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The partial oxidation of propane to formaldehyde using uranium mixed oxide catalysts

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Abstract

A series of mixed metal oxide catalysts have been prepared and tested for the oxidation of propane and propene. Under the reaction conditions employed in these studies, Fe/Mo and U/Mo mixed oxide catalysts showing iron and uranium molybdate phases were inactive for propane and propene oxidation. A mixed U/Sb catalyst, with a USb_3O_{10} structure, was also inactive for propane oxidation, but demonstrated the expected selective oxidation activity to form acrolein from propene. Outstanding results for the selective oxidation of propane and propene to formaldehyde were obtained using Fe/U catalysts prepared with ratios of 0.5/3 and 1/3. At 450 °C, a selectivity towards formaldehyde of 44% was achieved at 42% propane conversion. Characterisation of the Fe/U catalysts by powder X-ray diffraction (XRD) and laser Raman spectroscopy identified a UO_3 phase with no evidence for an iron containing phase. Temperature-programmed reduction studies identified further reduction Features which cannot be attributed to UO_3 alone. The characterisation data can be interpreted in terms of a highly dispersed iron oxide phase supported on UO_3 and it is this combination which gives rise to the selective propane oxidation activity.

Keywords: Selective oxidation; Propane; Mixed oxide catalysts; Formaldehyde

1. Introduction

Formaldehyde is an important bulk chemical, it is manufactured world-wide on a large scale and is widely used as an intermediate for the manufacture of a variety of products. At present, the majority of formaldehyde is manufactured by a three-stage process via methanol. Methanol manufacture is a well established technology, involving an initial steam reforming stage, usually methane, to produce synthesis gas. The second stage is methanol synthesis using a $Cu/ZnO/Al_2O_3$ catalyst. In the final stage, formaldehyde is produced from methanol by selective oxidation using either a ferric molybdate or silver based catalyst. Although methanol, and ultimately formaldehyde, are produced in high yields using this approach it is nevertheless an energy intensive process, especially the highly endothermic steam reforming step. It is against this background, that investigation of a simplified more direct route to formaldehyde could be beneficial. In particular, there is also a drive to establish processes for efficient utilisation of low value abundant short chain saturated hydrocarbons. In particular, there is great incentive and it is now a major research aim to utilise directly such hydrocarbons to produce commercially more valuable oxygenated compounds. These concerns have been addressed and in this paper a heterogeneous catalytic route for the direct selective oxidation of propane to formaldehyde is presented.

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Catalysts for the singles step transformation have been investigated, in particular dual component oxides of uranium and iron have demonstrated promising activity.

2. Experimental

2.1. Catalyst preparation

The Fe/U (atomic ratio Fe/U = 0.5/3 and 1/3) were prepared using a co-precipitation method. One gram of $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich, >99.99%) was dissolved in 10 ml of de-ionised water and the solution was added to a solution of $UO_2(NO_3){\cdot}2H_2O$ (Strem Chemical, Inc., >99%), prepared by dissolving 5.85 g of the nitrate in 16 ml of de-ionised water. The two solutions were mixed and the excess water evaporated overnight at 150 °C. The solid obtained was calcined at 450 °C for 3 h in static air to produce the catalyst.

The U/Sb catalysts were synthesised using methods described in the literature [1,2]. It was prepared by reacting $UO_2(NO_3){\cdot}2H_2O$ (8.8 g, Strem Chemical, Inc., >99%) with Sb_2O_3 (8.7 g, Aldrich, 99.99%) dissolved in 70% nitric acid and refluxed for 3 h. After cooling, the solution was adjusted to pH 8 by adding 28% aqueous NH_4OH solution. The product was filtered, washed with de-ionised water and dried at 120 °C for 24 h to produce the precursor of the catalyst. The precursor was then calcined at 425 °C for 16 h and the temperature increased to 925 °C for a further 16 h. The catalysts produced by this procedure had an excess of antinomy and by X-ray diffraction (XRD) this was observed in the form of the oxide. The contaminating Sb_2O_3 was removed by refluxing the catalyst with HCl at 100 °C to produce the final catalyst.

