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The oxidative dehydrogenation of propane using gallium–molybdenum oxide-based catalysts

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Abstract

Catalysts based on a physical mixture of Ga_2O_3 and MoO_3 have been prepared and evaluated for propane partial oxidation to propene. The Ga_2O_3/MoO_3 catalysts produced appreciable propene yields and it has been demonstrated that the catalyst synergistically combined the alkane activation properties of Ga_2O_3 with the selective oxidation function of MoO_3. Studies have probed the influence of varying the Ga/Mo ratio. Catalysts with a 1/1 and 1/3 ratio showed similar catalytic activity, whilst reducing the ratio to 1/10 significantly reduced the propene yield. Comparison of the 1/1 Ga_2O_3/MoO_3 catalyst with a 6 wt.% V_2O_5/TiO_2 catalyst, which is known to be active for selective propane oxidation, showed that the propene yields were greater for Ga_2O_3/MoO_3.

Keywords: Propane; Propene; Partial oxidation; Oxidative dehydrogenation; Gallium oxide; Molybdenum oxide

1. Introduction

The catalytic partial oxidation of propene is commercially important and oxidation to higher value oxygenates has been a major research aim for many years. Given the increasing industrial demand for propene, for the production of acrolein, acrylic acid acrylonitrile and *iso*-propanol, it has been desirable to develop catalysts capable of producing propene by dehydrogenation of the more abundant alkane. Studies have probed the oxidative dehydrogenation of alkanes as a potential route for alkene production. Unlike non-oxidative dehydrogenation, oxidative propene dehydrogenation is exothermic and avoids the thermodynamic constraints that limit propene yield from non-oxidative dehydrogenation. However, the introduction of an oxidant may also lead to lower than maximum predicted propene yields as deep oxidation to carbon oxides are more thermodynamically favoured.

A number of catalysts have been reported for propane oxidative dehydrogenation, including supported chromium oxide [1], molybdenum containing catalysts [2–4] and more recently, complex multi-component metal oxide catalysts containing both molybdenum and vanadium. These multi-component catalysts, such as V–Mo–Te–Nb mixed oxides [5], are complex, and the formation of the active phase is critical to maximise performance. The most extensively studied catalysts are those based on supported vanadium oxide. The acidic/basic properties of the supported catalysts are found to be a strong determining factor in the catalytic performance, additionally the vanadia loading and its interaction with the support are also important. In general, reports detailing the use of vanadia on amphoteric supports are most common, although basic supports have also been used. It is accepted that the basic supports give more selective catalysts due to the easier desorption of propene from the surface. To date, a number of catalysts supports have been tested and characterised, these include Al_2O_3 [6–8], TiO_2, SiO_2 and MgO [7,8]. In particular, vanadia supported on MgO has demonstrated promising activity and selectivity to propene although there still seems to be general disagreements in the literature about the active site and V–Mg–O phase responsible for the higher selectivity [9–11]. V_2O_5/TiO_2 catalysts have also proved to be successful, demonstrating relatively high activity and a low temperature of activation, which has led to further studies focusing on the addition of various promoters [12,13]. Al-

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though it is often the case that promoted catalysts showed an increase of propane conversion they also showed a simultaneous decrease of propene selectivity.

In previous studies, catalysts based on a mixture of Ga_2O_3 and MoO_3 have been developed for the partial oxidation of methane [14]. The Ga_2O_3/MoO_3 catalyst showed an increased yield of partial oxidation products by combining the alkane activation properties of Ga_2O_3 and the partial oxidation behaviour of MoO_3 in a synergistic manner. It is apparent that similar catalytic properties are also required for the partial oxidation of propane to propene. It is against this background that the current study has been undertaken to probe the efficacy of Ga_2O_3/MoO_3 catalysts for the partial oxidation of propane.

