Catalysis Letters 58 (1999) 147–152

The formation of active species for oxidative dehydrogenation of propane on magnesium molybdates

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Received 10 August 1998; accepted 3 February 1999

Pure and mixed magnesium molybdate phases (MoO_3, $MgMoO_4$, and $MgMo_2O_7$) have been examined for the oxidative dehydrogenation reaction of propane. The results are very sensitive to the stoichiometry and method of preparation. The catalysts exhibiting superior activity and selectivity are characterized by a unique temperature-programmed reduction peak that is not present for the poorly active or selective catalysts. Mixtures of $MgMoO_4$ and MoO_3 or $MgMoO_4$ and $MgMo_2O_7$, materials that perform poorly by themselves, show significant improvements in performance upon heating. The solid-state interactions leading to these improvements correspond to the appearance of the characteristic reduction peak. The results suggest that the beneficial synergistic effects seen with mixtures of inactive phases are due to formation of a new phase or species, rather than remote communication between phases (e.g., oxygen spillover).

Keywords: oxidative dehydrogenation, propane, magnesium molybdates, temperature-programmed reduction

1. Introduction

Several papers concerning the oxidative dehydrogenation (ODH) of propane over magnesium molybdates have recently been published [1–5]. There have also been studies of this system for the ODH of ethylbenzene [6,7]. Each of these works points out the importance of excess molybdenum relative to the $MgMoO_4$ stoichiometry. In their recent study [3], Cadus and coworkers concluded that excess molybdenum results in a synergistic cooperation between the $MgMoO_4$ and MoO_3 phases in the ODH of propane. They suggest the effect is similar to that observed for excess Mo in the selective oxidation of C_4 hydrocarbons over $MnMoO_4$ [8] or $CdMoO_4$ [9], or the synergy between magnesium vanadate phases reported for the ODH of propane [10]. In each of these cases, the synergistic effect has been attributed to oxygen spillover from one phase to another [8,9,11]. Cadus and coworkers based their conclusions on the observation that their active $MgMoO_4$–MoO_3 catalyst mixtures were always composed of two phases. They were unable to detect the formation of new phases, phase decomposition, or phase contamination. However, EPR measurements showed the formation of Mo^{5+} indicating alterations in redox properties.

In contrast to the conclusion of Cadus and coworkers, Lee et al. [5] have concluded that the benefit of excess molybdenum in the ODH of propane is derived from active MoO_x clusters that form on the surface of $MgMoO_4$. Their conclusion is based on results obtained by supporting Mo on inactive magnesium molybdate surfaces and by treating materials with acid and base solutions to modify the surface chemistry. In the present study, we provide evidence that the combination of excess molybdenum (as MoO_3 or $MgMo_2O_7$) combined with $MgMoO_4$ does result in altered redox properties that lead to improved catalytic performance. Our evidence suggests that this alteration is the result of the direct contamination or reaction between the two phases to create new species, rather than the result of remote communication of the phases, for example through an oxygen spillover mechanism.

2. Experimental

2.1. Catalyst preparation

Several catalysts were prepared or obtained to serve as baseline materials. Samples of $MgMoO_4$, $Mg_{0.95}MoO_{4-x}$ and $Mg_{1.05}MoO_{4+x}$ were prepared from solutions of $Mg(NO_3)_2$ (pH = 2) and $(NH_4)_6Mo_7O_{24}$ (pH = 9) according to [4]. Briefly, the solutions were stirred together, adjusted to a pH of 5, evaporated and dried, and calcined in air stepwise at 200, 250, and 300 °C, with a final 9 h calcination at 600 °C. "Phase pure" samples of $MgMoO_4$ were prepared by the citrate method [12] with a final calcination temperature of 550 °C. A solution of $Mg(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ was prepared, and citric acid was added so that the equivalents of citrate anions were equal to the cation equivalents ($Mg^{2+} + Mo^{6+}$) in solution. The solution was then evaporated and dried under vacuum. The resulting powder was ground and calcined in air for 8 h. Samples of "$Mg_2Mo_3O_{11}$" (see results below) were prepared by both the citrate method (600 °C calcine) and by heating a stoichiometric mixture of $MgMoO_4$ and MoO_3 fine powders for 48 h at 650 °C in an open tube. MoO_3 (ACS certified) was obtained from Fisher Scientific.