The U/Mo catalysts were synthesised using a method described in the literature [3]. A solution was prepared by dissolving 5.4 g $UO_2(CH_3COO)_2{\cdot}2H_2O$ (BDH AnalaR grade) in 19.6 ml of de-ionised water. The solution was added to another solution of 0.4 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Aldrich) dissolved in 20 ml of hot de-ionised water. The excess water was evaporated and the resulting solid calcined at 550 °C in flowing air for 4 h.

The Fe/Mo catalyst was prepared by a precipitation method [4]. Two gram $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich, >99.99%) was dissolved in 15 ml of de-ionised water and added to a solution of 1.3 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Aldrich) dissolved in 10.5 ml of de-ionised water. The resulting precipitate was dried and calcined at 400 °C in static air for 6 h and subsequently at 750 °C for a further 24 h in static air.

2.2. Catalyst characterisation

Catalyst surface areas were measured by the BET method, using a Micromeritics ASAP 2010 apparatus. Prior to surface area determination catalysts were degassed at 75 °C for 6 h. Measurements were carried out at 77 K using multiple point high purity nitrogen adsorption.

Powder XRD was performed using an Enraf Nonius FR590 diffractometer with a Cu source operated at 30 mA and 40 kV. A Ge(1 1 1) monochromator was used to select Cu $K\alpha_1$ X-rays. The powdered samples were compressed into an aluminium sample holder, which was rotated during data collection to compensate for any ordering of crystallite orientation which may occur during sample packing. Data were calibrated against a silicon standard and phase identification was performed by matching the experimental pattern against standard entries in the JCPDS powder diffraction file.

Raman spectra were recorded using a Renishaw system 1000 dispersive laser Raman microscope. An argon ion laser (514.5 nm) was used as excitation source and was typically operated at a power of 20 mW. Samples were used in powdered form and were placed on a microscope slide and the laser focused onto the sample to produce a spot size of ca. 3 μm in diameter. Spectra were collected using a back scattering geometry with a 180° angle between the illuminating and the collected light.

Temperature-programmed reduction was carried out in a TPR/TPO/TPD Micromeritics Autochem 2910 equipped with a TCD detector. The reducing gas used in all experiments was 10% H_2 in Ar, with a flow rate of 50 ml min^{-1}. The temperature range explored was from room temperature to 1000 °C. The heating rate was maintained at 10 °C min^{-1} for all samples whilst the sample mass was varied depending on the sample under study. Details of specific conditions are given with the TPR profiles and sample masses were in the range 25–200 mg.

2.3. Catalyst testing

Catalyst performance was established using a conventional microreactor. Gas rates were regulated using electronic thermal mass flow controllers, *P* ratio of C_3/oxygen/helium 1/1/10 was used with a total flow rate equivalent to 24 ml min^{-1}. The catalyst was placed in a Pyrex reactor and was supported upon a quartz frit. Studies were carried out using a GHSV of 9600 h^{-1}. Product and reactant analysis was performed on-line using a GC equipped with Porapak P and molecular sieve 13X columns using a thermal conductivity and flame ionisation detector.

3. Results

The results of propane oxidation are shown in Table 1. The Fe/Mo, U/Mo and U/Sb mixed oxide catalysts were inactive, showing no propane conversion below 500 °C. The Fe/U catalysts showed surprising behaviour for propane oxidation. Both of the Fe/U catalysts exhibited appreciable selectivity towards formaldehyde, the Fe/U (0.5:3) catalyst was initially active at 300 °C. Increasing the temperature resulted in an increase of propane conversion and at 400 °C, 54% selectivity towards formaldehyde was observed. The selectivity to formaldehyde decreased slightly as a reaction temperature was increased, however, selectivity remained surprisingly high even at 500 °C when propane conversion was 40%. A similar trend was also observed with the Fe/U (1/3) catalyst, although the trend was similar the activity was significantly greater, operating at approximately 100 °C lower. With both catalysts, the remaining product was predominantly CO_2, with a low selectivity towards CO. The propane conversions was limited by the concentration of oxygen in the reaction feed. Blank reactions demonstrated that propane conversion below 500 °C was zero.