2. Experimental

2.1. Catalyst preparation

Catalysts comprising physical mixtures of Ga_2O_3 (Aldrich 99.9+%) and MoO_3 (Aldrich 99.9+%) were prepared by grinding the oxides (1:1 molar ratio) in a pestle and mortar. The physical mixture was divided, half was calcined at 650 °C for 3 h in static air, whilst the other half was used uncalcined. The catalysts were denoted Ga_2O_3/MoO_3 calcined and Ga_2O_3/MoO_3 uncalcined. The single oxides tested were used as supplied without further treatment. A series of vanadium catalysts with various V_2O_5 loadings were prepared by impregnation of a TiO_2 support (Degussa P25, $50\,m^2\,g^{-1}$) with an aqueous solution of ammonium metavanadate. The resulting paste was dried for 16 h at 120 °C and calcined in static air at 450 °C for 5 h. The V_2O_5 loading was varied from 3 to 10 wt.%. All catalysts were pelleted to a uniform particle size range of 250–600 μm.

2.2. Catalyst characterisation

Catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic Cu Kα1 source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file. Surface areas were determined by multi-point N_2 adsorption at 77 K, and data were treated in accordance with the BET method.

Raman spectra were recorded using a Renishaw system 1000 dispersive laser Raman microscope. An argon ion laser (514.5 nm) was used for excitation, and was typically operated at 20 mW. Samples were investigated in powdered form, they 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.

2.3. Catalyst activity

Catalytic performance was measured at atmospheric pressure in a fixed bed micro-reactor using a quartz reactor tube (i.d. 9 mm). Catalyst activity was determined over the temperature range ca. 200–550 °C with constant propane/oxygen/helium ratio of 2/1/8.5. A constant catalyst volume of 0.25 ml was used with a total flow rate of $40\,ml\,min^{-1}$ giving a gas hourly space velocity of $9600\,h^{-1}$. The products were analysed online with a Varian 3800 chromatograph, using Porapak Q and Molsieve columns, equipped with thermal conductivity and flame ionisation detectors. Propane conversion was calculated on the basis of products detected and in all experiments the carbon balances were 100 ± 2%.

3. Results and discussion

Propane conversion over the Ga_2O_3/MoO_3 catalysts and comparison with Ga_2O_3 and MoO_3 are shown in Fig. 1. The data were obtained at steady state conversion and there was no measurable deactivation for any of the catalysts. The Ga_2O_3 catalyst showed initial propane conversion at 375 °C

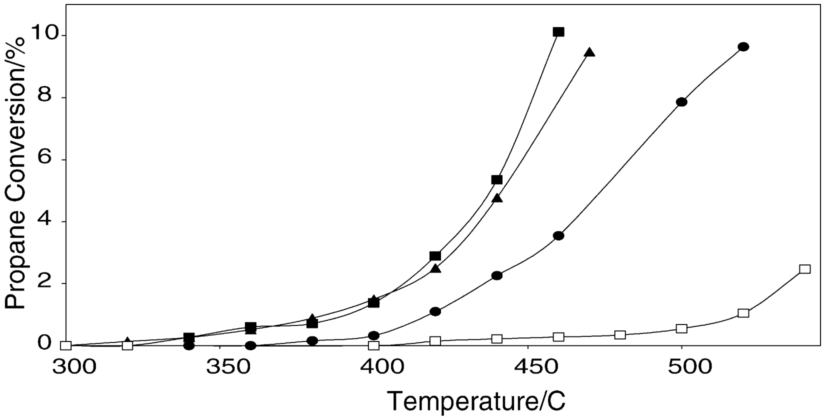

Fig. 1. Propane conversion over the Ga_2O_3/MoO_3 catalysts and comparison with Ga_2O_3 and MoO_3. (▲): Ga_2O_3/MoO_3 calcined; (■): Ga_2O_3/MoO_3 uncalcined; (●): Ga_2O_3; (□): MoO_3.