Mixtures of $MgMoO_4$ (from the citrate preparation) with MoO_3 and $Mg_2Mo_3O_{11}$ (from the solid-state preparation) were also made. The mixtures were prepared by first grinding the individual components to fine powders, then weighing the powders in a 9 : 1 ($MgMoO_4$: second component) ratio and mixing. Mixing was aided by suspending the powders in pentane and mechanically shaking. The pentane was allowed to evaporate following the mixing procedure. All catalysts used in this study were pelletized by pressing, crushed, and sieved to recover a $-40/+60$ mesh for reaction testing.

2.2. Catalyst characterization

Powder X-ray diffraction data were collected at room temperature on a Siemens model D500 automated diffractometer, with θ–2θ sample geometry and Cu K_α radiation, between $2\theta = 5$ and 60°, step size 0.05°. Nitrogen BET surface areas were measured with a Quantachrome Autosorb 6B automated gas sorption system. Temperature-programmed reduction (TPR) studies were carried out using a Micromeritics Autochem 2910. During TPR, samples (30 mg) were ramped from room temperature to 1050 °C at 10 °C/min in a 50 sccm stream of 10% H_2 in Ar.

2.3. Reaction tests

The ODH reaction of propane was conducted in a conventional flow reactor at atmospheric pressure. For each run, a 0.400 g bed (2 cm in height) of granulated catalyst was supported on a plug of quartz wool in the 5 mm I.D. quartz reactor tube. The feed, consisting of 18 mol% C_3H_8, 9 mol% O_2, and the balance N_2, was passed over the catalyst bed at a rate of 100 sccm. In all cases, conversion and selectivity were such that oxygen consumption was less than 100%. The reactor was heated to 400 °C in the flowing reaction mixture and data was collected for 1 h after which the temperature was increased. The procedure was repeated until data had been collected at temperatures typically ranging from 400 to 575 °C in 25 or 50 °C intervals. Some catalysts were also tested at 600 °C. For the catalyst mixtures, the tests were repeated with the used samples, again starting at 400 °C. The reaction temperature was monitored with two thermocouples external to the quartz tube (at the center and top of the bed) and a third thermocouple positioned inside the reactor tube just above the catalyst. The three thermocouples typically registered temperatures within at least 5 °C of one another. Tests conducted in an empty reactor tube indicated that the straight thermal contribution to the reaction was negligible below 550 °C, increasing to 1% propane conversion at 600 °C. These control experiments do not rule out the possibility of heterogeneously initiated homogeneous reactions. However, catalyst bed and downstream volumes were consistent from run to run, precluding the possibility that differences would result from different residence times in the "empty" reactor volume.

The reaction tests for each catalyst were carried out over the course of several working days. At the end of a test day, the reactor was cooled to room temperature under the reactive flow. At the start of the next day's testing, the reactor was heated in the reaction mixture to the final temperature of the previous day, and it was verified that the results were consistent prior to proceeding with higher-temperature tests. Following the reaction tests, the catalysts were recovered for X-ray diffraction and surface area analysis.

Reactants and products were analyzed with an on-line MTI gas chromatograph utilizing a 10 m molecular sieve 5A PLOT column (O_2, CH_4, CO) and a 8 m Poraplot Q column (CO_2, C_3H_6, C_3H_8). The reactor effluent passed through a condenser to remove excess water prior to analysis. No additional products other than water were detected. The carbon balances closed within ±5%.

3. Results

3.1. ODH of propane

The physical properties of catalysts used in this study are summarized in table 1. X-ray diffraction analysis of the materials revealed that, with the exceptions of $MgMoO_4$ prepared by the citrate method and MoO_3, the catalysts are composed of multiple crystalline phases. Samples prepared with a Mg : Mo ratio near 1 : 1 are primarily β-$MgMoO_4$, with small amounts of other phases. Similarly, diffraction patterns of the physical mixtures are dominated by the predominant β-$MgMoO_4$ phase.

