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A STUDY OF THE REDUCTION OF MOLYBDENUM TRIOXIDE ON A CARBON SUPPORT USING THERMOGRAVIMETRY/MASS SPECTROMETRY

P J O'CONNOR, L F WHITING and C B MURCHISON

The Dow Chemical Company, Midland, MI (U S A)

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ABSTRACT

Molybdenum catalysts used in the synthesis of hydrocarbons can be prepared by reduction of molybdenum trioxide with hydrogen to form water at elevated temperatures When carbon is used as the catalyst support material the possibility exists for the reduction of the metal oxide by the carbon support which would produce carbon dioxide Thermogravimetry/mass spectrometry (TG–MS) was utilized in this study to quantitate the amount of reduction of the molybdenum oxide by hydrogen and by the carbon support up to 700 °C Results show that in an inert atmosphere such as helium a significant amount of reduction is effected by the carbon support However, in a 5% hydrogen/95% helium atmosphere reduction of the oxide by hydrogen predominates with less than 2% reduction occurring via the carbon support

INTRODUCTION

Carbon supported molybdenum catalysts have proven to be useful for synthesizing high yields of C_2–C_5 hydrocarbons from hydrogen and carbon monoxide One mode of preparation of these catalysts includes the thermally induced reduction of an intermediate molybdenum trioxide on potassium carbonate activated carbon in the presence of hydrogen to give a distribution of molybdenum species of lower oxidation states including elemental molybdenum

There is an alternative reduction possible via oxidation of the activated carbon support by the molybdenum trioxide to yield a lower oxide of molybdenum and carbon dioxide A study was undertaken to qualitatively and quantitatively evaluate these reduction processes using thermogravimetry/mass spectrometry (TG–MS)

EXPERIMENTAL

The instrumentation used for qualitative analysis using TG–MS or optionally incorporating on-line capillary gas chromatography for resolution of complex gas mixtures (TG–GC–MS) has been described and characterized previously [1] Modification of the existing instrumentation and method was required to obtain reproducible quantitative results in the TG–MS mode A Mettler ME21 constant mass electronic microbalance and a TGA furnace were interfaced to a Hewlett Packard 86A microcomputer using a Hewlett Packard 3497A data acquisition/control unit with a Love Controls Corporation (Wheeling, IL) Model 151 with option 7188 temperature controller

The oxidized catalyst was prepared by first soaking the support material with an aqueous solution of potassium carbonate (reagent grade, Baker) and ammonium heptamolybdate tetrahydrate (Climax Molybdenum Company), then air drying at ambient temperature for several hours, followed by programmed heating to 300 ° C in an air atmosphere to drive off adsorbed water, water of hydration and ammonia The samples used in this study included (1) non-activated carbon, (2) a "blank" consisting of support carbon activated with potassium carbonate (4% w/w elemental potassium), and (3) molybdenum trioxide catalyst on activated carbon support which was 21% w/w molybdenum and 3 7% w/w potassium

Calcium oxalate monohydrate (Du Pont Instruments) was used as a standard The inert carrier gas was high purity helium passed through a gettering device (Go-Getter by General Electric) and the reducing atmosphere was 5% v/v hydrogen in high purity helium (both gases from Scott Specialty Gases)

INSTRUMENT DESIGN AND OPERATION

The instrument configuration for TG–MS analysis is shown in Fig 1 Much of the glassware design was influenced by the need to minimize the concentration of background air in the sample atmosphere. Rubber O-rings were used in all of the glass to glass joints and a controllable gas-flow system was incorporated. A continuous flow of helium swept through the balance mechanism area and exited via the intermediate exit port The desired sample purge gas was introduced through an inlet port located directly above the furnace zone and split so that a fraction of the gas swept upward through a series of flow restricting PTFE disks and out the intermediate exit port Diffusion into the furnace zone of any air that might have entered the system through O-ring joints was greatly reduced by the upward purge flow The majority of the sample purge gas was directed past the sample and out through the main exit port below the TGA furnace The