The range of catalysts have also been tested for propene oxidation under the same conditions (Table 2). With the exception of the mixed Fe/U and U/Sb catalysts the other mixed oxide systems only demonstrated deep oxidation under the reaction conditions in our study. The 1/3 Fe/U catalyst demonstrated similar behaviour for propene oxidation that gas also been observed during propane oxidation. Using propene the conversion at 300 °C was 27% opposed to 5% with propane, indicating the relative ease for propene activation compared with propane. The product selectivities from propane and propene are also broadly similar, selectivity comparison at a constant conversion of ca. 25% showed that propane oxidation was 48% selective towards formaldehyde whilst propene had a selectivity of 46%. The selectivity towards CO was slightly higher from propene oxidation when compared with propane. The U/Sb catalysts showed appreciable selectivity towards acrolein with the balance of products CO_2 and some CO at higher temperatures. The activity of U/Sb for propene oxidation

Table 1
Activity and selectivity of mixed oxide catalysts for propane oxidation (propane/oxygen/helium = 1/1/10, GHSV = 9600 h^{-1})

Catalyst	Temperature (°C)	Conversion (%)	Selectivity		
			%FM	%CO	%CO_2
Blank reaction	200	0	0	0	0
	300	0	0	0	0
	400	0	0	0	0
	500	0	0	0	0
Fe/U 0.5:3	200	0	0	0	0
	300	tr	0	0	100
	350	0.8	0	0	100
	400	6	54	0	46
	450	23	44	6	50
	475	37	43	1	56
	500	40	41	0	59
Fe/U 1:3	200	0	0	0	0
	300	5	55	0	45
	325	7	38	3	59
	350	13	40	3	57
	375	23	48	2	50
	400	35	43	7	49
	425	42	44	1	55
U/Sb	300	0	0	0	0
	325	0	0	0	0
	350	0	0	0	0
	375	0	0	0	0
	400	0	0	0	0
U/Mo	300	0	0	0	0
	325	0	0	0	0
	350	0	0	0	0
	400	0	0	0	0
Fe/Mo	300	0	0	0	0
	350	0	0	0	0
	400	0	0	0	0
	450	0	0	0	0

Table 2
Activity and selectivity of mixed oxide catalysts for propene oxidation (propene/oxygen/helium = 1/1/10, GHSV = 9600 h^{-1})

Catalyst	Temperature (°C)	Conversion (%)	Selectivity			
			%FM	%AC	%CO	$\%CO_2$
Blank reaction	200	0	0	0	0	0
	300	0	0	0	0	0
	400	0	0	0	0	0
	500	0	0	0	0	0
Fe/U 1:3	200	0	0	0	0	0
	300	27	46	0	12	42
	325	34	37	0	9	54
U/Sb	300	0	0	0	0	0
	325	0.6	0	100	0	0
	350	1.8	0	53	0	47
	375	1.9	0	61	0	39
	400	3.7	0	42	0	59
	450	12	0	35	17	47
U/Mo	300	0	0	0	0	0
	325	9	0	0	0	100
	350	11	0	0	0	100

FM = formaldehyde, AC = acrolein.

is in clear contrast to the inactivity for propane oxidation. The selective oxidation of propene to acrolein has been studied extensively and the results obtained in this study are consistent with the activity expected from previous work [2]. Over the same temperature range, the conversion in the empty reactor tube was again negligible using the same gas flow rates.

The BET surface area of the catalysts and the phases identified from powder XRD studies are summarised in Table 3. The surface area of catalyst systems were diverse, surface area <1 $m^2 g^{-1}$ were determined for the U/Mo, and Fe/Mo catalysts. The surface areas of U/Sb and Fe/U 0.5/3 were significantly greater, at 25 and 18 $m^2 g^{-1}$, respectively. The highest surface area was 116 $m^2 g^{-1}$ for Fe/U 1/3.