Diffraction patterns of materials prepared with Mg : Mo ratios of 2 : 3 exhibit intense peaks for both β-$MgMoO_4$ and the polymolybdate reported by Meullemeestre to be $Mg_2Mo_3O_{11}$ [13]. Similar difficulties in obtaining phase-pure samples of $Mg_2Mo_3O_{11}$ have been reported by Tsuzuki and coworkers [14]. These researchers concluded that the material corresponding to the $Mg_2Mo_3O_{11}$ diffraction pattern reported is actually a low-temperature phase of $MgMo_2O_7$. We have recently prepared a sample exhibiting only the XRD peaks reported by Meullemeestre for "$Mg_2Mo_3O_{11}$" by heating a 1 : 1 molar ratio of $MgMoO_4$ and MoO_3 to 650 °C. Thus, we conclude that the material purported in the literature to be $Mg_2Mo_3O_{11}$ is actually $MgMo_2O_7$. In this work, we will refer to materials prepared with a Mg : Mo ratio of 2 : 3 as $Mg_2Mo_3O_{11}$, and we will refer to the phase exhibiting Meullemeestre's "$Mg_2Mo_3O_{11}$" X-ray diffraction pattern as $MgMo_2O_7$. The 2 : 3 stoichiometry would be expected to yield equivalent molar amounts of $MgMo_2O_7$ and $MgMoO_4$.

Conversion and selectivity are shown as a function of temperature for the active and selective baseline materials ($Mg_{0.95}MoO_{4-x}$, $MgMoO_4$ from salts, and $Mg_2Mo_3O_{11}$ from citrate) in figure 1. Consistent with previous results [1–5], the best overall performing material ($Mg_{0.95}MoO_{4-x}$) is that containing only a small excess of Mo relative to the 1 : 1 $MgMoO_4$ stoichiometry. At conver-

Table 1
Properties of Mg–Mo–O catalysts.

Catalyst stoichiometry (Mg : Mo ratio)	Preparation method	As-prepared Phase[a] (by XRD)	As-prepared Surface area (m^2/g)	After reaction testing Phase (by XRD)	After reaction testing Surface area (m^2/g)
0.95 : 1	Metal salts	β, P	5.1	β, P	5.0
1 : 1	Metal salts	β, α	7.0	β, α	6.0
1 : 1	Citrate	β	19.0	β	16.7
1.05 : 1	Metal salts	β, α	8.1	β, α	8.0
2 : 3	Citrate	P, β	6.6	P, β	3.7
2 : 3	Solid state	P, β	0.7	P, β	0.7
0.88 : 1	$0.9MgMoO_4$ $0.1MoO_3$	β, M	17.0	β, P	4.4
0.96 : 1	$0.9MgMoO_4$ $0.1Mg_2Mo_3O_{11}$	β, P	18.0	β	7.7
MoO_3	Fisher	M	1.7	M	0.7

[a] $\beta = \beta$-$MgMoO_4$, P = $MgMo_2O_7$, $\alpha = \alpha$-$MgMoO_4$, M = MoO_3; phase with most intense peaks in XRD is listed first.