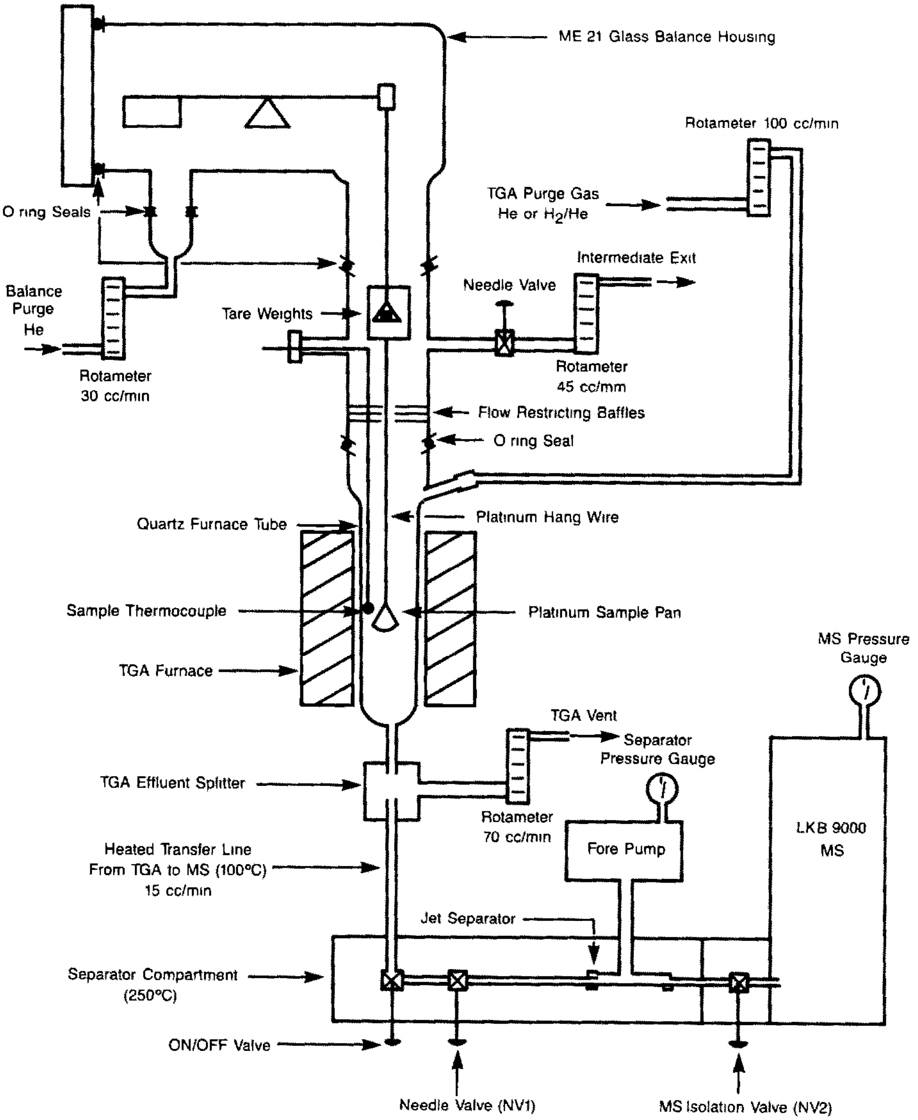

Fig 1 Diagram of TGA glassware and gas-flow scheme for TG–MS operation

flow rates of all gases entering and leaving the system were controlled by needle valves and monitored with rotameters or Gas Met flowmeters to provide reproducible dilution of the gases evolved from the sample reaction The flow to the mass spectrometer was set by adjusting the MS isolation needle valve 2 (NV2) Typically, 15 cm^3 min^{-1} of TGA effluent (85 cm^3 min^{-1} total) were drawn into the jet separator

RESULTS AND DISCUSSION

Instrument response factors

In the preparation of the catalyst, the ammonium heptamolybdate tetrahydate impregnated potassium activated support is calcined at 300 °C in air to drive off ammonia and water. This leaves molybdenum trioxide on the activated support

$$(NH_4)_6Mo_7^{VI}O_{24}\cdot 4H_2O \xrightarrow[300\,°C]{} 7Mo^{VI}O_3 + 6NH_3 + 7H_2O$$