Table 3
Summary of catalysts BET surface areas and phases identified from powder X-ray diffraction studies

Catalyst	Atomic ratio	SA_{BET} ($m^2 g^{-1}$)	Phases identified
U/Mo	1/2	0.7	$UO_2(MoO_4)_2$
Fe/Mo	2/3	0.9	$Fe_2(MoO_4)_3$
U/Sb	1/3	25	USb_3O_{10}
Fe/U	0.5/3	18	UO_3
	1/3	116	UO_3

Powder XRD showed the presence of bulk mixed oxide phases for the Fe/Mo, U/Mo, and U/Sb catalysts, no other phases were identified by XRD. In the first two systems, molybdate phases were identified, these were iron molybdate ($Fe_2(MoO_4)_3$) and uranyl molybdate (UO_2MoO_4), respectively. In the case of the U/Sb catalyst, the USb_3O_{10} phase was observed and there was no evidence for excess Sb_2O_3 which was identified during preparation. On the contrary, the U/Fe catalyst only showed diffraction from a UO_3 phase with no evidence for an iron containing diffracting phase.

Laser Raman spectroscopy characterisation has been carried out on all of the mixed oxide catalysts. However, considering the interesting a catalytic results from the Fe/U catalyst only the Raman spectra of this catalyst will be presented. The Fe/U mixed oxide catalyst showed relatively few active bands which were also relatively broad (Fig. 1). The most intense band in the U/Fe spectrum was at 762 cm^{-1} with much less intense broad features at 821, 477 and 322 cm^{-1}.

The temperature-programmed reduction profile of the 1/3 Fe/U catalyst was measured using 10% H_2 in Ar at a ramp rate of 10 °C min^{-1} (Fig. 2). The TPR profile of the Fe/U mixed oxide revealed important information, regarding the structure of the catalyst. Two broad reduction features were observed, the most

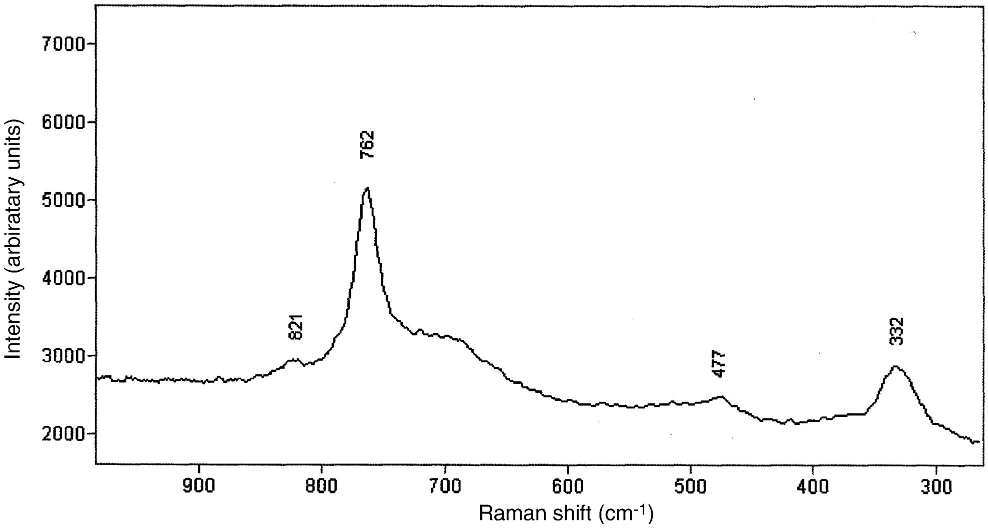

Fig. 1. Micro-laser Raman spectrum of the Fe/U oxide catalyst.