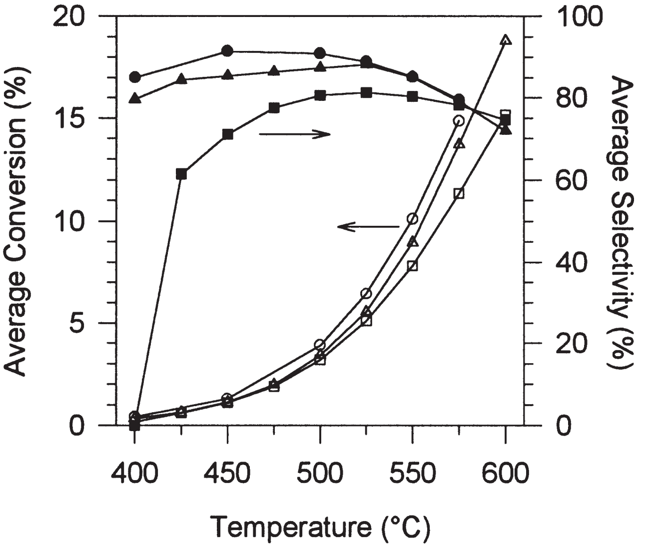

Figure 1. Temperature dependence of propane conversion and selectivity over active and selective baseline magnesium molybdate catalysts. (○) $Mg_{0.95}MoO_{4-x}$ conversion, (●) $Mg_{0.95}MoO_{4-x}$ selectivity, (□) $MgMoO_4$ from salts conversion, (■) $MgMoO_4$ from salts selectivity, (△) $Mg_2Mo_3O_{11}$ from citrate conversion, and (▲) $Mg_2Mo_3O_{11}$ from citrate selectivity. Points shown are an average of data taken over the course of 1 h at the given temperature.

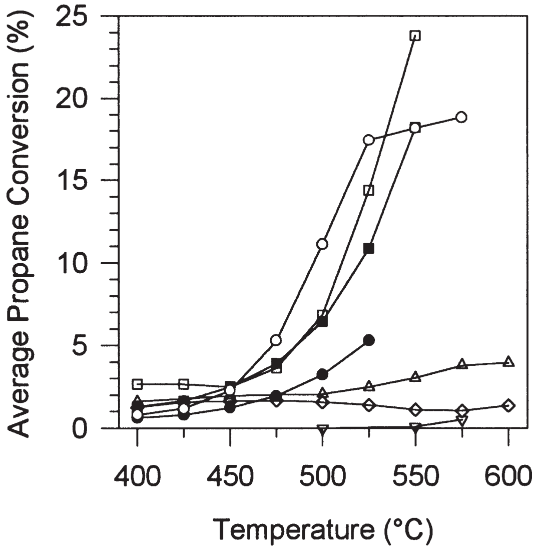

Figure 2. Temperature dependence of propane conversion over several poorly active and selective catalysts and physical mixtures of those same catalysts. (△) $MgMoO_4$ from citrate, (▽) MoO_3, (◇) $Mg_2Mo_3O_{11}$ from solid state, (○) $0.9MgMoO_4$ from citrate + $0.1MoO_3$, (●) repeat run with used $0.9MgMoO_4$ from citrate + $0.1MoO_3$, (□) $0.9MgMoO_4$ from citrate + $0.1Mg_2Mo_3O_{11}$ from solid state, (■) repeat run with used $0.9MgMoO_4$ from citrate + $0.1Mg_2Mo_3O_{11}$ from solid state. For clarity, conversion shown is the average of data points taken at given temperature.

sions greater than 5%, these active catalysts show the decrease in selectivity with increasing conversion typical of most ODH catalysts. This behavior is generally attributed to a secondary combustion reaction of the product olefin. The active catalysts converge to nearly identical selectivity behavior at higher conversions. At low conversions, the active catalysts are strikingly nontypical. Rather than exhibiting the highest selectivities as the conversion approaches zero, there is a break point after which selectivities decrease with decreasing conversion. At 400 °C, no detectable propene is produced over the 1 : 1 catalyst. The surface areas of the active 0.95 : 1, and 1 : 1 catalysts were relatively stable during testing. The surface area of the active 2 : 3 catalyst decreased by about 50%. The other baseline materials ($MgMoO_4$ from citrate, $Mg_{1.05}MoO_{4+x}$, and $Mg_2Mo_3O_{11}$ from the solid state) are poorly active and selective, with conversions of less than 5% at 600 °C (figure 2). Maximum selectivities over these materials vary from <40% for the $MgMoO_4$ from the citrate preparation and $Mg_{1.05}MoO_{4+x}$, to 50% for the $Mg_2Mo_3O_{11}$ from the solid-state preparation, to 68% for MoO_3. No major changes are observed in the X-ray diffraction patterns as a result of reaction testing any of the baseline samples.