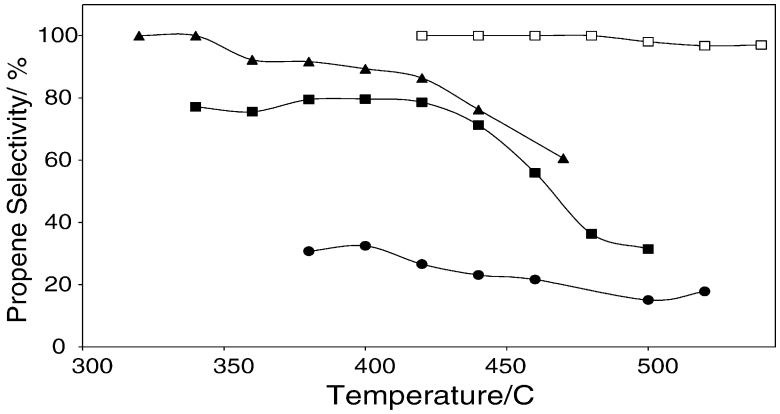

Fig. 2. Selectivity to propene as a function of temperature. (▲): Ga_2O_3/MoO_3 calcined; (■): Ga_2O_3/MoO_3 uncalcined; (●): Ga_2O_3; (□): MoO_3.

increasing to ca. 8% at 500 °C. On the contrary, the rate of propane oxidation over MoO_3 was considerably lower. Initial activity was detected at 425 °C and only increased to ca. 3% at 500 °C. Both of the Ga_2O_3/MoO_3 catalysts showed considerably higher rates of propane oxidation. The profile of propane conversion with temperature was broadly similar for the calcined and uncalcined catalysts. However, above 425 °C the propane conversion over the uncalcined catalyst was marginally greater than the calcined material. No appreciable activity was observed below 550 °C in an empty quartz reactor.

Propene, CO_2 and CO were the only reaction products over the calcined Ga_2O_3/MoO_3, Ga_2O_3 and MoO_3 catalysts. The same products were observed with the uncalcined Ga_2O_3/MoO_3 catalyst, but it also showed <2% selectivity to acrolein above 440 °C. Propene was a major partial oxidation product and the selectivity as a function of temperature is shown in Fig. 2. Propene selectivity was lowest for the Ga_2O_3 catalyst, gradually decreasing from ca. 35% at 375 °C to ca. 20% at 520 °C. MoO_3 was most selective for the partial oxidation of propane to propene. Selectivities in excess of 95% were observed even at 540 °C, but it must be noted that these high selectivities were obtained at low propane conversion. The propene selectivity over the calcined and uncalcined Ga_2O_3/MoO_3 catalysts demonstrated the same trends with temperature. The calcined catalyst showed initially 100% selectivity to propene, this decreased gradually to 61% at 470 °C. The propene selectivity was lower over the uncalcined catalyst across the entire temperature range, but still remained greater than the Ga_2O_3 catalyst.

Studies have been performed replacing either the Ga_2O_3 or MoO_3 components of the catalysts with SiC. The aim of these studies was to probe the effect of possible dilution for the two component catalysts. Representative data for comparison are presented in Table 1. The replacement of the Ga_2O_3 component with SiC suppressed the propane conversion relative to MoO_3 alone. The propane conversion was also significantly lower than with the Ga_2O_3/MoO_3 catalysts. The selectivity to propene was also very similar to MoO_3. Replacement of MoO_3 with SiC showed that propane conversion was increased slightly when compared to Ga_2O_3 alone. This increase was minor, however, the propene selectivity was not affected by the addition of SiC. In conclusion, the effect of diluting the Ga_2O_3 and MoO_3 catalysts did not significantly alter their activity and selectivity. The results from studies using SiC to dilute Ga_2O_3 and MoO_3 showed that the enhanced performance of the Ga_2O_3/MoO_3 catalysts was not a simple consequence of diluting either component.

The per pass yields of propene for the 1/1 Ga_2O_3/MoO_3, Ga_2O_3 and MoO_3 catalysts are shown in Fig. 3. The MoO_3 catalyst gave the lowest propene yields. The propene yields over Ga_2O_3 were higher than MoO_3 and this was due to the higher propane conversion. It must also be noted that considerably higher temperatures where required with the MoO_3 catalyst. The propene yields over both Ga_2O_3/MoO_3 catalysts where markedly similar. Both exhibited a 5.7% per pass yield at 470 °C for the calcined catalyst and, at 460 °C for the uncalcined catalyst.