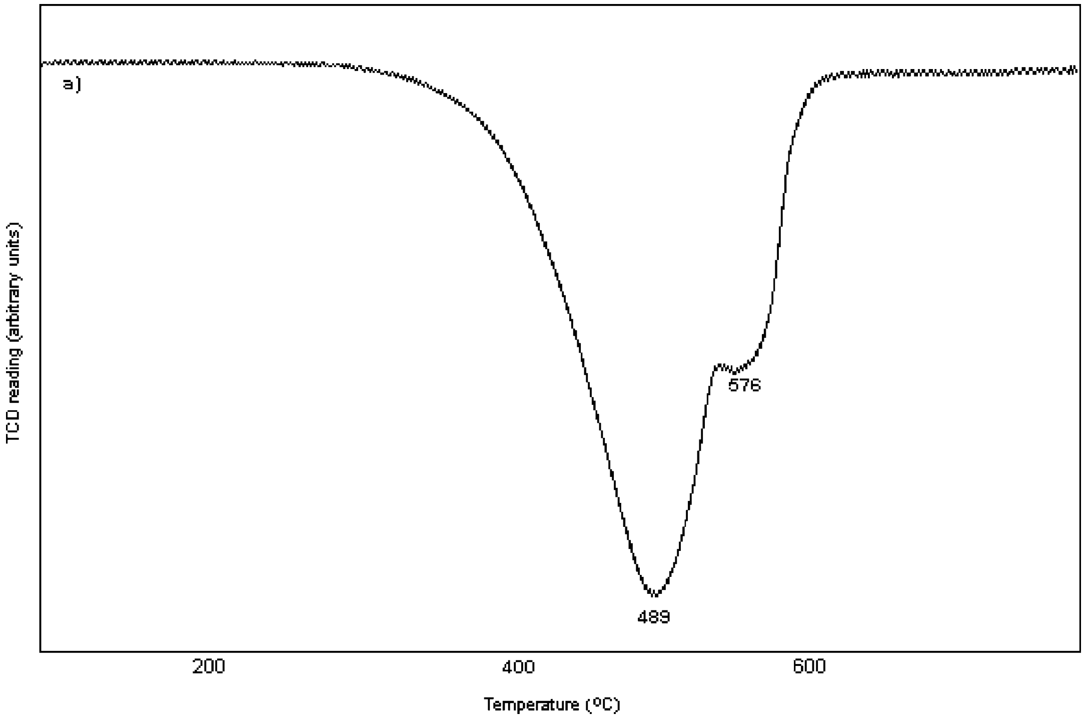

Fig. 2. Temperature-programmed reduction profile of the 1/3 Fe/U mixed oxide catalyst: 70 mg catalyst, 10 °C min^{-1} heating rate, 10% H_2/Ar.

intense feature had a maximum at 489 °C with a second less intense feature at 576 °C.

4. Discussion

The oxidation of propene and propane in the empty reactor showed negligible conversion below 500 °C, demonstrating that the influence of homogeneous gas phase reactions were minimal. To the mixed oxide catalysts U/Sb, Fe/Mo and U/Mo where all inactive for propane oxidation. Clearly, these catalysts do not have the surface active sites required to activate the propane molecule for oxidation under our reaction conditions. The uranium and iron molybdate catalysts were also inactive for propene oxidation. The U/Sb catalyst that consisted of the single phase USb_3O_{10} showed the activity expected [1,2], by producing appreciable selectivity towards acrolein. However, the most significant reactivity in this study was demonstrated by the Fe/U catalyst, both with the Fe/U ratios of 0.5/3 and 1/3, which oxidised propene and propane giving high selectivity towards formaldehyde at high levels of conversion. The catalyst with the higher Fe/U ratio was more active (Fig. 3) and it also had a significantly higher surface area than the 0.5/3 catalyst. Comparison of the propane oxidation rate at 400 °C normalised for surface area shows that the rates are similar for the F e/U 0.5/3 and 1/3 catalysts. The normalised rate for 0.5/2 Fe/U is $(9.2\pm0.9)\times10^{-9}$ and $(8.4\pm0.8)\times10^{-9}$ mol s^{-1} m^{-2} for the 1/3 Fe/U oxide catalyst. It is therefore clear that the catalyst surface has a vital role in selective propane oxidation to formaldehyde. The selectivity towards formaldehyde remains relatively high across the range of temperature and conversion and this suggests that formaldehyde is also particularly stable over the catalysts active for formaldehyde production.