Reaction results for catalysts prepared by mixing phases are shown in figures 2–4. Figure 2 clearly demonstrates the positive influence of mixing phases on catalyst activity. Synergistic effects are observed when either MoO_3,

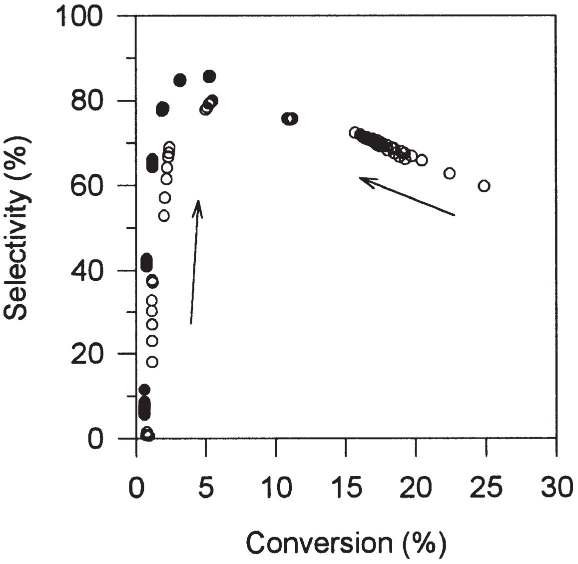

Figure 3. Selectivity of propane to propene over a catalyst mixture and the components of the mixture. (○) $0.9\mathrm{MgMoO_4}$ from citrate $+ 0.1\mathrm{MoO_3}$, and (●) repeat run with used $0.9\mathrm{MgMoO_4}$ from citrate $+ 0.1\mathrm{MoO_3}$. Clusters of points result from the time dependence of conversion and selectivity at a given temperature. Arrows indicate direction of change with increasing time on stream.

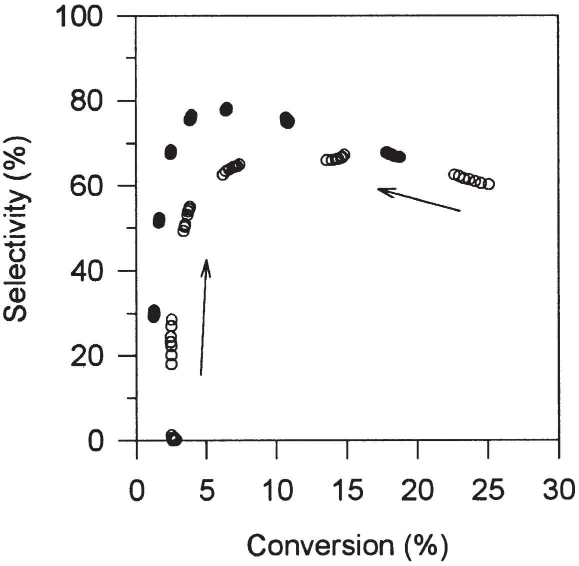

Figure 4. Selectivity of propane to propene over a catalyst mixture and the components of the mixture. (○) $0.9\mathrm{MgMoO_4}$ from citrate $+ 0.1\mathrm{Mg_2Mo_3O_{11}}$ from solid state, and (●) repeat run with used $0.9\mathrm{MgMoO_4}$ from citrate $+ 0.1\mathrm{Mg_2Mo_3O_{11}}$ from solid state. Clusters of points result from the time dependence of conversion and selectivity at a given temperature. Arrows indicate direction of change with increasing time on stream.