For comparison with the catalytic data in this study a series of V_2O_5/TiO_2 catalysts were also prepared and tested. The V_2O_5/TiO_2 catalyst system is one of the most widely studied for this reaction and it is generally accepted to be one of the most efficient catalysts. The best performance of the V_2O_5/TiO_2 catalysts was shown with a 6 wt.% V_2O_5 loading. A comparison of propane partial oxidation, at ap-

Table 1
Comparison of catalyst performance and the effect of dilution with SiC

Catalyst	Temperature (°C)	Propane conversion (%)	Propene selectivity (%)
MoO_3/SiC	560	0.3	100
	580	1.0	95
MoO_3	520	1.0	97
Ga_2O_3/SiC	400	0.5	30
	420	1.4	32
Ga_2O_3	420	1.1	28
Ga_2O_3/MoO_3 calcined	380	0.9	92
Ga_2O_3/MoO_3 uncalcined	380	0.7	80

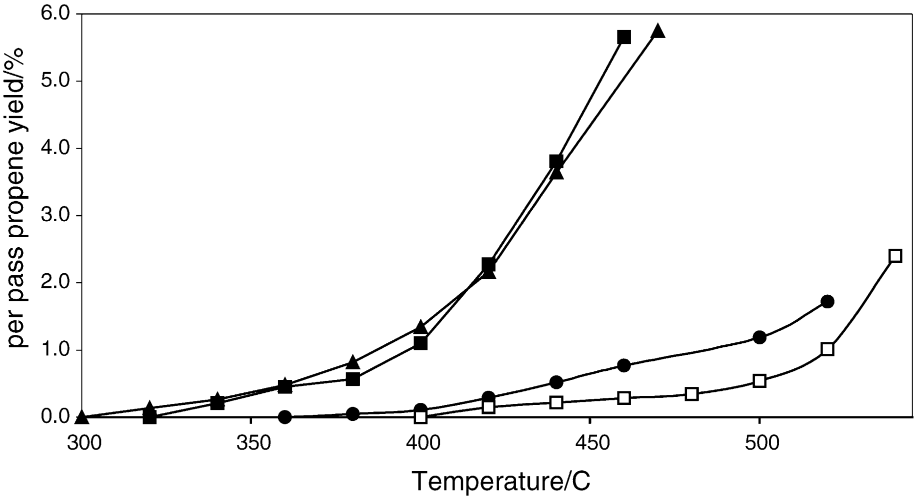

Fig. 3. Per pass yield of propene as a function of temperature. (▲): Ga_2O_3/MoO_3 calcined; (■): Ga_2O_3/MoO_3 uncalcined; (●): Ga_2O_3; (☐): MoO_3.

proximately constant conversion, ca. 10% where possible, is presented in Table 2.

Although the reaction conditions differ, the performance of the 6 wt.% V_2O_5/TiO_2 catalyst was in agreement with the published data in the literature.

The V_2O_5/TiO_2 catalysts were active at lower temperatures than the Ga_2O_3/MoO_3 catalysts, and such a decrease in temperature could be expected to produce higher propene selectivity by reducing over oxidation. However, this was not the case and the propene yield from the 6 wt.% V_2O_5/TiO_2 catalyst was lower than that for the Ga_2O_3/MoO_3 catalysts. Despite the higher temperatures, the propene selectivities and yields for the Ga_2O_3/MoO_3 catalysts were superior. These data clearly demonstrate that the Ga_2O_3/MoO_3 catalysts showed promising activity for propane oxidative dehydrogenation. Furthermore, at this stage no attempt has been made to maximise the performance of the Ga_2O_3/MoO_3 catalysts and it is envisaged that further improvements in catalyst performance are possible.

The influence of changing the Ga_2O_3 to MoO_3 ratio has been investigated and the effect on propane conversion is shown in Fig. 4. The catalyst with Ga/Mo = 1/1 was most active showing the greatest propane conversion across the temperature range. Decreasing the ratio to 1/3 resulted in a marginal decrease of propane conversion, but it remained close to the 1/1 catalyst. Decreasing the Ga_2O_3 content further to 1/10 resulted in a marked decrease of propane conversion when compared to the 1/1 catalyst. However, the rate of propane oxidation remained significantly greater than MoO_3 alone and indicated that even the addition of a relatively low concentration of Ga_2O_3 improved propane conversion.

