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The oxidative dehydrogenation of propane using gallium–molybdenum based catalysts

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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 demonstrated propene yields greater than a 6 wt% V_2O_5/TiO_2 catalyst, which is known to be active for the reaction. The higher yield of propene was achieved by the alkane activation properties of Ga_2O_3 and the selective oxidation function of MoO_3 combining in a synergistic manner.

KEY WORDS: propane; propene; partial oxidation; gallium oxide; molybdenum oxide.

1. Introduction

The catalytic partial oxidation of propene is commercially important and oxidation to higher value oxygenates have 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 reactions, 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. Catalysts based on supported vanadium oxide are the most extensively studied. V_2O_5/TiO_2 catalysts have proved to be some of the most successful, demonstrating appreciable activity and selectivity for propane partial oxidation to propene [1,2]. In general, reports detailing the use of vanadia on amphoteric supports are most common although basic supports have also been used. In particular vanadia supported on MgO has demonstrated promising activity and selectivity to propene [3]. Molybdenum containing catalysts have also shown promising performance for propane partial oxidation [4]. Most recently complex multi-component metal oxide catalysts containing both molybdenum and vanadium have been developed. 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.

Previously, catalysts based on a mixture of Ga_2O_3 and MoO_3 have been developed for the partial oxidation of methane [6]. 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 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

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.

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Catalytic performance was measured at atmospheric pressure in a fixed bed micro reactor using a quartz reactor tube (ID 9 mm). Catalyst activity was determined over the temperature range 200–540 °C with a 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 catalyst temperature was monitored by a thermocouple placed in the catalyst bed. 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 within 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 figure 1. The Ga_2O_3 catalyst showed initial propane conversion at 375 °C increasing to ca. 10% 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 low selectivity (<2%) to acrolein. Propene was a major partial oxidation product and the selectivity as a function of temperature is shown in figure 2. Propene selectivity was lowest for the Ga_2O_3 catalyst, gradually decreasing from ca. 35% at 375 °C two 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 $Ga_2O_3MoO_3$ 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. The activity and selectivity of the catalysts remained stable for the duration of the test period, which lasted approximately 10 h. Studies have also used catalysts diluted with SiC and similar results were obtained with and without dilution. The per pass yields of propene for the catalysts investigated in this study are shown in figure 3. The MoO_3 catalyst showed the lowest propene yields. The propene yields over Ga_2O_3 were higher than MoO_3 and this was a 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 yields at 470 °C for the calcined catalyst and, at 460 °C for the uncalcined catalyst.

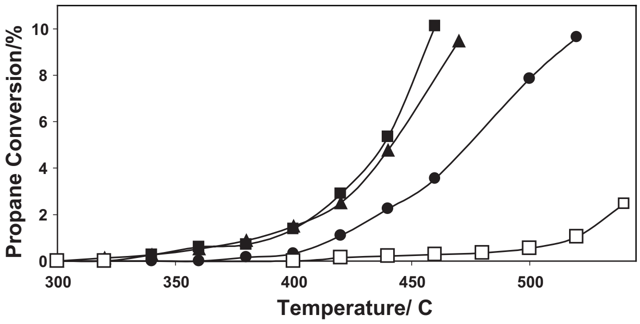

Figure 1. Propane conversion over the Ga_2O_3/MoO_3 catalysts and comparison with Ga_2O_3 and MoO_3. (▲) Ga_2O_3/MoO_3 calcined; (■) Ga_2O_3/MoO_3 uncalcined; (●) Ga_2O_3; (□) MoO_3.

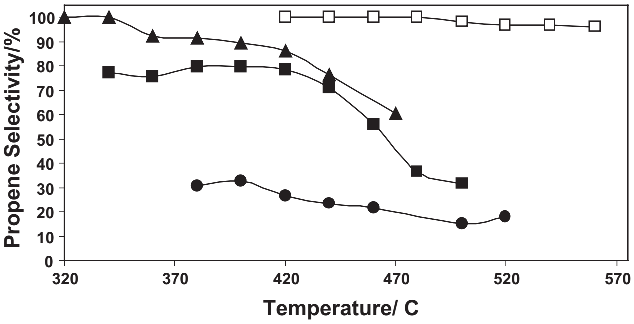

Figure 2. Selectivity towards propene as a function of temperature: (▲) Ga_2O_3/MoO_3 calcined; (■) Ga_2O_3/MoO_3 uncalcined; (●) Ga_2O_3; (□) MoO_3.

For comparison with the catalytic data in this study a series of V_2O_5/TiO_2 catalysts where 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 approximately constant conversion (ca. 10% if possible) is presented in table 1.

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 propene yield from the 6 wt% V_2O_5/TiO_2 catalyst was lower than that for the Ga_2O_3/MoO_3 catalysts. An increase of temperature was required with the Ga_2O_3/

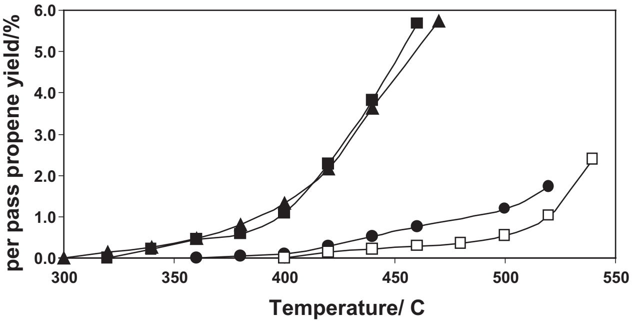

Figure 3. Per pass yield of propene as a function of temperature: (▲) Ga_2O_3/MoO_3 calcined; (■) Ga_2O_3/MoO_3 uncalcined; (●) Ga_2O_3; (□) MoO_3.

MoO_3 catalysts, however, in terms of achievable propene yields the performance of the Ga_2O_3/MoO_3 catalysts were superior. This data clearly demonstrates 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 Catalyst surface areas determined by the BET method are summarised in table 1. 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. X-ray diffraction confirmed that the phases Ga_2O_3 and MoO_3 were present in the single oxides. The pattern for Ga_2O_3 indicated broad diffraction peaks with a relatively high background, whilst MoO_3 was highly crystalline. The diffraction patterns for both of the Ga_2O_3/MoO_3 catalysts only showed diffraction from the MoO_3 phase and the low intensity Ga_2O_3 diffraction peaks were difficult to distinguish from the background. Similar results were obtained from the Raman spectra. The Ga_2O_3/MoO_3 catalysts only showed Raman active vibrations that were assigned to MoO_3. This was not surprising since Raman studies on the Ga_2O_3 alone did not produce a discernible spectrum. 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 also apparent that calcined and uncalcined catalysts were not significantly different.

It is clear that 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 [7]. 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 alkene activation through a dehydrogenation step [8].

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. 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 [1]. 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 com-

Table 1
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/$m^2\ g^{-1}$	Temp. /°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
6 wt% V_2O_5/TiO_2		315	7.5	28	2.0
	46	340	11.0	22	2.5

prised 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 [9], 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_2O3 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.

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