or $\mathrm{MgMo_2O_7}$ (from the solid-state 2 : 3 catalyst preparation) is combined with $\mathrm{MgMoO_4}$. A number of interesting changes are observed in the behavior of both the mixed catalysts during reaction testing. At reaction temperatures of 475 °C or less (low conversion regime), the selectivity of the reaction to propene steadily increases as a function of time on stream. Slight increases in conversion also occur. This can be seen in figures 3 and 4 as clusters of data points that result from changes in the activity and selectivity of the catalyst over time at a given temperature. At higher temperatures (525 °C or greater) and conversions, the main effect is a significant decrease in conversion over time. Coupled with the decrease in conversion is the expected increase in selectivity. Again this is illustrated as clusters of data points in figures 3 and 4. This loss of activity is particularly pronounced for the $\mathrm{MgMoO_4/MoO_3}$ mixed catalyst. The effect can readily be seen in figure 2, where the average conversion at 550 and 575 °C falls far short of the values one would expect by extrapolating the data points from lower temperatures. At intermediate temperatures (475–525 °C) the catalytic behavior is relatively stable. The selectivity–conversion relationship is improved when the experiment is repeated with the used mixed catalysts (figures 3 and 4), although conversion at a given temperature is diminished (figure 2). These differences are attributable only to changes in the catalysts as the initial data is reproduced when the experiments are repeated with fresh catalysts.

Characterization of the mixed catalysts recovered from the reactor shows that significant changes occur in the materials during reaction testing. In both cases, the surface areas were drastically reduced. Further, X-ray diffraction analyses indicates changes in the phase composition. For the $\mathrm{MgMoO_4/MoO_3}$ case, solid-state reactions occurred between $\mathrm{MgMoO_4}$ and $\mathrm{MoO_3}$ to produce the $\mathrm{MgMo_2O_7}$ phase. For the $\mathrm{MgMoO_4/Mg_2Mo_3O_{11}}$ case, the $\mathrm{MgMo_2O_7}$ phase evidently reacted away as β-$\mathrm{MgMoO_4}$ was the only crystalline phase observed after reaction testing.

3.2. TPR of magnesium molybdate catalysts

Figure 5 shows the results from the TPR of the baseline catalysts. Reduction profiles (A)–(C) were obtained for catalysts that are inactive and nonselective for the ODH of propane under the conditions studied. Profiles (D)–(F) were obtained for materials that show significant activity and selectivity for the propane ODH reaction. Each of the active catalysts exhibits a unique reduction peak, centered at about 650 °C, that is not present for the inactive materials. Figure 6 shows TPR results for the mixed $\mathrm{MgMoO_4/MoO_3}$ catalyst. Neither the $\mathrm{MgMoO_4}$ or $\mathrm{MoO_3}$ pure phases show the characteristic 650 °C reduction peak, and neither are active for the ODH reaction (figure 2). The mixed phases, however, do show some evidence of a peak at 650 °C. Heating the mixed phases in air for 1 h at 425 °C results in the characteristic peak becoming a dominant feature in the reduction profile. Similar results were obtained for the mixed $\mathrm{MgMoO_4/Mg_2Mo_3O_{11}}$ catalyst (figure 7). Neither the $\mathrm{Mg_2Mo_3O_{11}}$ or the mixed $\mathrm{MgMoO_4/Mg_2Mo_3O_{11}}$ phases initially exhibit the characteristic reduction peak. However, after pretreating the mixture in air for 30 min at 475 °C, a reduction peak centered at 650 °C becomes evident.