Selectivity to propene for the Ga_2O_3/MoO_3 catalysts with varying Ga/Mo ratios are presented in Fig. 5. The propene selectivity for Ga_2O_3/MoO_3 catalysts with ratios 1/1 and 1/3 were similar over the investigated temperature range. Propene selectivity decreased from 100% at 340 °C to approximately 40% at 470 °C and above. Decreasing the Ga/Mo ratio to 1/10 resulted in an increased selectivity to propene. This was evident across the whole temperature range, although it must be noted that propane conversion was generally lower over the 1/10 Ga_2O_3/MoO_3 catalyst.

Table 2
Comparison of catalyst performance for propane oxidative dehydrogenation ($C_3H_8/O_2/He = 2/1/8.5$, GHSV = $9600\,h^{-1}$)

Catalyst	BET surface area ($m^2\,g^{-1}$)	Temperature (°C)	Propane conversion (%)	Propene selectivity (%)	Per pass propene yield (%)
Ga_2O_3/MoO_3 calcined	13	470	9.9	62	5.7
Ga_2O_3/MoO_3 uncalcined	13	460	10.1	56	5.7
Ga_2O_3	25	520	9.6	18	1.7
MoO_3	1.5	540	2.5	97	2.4
3 wt.% V_2O_5/TiO_2	50	260	0.9	50	0.5
		300	3.6	32	2.0
		325	10.1	19	1.9
6 wt.% V_2O_5/TiO_2	47	240	0.8	69	0.5
		315	7.5	28	2.0
		340	11.0	22	2.5
10 wt.% V_2O_5/TiO_2	46	240	1.2	65	0.7
		290	8.7	3	0.2

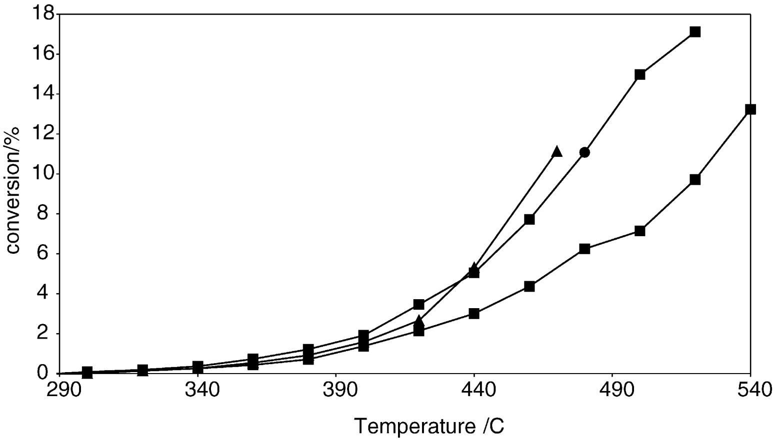

Fig. 4. The influence of Ga_2O_3 to MoO_3 ratio for propane conversion over dual component $Ga_2O_3MoO_3$ catalysts. (▲): 1/1 Ga_2O_3/MoO_3 calcined; (●): 1/3 Ga_2O_3/MoO_3 calcined; (■): 1/10 Ga_2O_3/MoO_3 calcined.

Catalyst surface areas determined by the BET method are summarised in Table 2. The MoO_3 surface area was low whilst Ga_2O_3 was considerably greater at $25\,m^2\,g^{-1}$. The surface areas for the calcined and uncalcined Ga_2O_3/MoO_3 catalysts were $13\,m^2\,g^{-1}$, the expected value for a 1:1 physical mixture. It was also apparent that the surface area was not decreased by calcination.

The catalysts were characterised using powder X-ray diffraction and laser Raman spectroscopy. The powder X-ray diffraction patterns for MoO_3 and the 1/1 Ga_2O_3/MoO_3 catalysts are shown in Fig. 6. The powder pattern from Ga_2O_3 showed that diffraction peaks were broad and relatively low in intensity demonstrating that the structure was relatively disordered. On the other hand, diffraction data from MoO_3 showed that the phase was highly crystalline. The Ga_2O_3/MoO_3 catalysts showed largely diffraction peaks from MoO_3. Careful inspection of the diffraction data revealed that diffraction from Ga_2O_3 was observed, but due to the low intensity of the peaks they were barely discernable. This is not surprising considering the differences of diffraction intensity between the diffraction patterns from MoO_3 and Ga_2O_3. However, it is important to note that no new mixed Ga/Mo phases were produced, neither was there any recordable distortion of the MoO_3 unit cell. Furthermore, after use there were no significant changes to the powder XRD patterns. An additional diffraction peak at ca. 22° was observed in the uncalcined 1/1 Ga_2O_3/MoO_3 catalyst. The peak was attributed to the presence of GaO(OH) and it is interesting that this catalyst alone also demonstrated low selectivity to acrolein.