The molybdenum trioxide species is then heated in hydrogen yielding reduced molybdenum species including the metal, giving off water as a byproduct

$$Mo^{VI}O_3 \xrightarrow{H_2} Mo^0 + 3H_2O$$

If an alternative mechanism of reduction is occurring via oxidation of the carbon support, then carbon dioxide will be evolved from the catalyst upon heating

$$2Mo^{VI}O_3 \xrightarrow{C} 2Mo^0 + 3CO_2$$

To evaluate properly the extent of reduction by each mechanism, the precise amounts of CO_2 and H_2O evolved from the sample reaction must be determined. First, response factors for CO_2 and H_2O were calculated by evolving known quantities of both gases in the TG-MS apparatus. For an inert atmosphere, calcium oxalate monohydrate was chosen as a standard. Figure 2 illustrates a TGA curve of the thermal decomposition of calcium oxalate monohydrate in helium. Three distinct weight loss regions are observed. The first 12% of sample weight loss recorded in the drop to the second plateau between 100 and 200 °C corresponds to the evolution of one mole of H_2O per mole of calcium oxalate. The theoretical weight for release

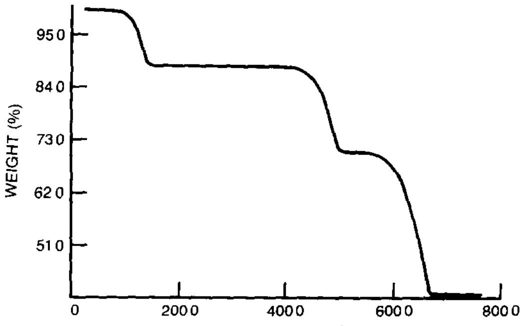

Fig. 2. TGA curve of calcium oxalate monohydrate in helium (5 °C min^{-1}, 4.107 mg)

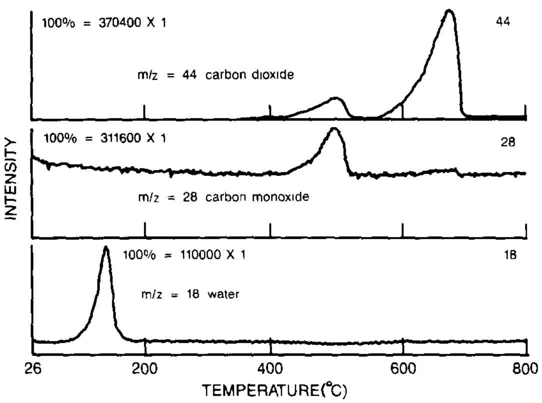

Fig 3 Ion current vs temperature plots from TG–MS experiment on calcium oxalate monohydrate (5 °C $\min^{-1}$, 4 107 mg)

of the water of hydration is 12 3% The second 19% of sample weight loss recorded between 350 and 540 °C corresponds to the decomposition of calcium oxalate to calcium carbonate and carbon monoxide The evolution of carbon monoxide has a theoretical weight loss of 19 2% The third recorded sample weight loss of 29% is attributed to the decomposition of calcium carbonate to calcium oxide and carbon dioxide The theoretical weight loss for this reaction is 30 1%

During the heating of the sample in the TGA, a portion of the effluent was analyzed by TG–MS Mass spectra were acquired at 19 s intervals between *m/z* 14 and *m/z* 100 The plots of intensity vs time (temperature) for masses 18, 28 and 44 corresponding to the parent ions of water, carbon monoxide and carbon dioxide, respectively, are shown in Fig 3 These mass plots clearly depict the chemistry of the three separate reactions involved in the thermal decomposition of the calcium oxalate monohydrate

$$\underset{(\mathrm{FW}=146\ 1)}{\mathrm{CaC_2O_4\ H_2O}} \xrightarrow[100-200\,^\circ\mathrm{C}]{} \mathrm{CaC_2O_4(s) + H_2O(g)}$$

$$\mathrm{CaC_2O_4(s)} \xrightarrow[350-540\,^\circ\mathrm{C}]{} \mathrm{CaCO_3(s) + CO(g)}$$

$$\mathrm{CaCO_3(s)} \xrightarrow[560-700\,^\circ\mathrm{C}]{} \mathrm{CaO(s) + CO_2(g)}$$

The response factor for water is obtained from calcium oxalate monohydrate by first integrating the area above baseline intensity under the peak found on the intensity vs time plot for mass 18 (H_2O) of Fig 3 This peak is associated with the evolution of the water of hydration from the sample which is known to be 12% of the total sample weight This exact quantity of water evolved is then used to quantitate the relationship of the integral area detected per mass of H_2O actually evolved

