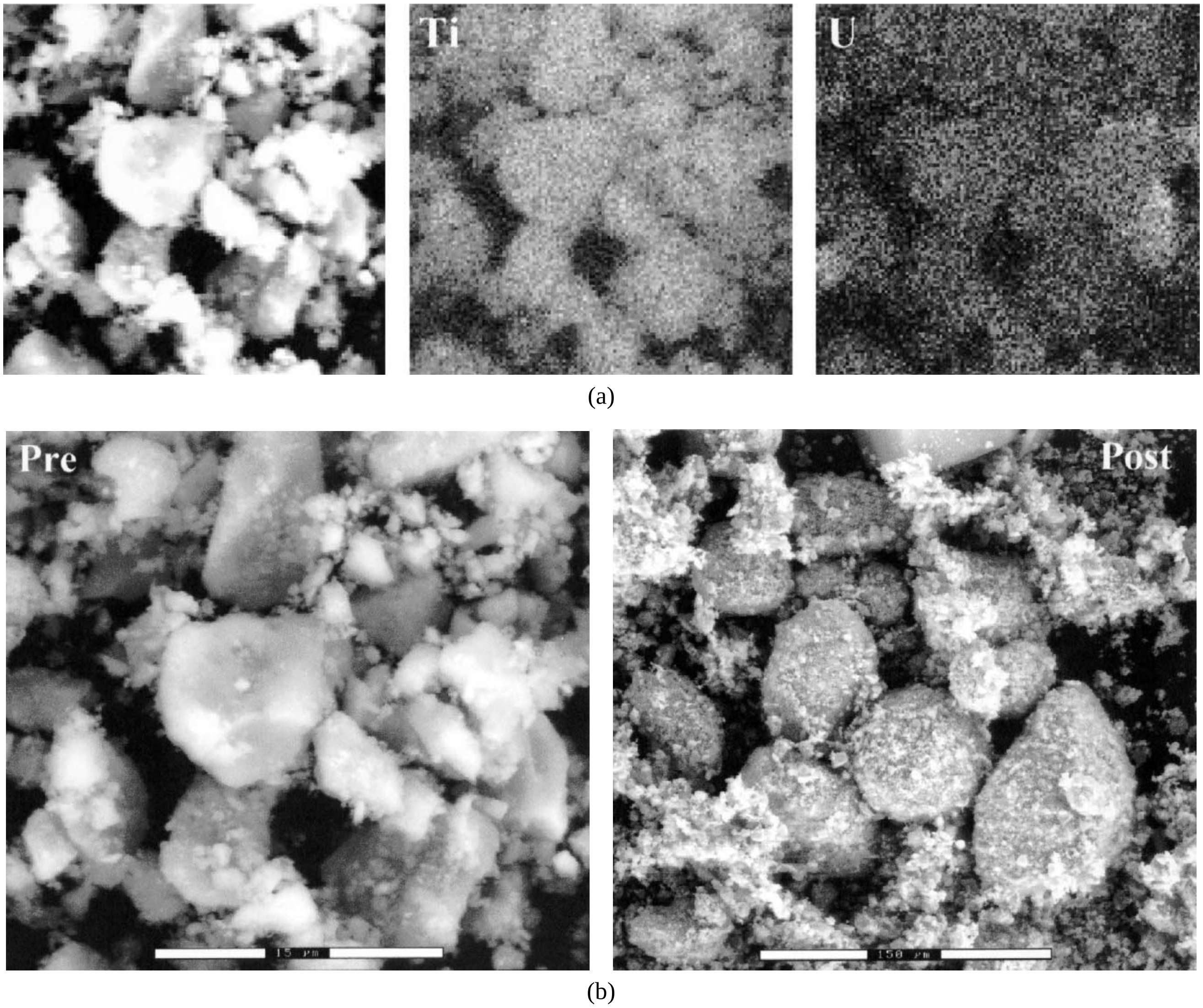

Figure 2. (a) Chemical micrographs (30 μm × 30 μm) showing the topography, uranium and titanium distributions within a fresh 9 mol% UO_x/TiO_2 catalyst. (b) Topography of a pre- and post-reaction 9 mol% UO_x/TiO_2 catalyst. $T_{\text{reaction}} = 600\,^{\circ}C$, $C_4H_8 : O_2 = 1$.