It was evident that the MoO_3 diffraction intensities from the Ga_2O_3/MoO_3 catalysts were altered when compared to the MoO_3 starting material. These differences were not observed between the Ga_2O_3/MoO_3 catalysts and they are not due to modification of the MoO_3 during calcination. Therefore, it is more likely that the grinding process effects the change in morphology during the catalyst preparation.

The Raman spectra for representative catalysts are presented in Fig. 7. It was not possible to obtain Raman data

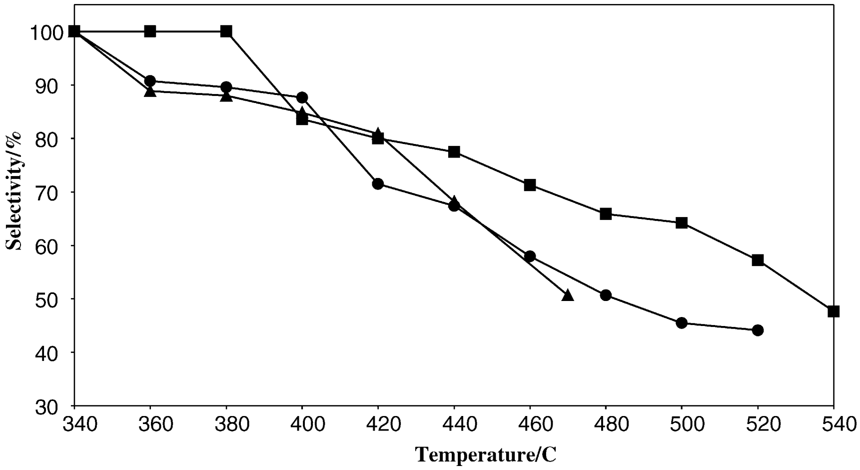

Fig. 5. Selectivity to propene as a function of temperature over Ga_2O_3/MoO_3 catalyst with varying Ga/Mo ratio. (▲): 1/1 Ga_2O_3/MoO_3 calcined; (●): 1/3 Ga_2O_3/MoO_3 calcined; (■): 1/10 Ga_2O_3/MoO_3 calcined.