A similar procedure is used to obtain the response factor for CO_2 using the weight of evolved CO_2 from calcium oxalate monohydrate between 560 and 700 °C and the corresponding normalized integral peak area for mass 44

Response factor values used in the catalyst reduction experiments were the mean average of six different runs with a relative error range of about ±10%

Catalyst support effects

The catalyst reductions were evaluated by subjecting the samples to programmed heating in either a He or 5% H_2/95% He atmosphere and analyzing the off gas using TG–MS During heating, mass spectra were acquired from m/z 14 to m/z 100 at 13 s to 19 s intervals depending on the total run time and number of data points taken, usually 500 The ion current plots for CO_2 and H_2O were integrated and the quantity of both gases evolved during the reaction was computed using response factors as described previously Under conditions of heating, the carbon support will evolve both H_2O and CO_2 Correction for evolution of these species from the carbon support was made by running a blank consisting of K_2CO_3 activated carbon under identical conditions as the catalyst and determining, as a function of temperature, the amounts of CO_2 and H_2O generated per unit mass of carbon support The blank was 93% carbon by weight Likewise, the quantities of H_2O and CO_2 evolved from the catalyst per unit mass of carbon support (the catalyst was 63% carbon by weight) were calculated By subtracting the contribution of evolved gases by the support, the net production of CO_2 and H_2O from the catalyst per unit mass of carbon support was determined This value was then multiplied by the mass of the carbon support in the catalyst sample to yield the absolute net evolution of CO_2 and H_2O The sum of CO_2 and H_2O evolved can be checked against the total weight loss observed by TGA as a cross-check of the results

In all experiments, some sample weight loss occurred below 200 °C due to the removal of chemisorbed and physisorbed water and also from decomposition of potassium bicarbonate impurity in the potassium carbonate Hence, the mass of the catalyst and blank at 200 °C was used in all calculations Previous reduction studies on similar molybdenum catalysts indicate that no interfering thermally induced reactions of substances possibly formed during impregnation (e g $(NH_4)_2CO_3$, K_2MoO_4) should occur between 200 and 720 °C Also the decomposition of K_2CO_3 to form K_2O and CO_2 is expected only if temperatures greatly exceed 650 °C

Catalyst reduction by the carbon support

Several experiments were performed in a helium atmosphere to observe the extent of MoO_3 reduction via oxidation of the carbon support in the

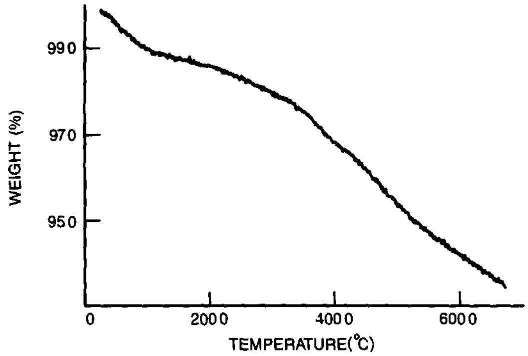

Fig 4 TGA curve of molybdenum trioxide on potassium carbonate/carbon support in helium (5 °C min^{-1}, 10 311 mg)

absence of hydrogen Figure 4 shows the TGA curve for the catalyst heated at 5 °C min^{-1} in helium By visual observation of the slope of the weight loss curve, the maximum rate of weight loss above 200 °C occurs between 340 and 540 °C The corresponding reconstructed ion thermogram of mass 44 shown in Fig 5 indicates that a maximum rate of CO_2 evolution takes place between 455 and 530 °C The TGA curve for the blank run under identical conditions is shown in Fig 6 From this curve the highest rate of weight loss is observed above 600 °C and is probably due to the onset of K_2CO_3 decomposition, since the rate continues to increase until programmed heating ceases at 670 °C Figure 7 contains the reconstructed ion thermogram of mass 44 The first temperature region of CO_2 detection below 200 °C is associated with the decomposition of $KHCO_3$ impurity The catalyst sample does not exhibit $KHCO_3$ decomposition since it has already