Powder XRD studies identified a bulk UO_3 phase, with no evidence for an iron containing phase. The relatively simple Raman data for the Fe/U catalyst are summarised in Table 4. The main band in the spectra at 762 cm^{-1} was due to U–O vibration, which along with the weaker band at 822 cm^{-1} are characteristic of the simple Raman spectra of UO_3 (Table 3). Both bands are slightly shifted to lower wave number when compared to UO_3, and this is probably due to a chemical interaction between iron and uranium components. There is no strong evidence for the presence of a discrete iron oxide phase, although the low

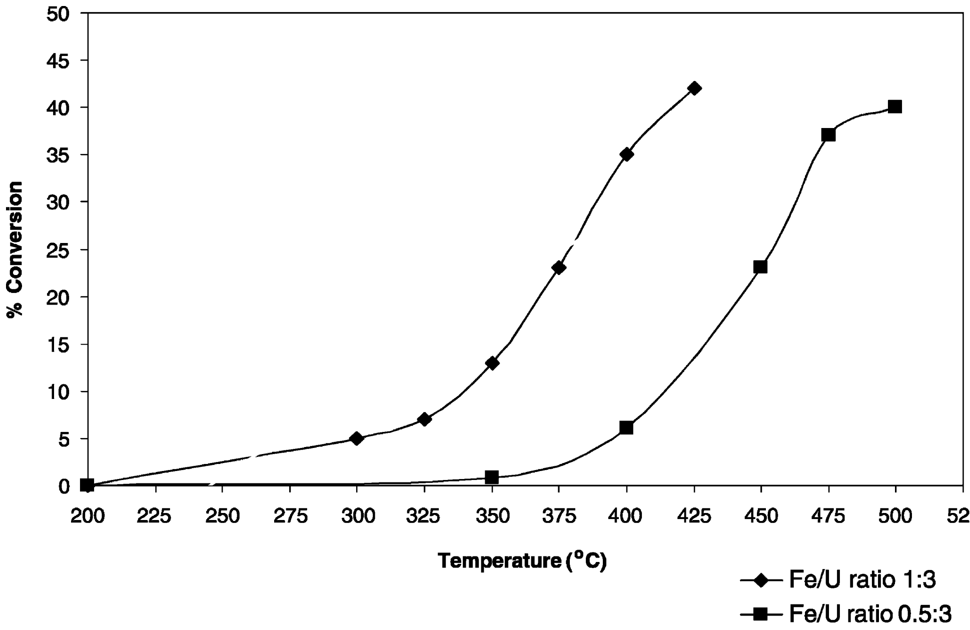

Fig. 3. Propane conversion over the 0.5/3 and 1/3 Fe/U mixed oxide catalysts.

Table 4
Summary and assignment of Fe/U oxide catalyst Raman spectroscopy

Fe/U oxide	Band assignment
	Asymmetric stretching vibration Fe–O–Fe
332 (M)	Asymmetric stretching vibration Fe–O–Fe
477 (W)	U–O stretching vibration
762 (S)	U–O stretching vibration
821 (W)	U–O stretching vibration

All frequencies are measured in cm^{-1}. VS = very strong, S = strong, M = medium, W = weak.

frequency Raman feature at 322 cm^{-1} is centred in the region of the most intense features in the spectra of Fe_2O_3, and bands from UO_3 are not generally observed in this region [5]. The presence of iron oxide is a tentative suggestion based on the Raman studies and the absence of any X-ray diffracting domains indicates that the iron oxide is either amorphous or has a crystallite size less than ca. 30 Å.

Characterisation of the Fe/U oxide catalyst by XRD and laser micro-Raman spectroscopy concluded that UO_3 was the only identifiable phase, with no obvious evidence for the formation of a mixed oxide or iron oxide phase. The absence of a reduction peak in the Fe/U catalyst profile in the region 320–350 °C suggests that iron was not present as bulk Fe_2O_3. However, the peaks observed in the TPR profile at 489 °C and this can be assigned to the reduction of Fe_3O_4 which was observed at 655 °C for the oxide alone [3]. The observation of a second reduction feature at 576 °C is assigned to the reduction of UO_3. The reduction of UO_3 alone under identical experimental conditions is typically ca. 690 °C. The definite assignment of the reductions features cannot be certain, and it is possible that the order may be reversed. Studies of iron oxide reduction have indicated that the Fe_3O_4 was reduced at temperatures around 700 °C. Under the conditions used in our experiments, we have observed this reduction at a lower temperature. The temperature for iron oxide reduction is influenced by the particle size, as reducing the size results in a lower reduction temperature. It is possible that the co-precipitation procedure used to prepare the Fe/U catalysts resulted in an iron oxide phase with a highly dispersed small crystallite size. This would not only be a contributing factor the lower reduction temperature may also explain why the iron oxide phase was amorphous to X-rays and the increased indeterminate scattering capacity of small crystallites may also effect the Raman spectroscopy. However, in the case of the uranium and iron components, the mixture of Fe_3O_4 and UO_3 facilitates the reduction of both oxides.