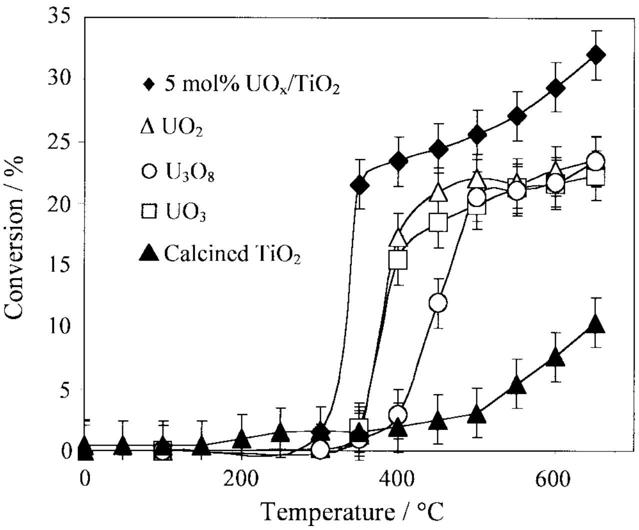

Figure 3. Effect of temperature on isobutene conversion for bulk TiO_2, UO_x and supported UO_x/TiO_2 catalysts.

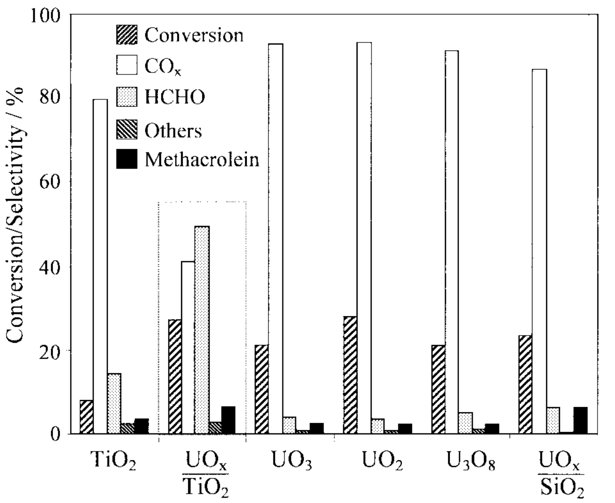

Figure 4. Effect of UO_x/TiO_2 synergy on isobutene partial oxidation at 600 °C. Performance of a 7 mol% UO_x/SiO_2 catalyst is shown for comparison.

a dramatic effect on selectivity towards partial oxidation products. Selectivity to CO and CO_2 falls from 79 to 40% with a concomitant rise in partial oxidation products, in particular formaldehyde, figure 4. Experiments in which the isobutene : O_2 ratio was varied (not shown) demonstrate that methacrolein and formaldehyde yields mirror each other, suggesting the latter is formed as a secondary product. Both display a typical volcano profile, with significant yields only for intermediate ratios $\sim$1. Combustion products show a markedly different profile, increasing monotonically with gas phase oxygen content as often observed in oxidation catalysis. We infer that partial oxidation and combustion reactions occur at different sites. Unoptimised formaldehyde and methacrolein yields of 15 and 6%, respectively, were obtained at 600 °C (yield = conversion × selectivity).

The enhanced selectivity is most likely the result of a synergic interaction between UO_x and support phases, and not simply attributable to an increased dispersion of uranium oxide. Comparative results for silica-supported urania (figure 4) reveal that small ($\sim$80 Å) UO_2 crystallites, stable under reaction conditions, behave essentially the same as bulk UO_2 strongly favouring isobutene combustion. High UO_x loadings do not further promote partial oxidation again consistent with a localised interaction at the interfacial/monolayer level. Our structural data support cooperative restructuring of both active and support phases prior to and during reaction. A similar synergy has been reported for a range of dual-oxide oxidation catalysts [7], notably isobutene oxidation over Sb_2O_4/MoO_3 wherein a remote control mechanism for the spillover of oxygen from support to active phase was advanced. Titania is a readily reducible oxide and strong metal–support effects in its catalysis are well documented. It is thus conceivable that anatase provides activated oxygen species to the UO_2/titania/gas phase interface, which facilitate partial oxidation of chemisorbed isobutene.

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