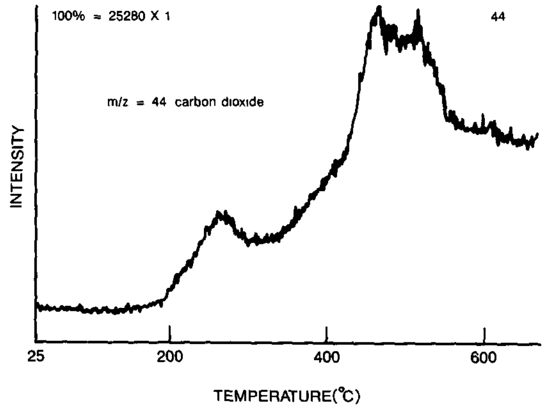

Fig 5 Ion current vs temperature plot from TG–MS experiment on molybdenum trioxide on potassium carbonate/carbon support in helium (5 °C min^{-1}, 10 311 mg)

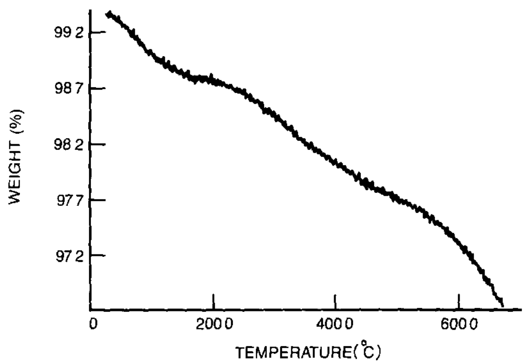

Fig 6 TGA curve of potassium carbonate/carbon support blank in helium (5 °C min^{-1}, 15 696 mg)

been heated to 300 °C in air during preparation Two other distinct regions of CO_2 evolution are found at higher temperatures possibly from the decomposition of two or more different types of oxygenated carbon species on the support.

Whatever the origin of gas evolved from the blank, it is assumed in the following calculation that the quantitative amount evolved per unit mass of carbon will be the same as the contribution of gas evolved from the carbon support of the catalyst sample Based on this assumption, reduction results calculated from the net quantity of oxygen (associated with CO_2) evolved from the catalyst relative to the total quantity of oxygen available (associated with MoO_3) are listed in Table 1 The results reported in Table 1 may represent minimum values for reduction by the support When one examines the CO_2 evolution curves for catalyst and blank (Figs 5 and 7) it is evident

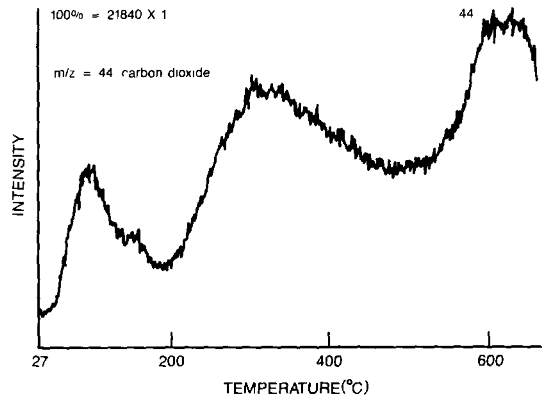

Fig 7 Ion current vs temperature plot from TG–MS experiment on potassium carbonate/carbon support blank in helium (5 °C min^{-1}, 15 696 mg)

TABLE 1

Reduction in helium (programmed at 5 °C min^{-1})

Temperature range (°C)	% Reduction by carbon support
200–350	0 6
350–500	6 0
500–670	6 3
	Total 12 9

that the rates of CO_2 evolution are very different in the two materials as a function of temperature The reason for this difference is not known One possible explanation for the differences observed at lower temperatures is that the catalyst had already been calcined at 300 °C in air during preparation, while the support blank had only been air dried at much lower temperatures If prior calcination of the support blank in air at 300 °C would have reduced the evolution of CO_2 from the blank during the TG–MS experiment in helium, it is estimated that this would yield an additional 3% reduction by the carbon support to give a total of approximately 16% reduction It appears from Figs 5 and 7 that at higher temperatures a significant amount of CO_2 evolution from the catalyst occurs between 400 and 500 °C and that CO_2 production decreases in rate above 550 °C In contrast, the CO_2 curve for the blank increases by a factor of two between 500 and 600 °C One explanation for this difference is that the catalyst coating the support accelerates the decomposition of the oxygen-containing species on the support to produce CO_2 at lower temperatures However, the total amount of CO_2 evolved from the support would not be expected to change the total percentage reduction value listed in Table 1 Another explanation for differences in the CO_2 evolution curves is that the catalyst coating on the carbon support protects the support from oxidation by background oxygen and/or stabilizes the oxygen-containing species originally present on the support surface In this case, less CO_2 would be evolved by the support coated with catalyst than expected and the total reduction of MoO_3 by the support would be higher than that reported in Table 1