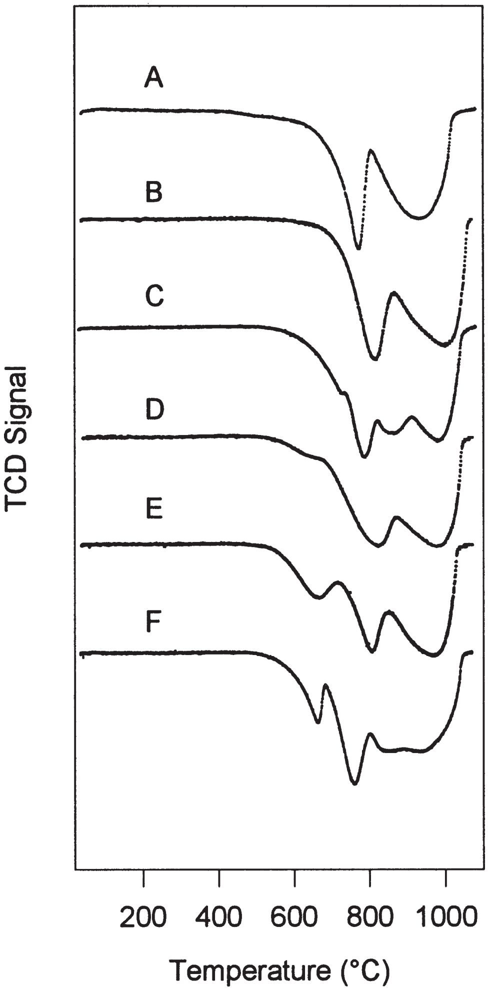

Figure 5. Temperature-programmed reduction of inactive and active catalysts. (A) $MgMoO_4$ from citrate, (B) $Mg_{1.05}MoO_{4+x}$, (C) $Mg_2Mo_3O_{11}$ from solid state, (D) $Mg_{0.95}MoO_{4-x}$, (E) $MgMoO_4$ from salts, and (F) $Mg_2Mo_3O_{11}$ from citrate.

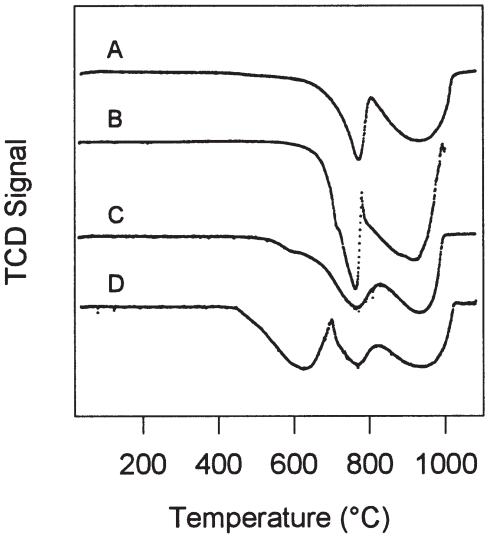

Figure 6. Temperature-programmed reduction of (A) $MgMoO_4$ from citrate, (B) MoO_3 and (C) $0.9MgMoO_4$ from citrate + $0.1MoO_3$, (D) $0.9MgMoO_4$ from citrate + $0.1MoO_3$ heated for 1 h at 425 °C.

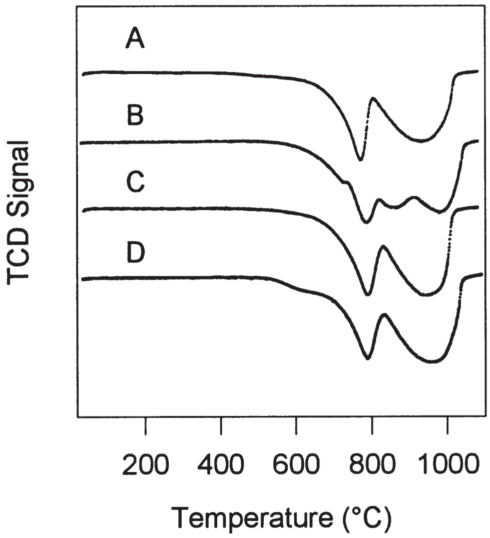

Figure 7. Temperature-programmed reduction of (A) $MgMoO_4$ from citrate, (B) $Mg_2Mo_3O_{11}$ from solid state, (C) $0.9MgMoO_4$ from citrate + $0.1Mg_2Mo_3O_{11}$ from solid state, (D) $0.9MgMoO_4$ from citrate + $0.1Mg_2Mo_3O_{11}$ from solid state heated for 1 h at 475 °C.