It is interesting to consider possible mechanisms for the formation of formaldehyde from propane and propene. The allylic C–H bond in propene is weaker (361 $kJ\,mol^{-1}$) than the C–H bond in propane (methylene 420 $kJ\,mol^{-1}$, methyl 413 $kJ\,mol^{-1}$), therefore, it can be concluded that propane is more difficult to activate than propene. It is reasonable to assume that propene and propane activation occurs by hydrogen abstraction from the allylic and from the methylene position, respectively. In addition, the bonding between the carbon skeleton of the reactant molecule and the catalyst surface is an important parameter after the first hydrogen abstraction. In the case of propene, allylic species will be formed directly after the first hydrogen abstraction. On the other hand, propane requires the abstraction of three hydrogens to form the allylic species. Interestingly, although light off temperatures for the Fe/U catalytic system (1/3 Fe/U) are equivalent for propene and propane oxidation (300 °C), the conversion for propene is much higher than for propane. This suggests that the abstraction of the third hydrogen atom to form the allylic intermediate could have an important influence on controlling the rate of reaction.

The Fe/U catalysts showed a very similar product distribution, which suggests that a similar mechanism may be operating in both cases. The lower conversion of propane compared to propene would be expected if propane was activated through an allylic surface intermediate in the manner described above.

In previous studies, propene is an intermediate from selective oxidation of propane to acrolein [6] and acrylic acid [7]. In this study, the fact that no propene was detected during propane oxidation indicates that once desorbed it is either reacted rapidly to form formaldehyde and carbon oxides or more likely it remains adsorbed on the catalyst surface undergoing further reaction. The reaction pathway leading to the production of formaldehyde is unclear. However, there are two studies in the literature that are interesting in light of this work. Teng and Kobayashi have reported the formation of formaldehyde during the selective oxidation of propane [8]. The catalyst used was silica impregnated with iron nitrate solution and calcined to produce a highly dispersed Fe/SiO_2 catalyst. At 450 °C with a propane/oxygen/nitrogen ratio of 5/4/16 and GHSV = $1050\,h^{-1}$, a selectivity towards formaldehyde of 18% was achieved at 2% conversion. It is the highly dispersed Fe^{3+} species that are considered important for the selective oxidation behaviour. Another notable study details the use of a urania-titania catalyst for the production of formaldehyde from oxidation of *iso*-butene [9]. It is considered that the modification of the redox behaviour of uranium oxide once sported on titania, gives rise to the selective oxidation activity. In the present work, the Fe/U mixed oxide catalyst has a highly dispersed iron phase in combination with UO_3 that has modified redox behaviour when compared with UO_3 alone. It is therefore possible that the combination of these elements in a single catalyst gives rise to the efficacy of the Fe/U oxide catalyst for the selective oxidation of propane and propene to formaldehyde.

5. Conclusions

A series of mixed metal oxide catalysts have been prepared and tested for the oxidation of propane and propene. Under the reaction conditions employed in these studies, Fe/Mo and U/Mo mixed oxide catalysts showing iron and uranium molybdate phases were inactive for propane and propene oxidation. A mixed U/Sb catalyst, with a USb_3O_{10} structure, was also inactive for propane oxidation, but demonstrated the expected selective oxidation activity to form acrolein from propene. The Fe/U catalysts prepared with 0.5/3 and 1/3 ratios were active for the selective oxidation of propane and propene to formaldehyde. Characterisation of the Fe/U catalysts by powder XRD and laser Raman spectroscopy identified a UO_3 phase with no evidence for an iron containing phase. Temperature-programmed reduction studies identified further reduction Features which cannot be attributed to UO_3 alone. The characterisation data can be interpreted in terms of a highly dispersed iron oxide phase supported on UO_3 and it is this combination which gives rise to the selective propane oxidation activity.

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