It should also be noted that a higher value for reduction of the MoO_3 by the carbon support can be obtained by not subtracting any support contribution to CO_2 evolution An upper limit of 23% reduction by the carbon support can be calculated in this manner

Catalyst reduction by hydrogen

The weight loss profile for the catalyst heated at 5 °C min^{-1} in a 5% H_2/95% He atmosphere is shown in Fig 8 The loss of weight occurring

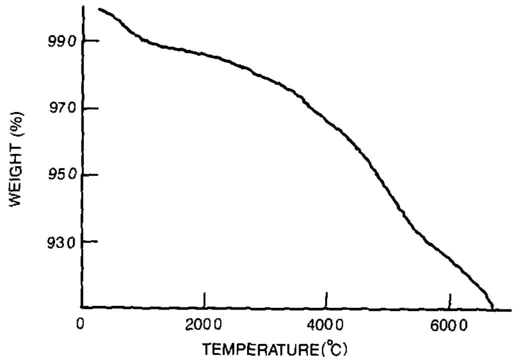

Fig 8 TGA curve of molybdenum trioxide on potassium carbonate/carbon support in 5% hydrogen in helium (5 °C min^{-1}, 18 083 mg)

from 200 to 670 °C is 7 5% compared with 5 1% catalyst weight loss for that temperature range for the similar previous experiment performed in helium atmosphere (Fig 4) A region of high rate of weight loss is observed between 460 and 540 °C with the slope of the TGA curve again increasing in magnitude above 240 °C Corresponding reconstructed ion thermograms for mass 44 and mass 18 (H_2O) are shown in Fig 9 CO_2 evolution appears to reach a maximum rate around 430 °C and recedes to virtual baseline levels as the temperature goes above 530 °C This is unlike the significant CO_2 evolution that continues beyond 540 °C when the catalyst is heated at the same rate in the absence of hydrogen (Fig 5) suggesting that little or no reduction takes place via the mechanism of carbon support oxidation in 5% H_2/95% He above 530 °C Observation of the H_2O evolution in Fig 9 reveals a peak between ambient temperature and 175 °C which is attributed

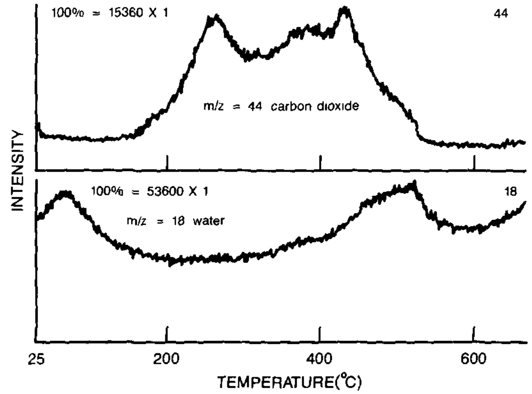

Fig 9 Ion current vs temperature plots from TG–MS experiment on molybdenum trioxide on potassium carbonate/carbon support in 5% hydrogen in helium (5 °C min^{-1}, 18 083 mg)

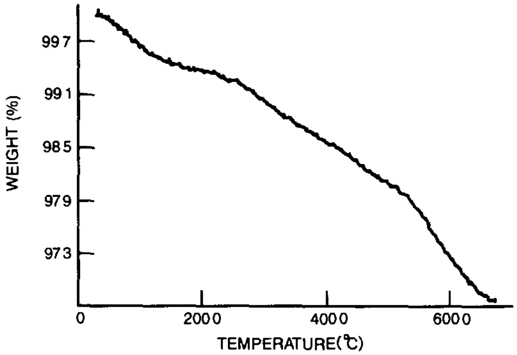

Fig 10 TGA curve of potassium carbonate/carbon support blank in 5% hydrogen in helium (5 ° C min^{-1}, 14 271 mg)