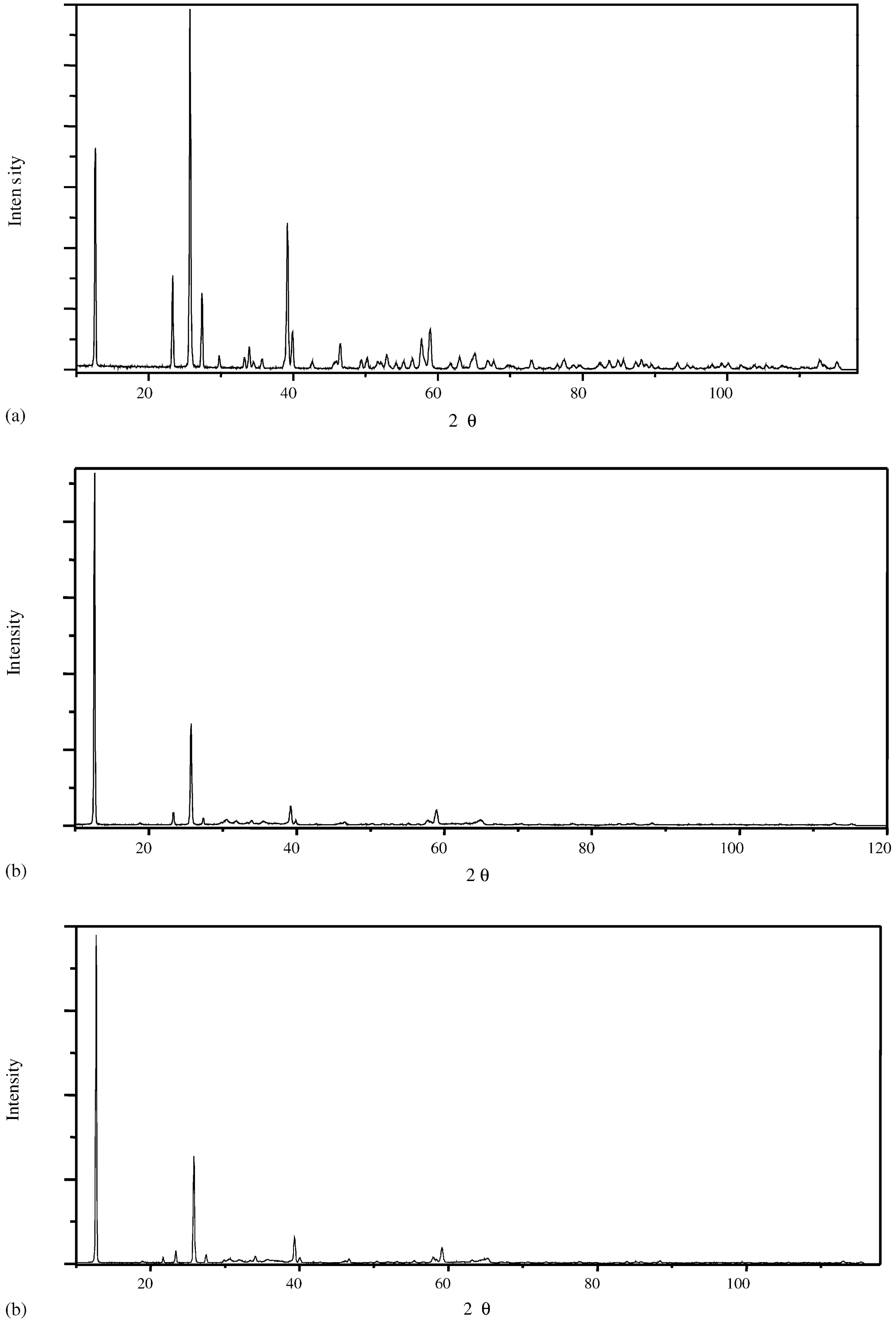

Fig. 6. Comparison of powder X-ray diffraction patterns for MoO_3 and Ga_2O_3/MoO_3 catalysts: (a) MoO_3; (b) Ga_2O_3/MoO_3 calcined; (c) Ga_2O_3/MoO_3 uncalcined.

for Ga_2O_3 as no structure was observed in the spectra. The Raman data for MoO_3 and the Ga_2O_3/MoO_3 catalysts confirms the conclusions obtained from the powder X-ray diffraction data. The Raman spectra for MoO_3 was the same as both of the Ga_2O_3/MoO_3 catalysts, reiterating the conclusion that MoO_3 is not significantly altered on production of the two component catalysts. The characterisation studies indicate that the Ga_2O_3/MoO_3 catalysts were comprised from a mixture of Ga_2O_3 and MoO_3 and there was no evidence for the formation of any new mixed phases. It was