4. Discussion

All of the active and selective catalysts tested in this study are composed of β-$MgMoO_4$ and another crystalline phase. There is no correlation between catalyst performance and the identity of the second phase. There is, however, a strong correlation between the catalyst performance and the TPR results. Each of the active and selective catalysts has a reduction peak centered at about 650 °C that is not present for the other materials, including β-$MgMoO_4$. This conclusion is not altered by comparing the catalysts on a surface area rather than mass basis. This result suggests that the active catalysts share a common phase or species that is not detected by X-ray diffraction. The different sizes of the characteristic TPR feature probably partly arise from the fact that the materials have different Mg : Mo ratios.

The presence of the active species is strongly dependent upon catalyst preparation conditions. For example, the two catalysts prepared with a 1 : 1 Mg : Mo stoichiometry give very different results. The citrate preparation, which presumably results in a more homogeneous product, yields an inactive and unselective material, despite its relatively high surface area. The reduction profile of the 1 : 1 citrate material is nearly identical to that of MoO_3. The 1 : 1 material prepared from precipitated salts contains multiple phases, exhibits the characteristic reduction peak, and its performance is comparable to the best material. On the other hand, the citrate preparation of the 2 : 3 stoichiometry yields a very active material with a prominent reduction peak at 650 °C while the solid-state preparation of the 2 : 3 stoichiometry yields an inactive and poorly selective, low surface area material without the characteristic peak.

The behavior of the mixed materials support the notion that a unique solid-state species is responsible for the catalytic ODH behavior rather than a remote communication of phases through reactive intermediates. Clearly, significant changes occur in the catalysts as a result of the reaction regimen. Surface areas are dramatically decreased, but more importantly, phase changes are observed. After testing, MoO_3 is no longer observed in the $MgMoO_4/MoO_3$ catalyst. Evidently, solid-state reactions consume the MoO_3, resulting in at least a partial conversion to $MgMo_2O_7$. In contrast, after testing the mixed $MgMoO_4$ and $MgMo_2O_7$ (as the 2 : 3 material prepared from the solid state) phases, the $MgMo_2O_7$ phase is no longer observed. Meullemeestre reported the decomposition of his "$Mg_2Mo_3O_{11}$" phase to β-$MgMoO_4$ and MoO_3 at temperatures above 600 °C [13]. In our case, we did not detect the appearance of MoO_3, only the loss of $MgMo_2O_7$. Evidence that these changes in the solid state are in fact related to "synergism" observed when the previously inactive phases are combined is provided by the consecutive reaction tests (figures 3 and 4). After the mixed catalysts are exposed to the complete reaction cycle, their selectivity at lower conversions is favorably altered. However, their activity at a given temperature is diminished.

Although our work does not entirely rule out the possibility of oxygen spillover, there are clearly changes in the solid state occurring simultaneously with improvements in catalyst performance. The evidence is thus consistent with a model, where the active and selective species for ODH of propane result from the spreading of small amounts of Mo onto the $MgMoO_4$ phase or from solid-state reactions between Mo and $MgMoO_4$ leading to a phase intermediate between $MgMoO_4$ and $MgMo_2O_7$. When more than a few percent of Mo is present relative to the 1 : 1 $MgMoO_4$ stoichiometry, the $MgMo_2O_7$ phase begins to form. Excess Mo also appears to enhance sintering, manifested by a loss of surface area. It appears then that for our mixed-phases catalysts at lower temperatures, new selective reactive sites are slowly evolving on the surface of the catalyst due to solid-state interactions of the two phases. This results in the observed increases in selectivity over time. The decrease in conversion at higher temperatures is at least partially due to a loss of surface area from catalyst sintering. The consumption of active sites through further solid-state reactions is also a possibility. The reason for the unexpectedly low selectivities observed for all the active catalysts at low conversions is not known, but it may be related to nonselective catalytic sites with a low activation energy, limited desorption of hydrocarbons at the lower temperatures, or to a self-poisoning of nonselective sites by reaction product carbon oxides. Further studies to characterize the active sites and their evolution are underway.

Acknowledgement

This work was supported by the US Department of Energy at Sandia National Laboratories under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, Lockheed Martin Company, for the US Department of Energy.

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