to the release of water adsorbed on the sample Catalyst samples consistently showed more water released below 200 ° C upon heating than blank samples Storing the catalyst sample in a more humid environment could account for this A maximum rate of H_2O evolution is achieved in the 440–540 ° C region. The rate decreases from 540 to 590 ° C and then steadily climbs as the catalyst temperature is raised from 590 to 670 ° C. Figure 10 is the TGA curve for the programmed heating of the K_2CO_3/carbon blank at 5 ° C min^{-1} in 5% H_2/95% He Final weight loss of 3 23% at 670 ° C is comparable with the 3 26% weight loss of the blank in helium (Fig 6). Corresponding reconstructed ion thermograms for mass 18 and mass 44 are shown in Fig 11 There are no temperature regions above 200 ° C that exhibit high rate of H_2O evolution although the mass of H_2O evolved accounts for 1.6% of the catalyst weight loss from 200 to 670 ° C For temperatures greater than 200 ° C, the ion current plot of CO_2 shows

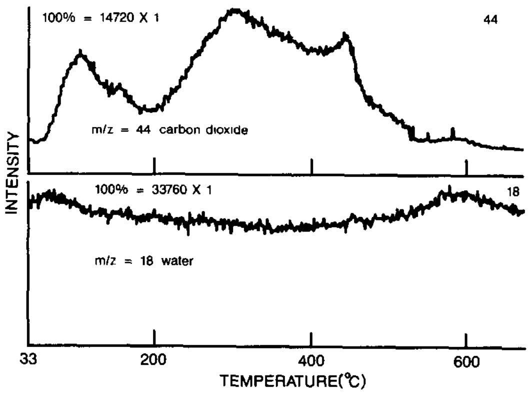

Fig 11 Ion current vs temperature plots from TG–MS experiment on potassium carbonate/carbon support blank in 5% hydrogen in helium (5 ° C min^{-1}, 14 271 mg)

TABLE 2

Reduction in 5% hydrogen (programmed at 5 °C min^{-1})

Temperature range (°C)	% Reduction by carbon support	% Reduction by H_2
200–350	0 3	1 2
350–500	0 9	14 0
500–670	0 0	13 6
	Total 1 2	Total 28 8

maximum intensity at 285 °C followed by a rapid drop in intensity at temperatures above 450 °C In contrast, the evolution rate of CO_2 from the blank in helium (Fig 7) is greatest from 600 to 670 °C TG–MS results indicate that CO_2 is not reduced to CO and H_2O by hydrogen under these experimental conditions

Table 2 lists percentage reduction values for three temperature ranges The net production of CO_2 is ascribed to oxidation of the carbon support, whereas the net production of H_2O is attributed to catalyst reduction via hydrogen Both contributions are tabulated separately and computed relative to the total quantity of oxygen in the catalyst sample available for removal (as MoO_3)

When the catalyst is programmed at 5 °C min^{-1} from ambient temperature to 670 °C, 30 0% of the available oxygen associated with MoO_3 was removed This percentage reduction value corresponds to an oxygen/molybdenum (mole/mole) ratio of 2 10 at the end of the experiment

It should be noted that the catalyst support evolution of H_2O and CO_2 in the various "blank" experiments has a significant effect on the calculated percentage reduction If one does not take into account these "blanks," the reduction values dramatically increase For purposes of comparison, the apparent reduction of the catalyst has been calculated from the weight loss curves without any correction for a blank These data are presented in Table 3 When the blank is not included, the reduction by the support in helium is about three times as large and the reduction in hydrogen is more than twice

TABLE 3

Reduction calculated from thermogravimetry curves without subtracting blank runs (5 °C min^{-1})

Temperature range (°C)	% Reduction by carbon support in helium	% Reduction by hydrogen
200–350	7	10
350–500	15	28
500–670	13	33
	Total 35	Total 71

as large as that listed in Table 2 where the blank is included These values represent an upper limit to the degree of reduction of the catalyst under these conditions The actual reduction is expected to be closer to the values listed in Tables 1 and 2

CONCLUSION

The experimental results from the TG–MS analysis of carbon supported molybdenum trioxide catalyst indicate that in an inert atmosphere such as helium, significant reduction can occur via oxidation of the carbon support beginning at temperatures above 200 ° C and continuing into the 700 ° C temperature region However, in a 5% hydrogen/95% helium atmosphere, the predominant catalyst reduction process between 200 and 670 ° C involves oxidation of hydrogen, albeit a small amount of reduction via carbon support oxidation can occur below 500 ° C

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