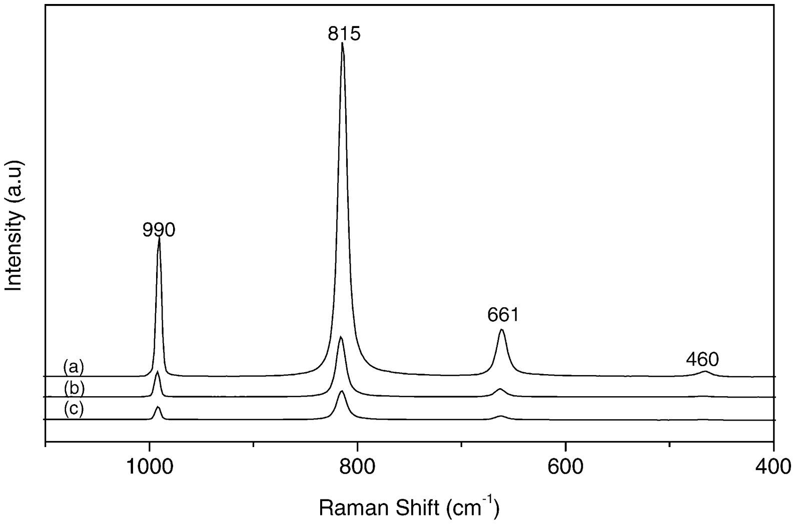

Fig. 7. Comparison of micro-laser Raman spectra for MoO_3 and Ga_2O_3/MoO_3 catalysts: (a) MoO_3; (b) Ga_2O_3/MoO_3 calcined; (c) Ga_2O_3/MoO_3 uncalcined.

also apparent that calcined and uncalcined catalysts were not significantly different.

The Ga_2O_3/MoO_3 catalysts produced a propene yield comparable with known active propane oxidative dehydrogenation catalysts. It is therefore interesting to consider the origin of this activity. In earlier studies investigating CH_4/D_2 exchange it has been shown that the rate of reaction for Ga_2O_3 was at least two orders of magnitude greater than any other metal oxide [15]. The exchange reaction is used as a probe for C–H bond activation and the data from the earlier study demonstrate that Ga_2O_3 is a very effective catalyst for alkane activation. It is also noteworthy that Ga_2O_3 is used in combination with H-ZSM5 for the Cyclar process to convert propane to aromatics. In the Cyclar process, Ga_2O_3 is implicated in alkane activation through a dehydrogenation step [16].

Comparison of the propane oxidation over Ga_2O_3 and MoO_3 showed that the conversion over Ga_2O_3 was considerably higher than that for MoO_3. This is consistent with the ability of Ga_2O_3 to activate alkanes. On the contrary MoO_3 alone was very selective for propane oxidative dehydrogenation to propene. The combination of the oxides into the Ga_2O_3/MoO_3 catalyst combines the beneficial properties of increased oxidation rate of Ga_2O_3 with the selective oxidation function of MoO_3 in a beneficial manner. The data from catalysts with varying Ga/Mo emphasize the importance of the synergy between Ga_2O_3 and MoO_3. As the Ga/Mo ratio was decreased from 1/3 to 1/10 the behaviour of the dual component catalyst tended towards the behaviour exhibited by MoO_3. These data reiterate that the Ga_2O_3 component is important for increasing the rate of propane conversion, whilst the MoO_3 imparts selectivity to propene.

Furthermore, the combination of the two oxides demonstrated a synergistic effect to produce a marked increase in propene yield. The Ga_2O_3/MoO_3 catalyst has been used successfully for methane partial oxidation to methanol [17]. It is interesting that the addition of Ga_2O_3 to MoO_3 resulted in an increased methanol yield by promoting methane conversion, whilst maintaining the higher methanol selectivity of MoO_3. The same type of synergy was observed for selective propane oxidation in the present study and it is apparent that both reactions have similarities, as the alkanes must be activated before undergoing partial oxidation. The characterisation data indicates that the Ga_2O_3/MoO_3 catalysts were comprised from a physical mixture of Ga_2O_3 and MoO_3. This being the case the synergy developed between the two oxides is associated with the boundary where the oxides are in contact with each other. This type of contact synergy is known for Ga_2O_3 in other reactions [18], and it appears that the effect is also important for propane partial oxidation.

4. Conclusions

Catalysts based on a physical mixture of Ga_2O_3 and MoO_3 have been prepared and evaluated for propane dehydrogenation by partial oxidation. Characterisation studies indicated that the catalyst was comprised of a mixture of the component Ga_2O_3 and MoO_3 oxides. The Ga_2O_3/MoO_3 catalyst synergistically combined the alkane activation properties of Ga_2O_3 with the selective oxidation function of MoO_3. The yield of propene of the non-optimised Ga_2O_3/MoO_3 catalyst was comparable with a V_2O_5/TiO_2 catalyst, which is known to show high activity. Reducing the Ga/Mo ratio from 1/1 resulted in a slight decrease of propene yield whilst reducing the ratio to 1/10 resulted in a significantly reduced yield.

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