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Investigation of Oxygen Insertion Mechanism in Selective Oxidation Reactions over $MnMoO_4/MoO_3$ Catalysts through Isotopic Labeling and Chemisorption Studies

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The role of lattice and gas-phase oxygen was investigated over a two-phase catalyst ($MnMoO_4/MoO_3$) and its pure-phase constituents, MoO_3 and $MnMoO_4$, in order to draw conclusions about the operation of the synergy mechanism observed over the $MnMoO_4/MoO_3$ catalysts in selective oxidation of C_4 hydrocarbons. Transient response experiments of 1,3-butadiene oxidation performed using isotopically labeled oxygen and high-temperature oxygen uptake measurements performed over fresh and reduced catalysts suggested a catalytic job distribution between the two phases of the $MnMoO_4/MoO_3$ catalysts where oxygen from the molybdenum trioxide lattice was incorporated into the hydrocarbon molecule, resulting in a partially oxidized product (i.e., furan, maleic anhydride), and the MoO_3 sites were regenerated through an oxygen spillover mechanism from the manganese molybdate phase. © 1990 Academic Press, Inc.

INTRODUCTION

Selective oxidation reactions play an important role in chemical and petrochemical industry, producing a large number of partially oxygenated hydrocarbon derivatives. In these reactions, one of the key questions is the mechanism of oxygen insertion into the hydrocarbon molecules, resulting in partial oxidation versus complete oxidation of the feed hydrocarbon. In the last decade, the partial oxidation of C_4 hydrocarbons to maleic anhydride has attracted much attention with C_4 hydrocarbons providing a more economical and environmentally safer feedstock. Although most of the work in this area has been performed over vanadium–phosphorus–oxide catalysts (*1–5*), there have also been studies reporting substantial selectivities to maleic anhydride over molybdate and/or molybdenum oxide-based catalysts (*6–13*). 1,3-Butadiene and furan have been commonly reported as two of the intermediates in the reaction pathway leading to the formation of maleic anhydride from 1-butene. There is no general consensus, however, about the role of lattice and gas-phase oxygen in selective and complete oxidation reactions of C_4 hydrocarbons. Trifiro and co-workers have proposed that 1-butene conversion to 1,3-butadiene occurs through lattice oxygen participation, but that some form of adsorbed oxygen is necessary for the formation of maleic anhydride (*8*). Although oxidative dehydrogenation of 1-butene to 1,3-butadiene has been investigated more extensively and the view that conversion of 1-butene to 1,3-butadiene takes place through use of lattice oxygen is shared by other researchers, the number of studies on the following steps leading to the formation of maleic anhydride is rather limited and therefore the question about the role of lattice and gas-phase oxygen in these reactions is far from being resolved.

The isotopic labeling technique is a powerful tool which can be of great value in elucidating reaction mechanisms. The use of isotopically labeled oxygen as an investi-

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gative tool has taken place mainly in the selective oxidation of propylene to acrolein (*14–19*). Switching from $^{16}O_2$ to $^{18}O_2$ during a steady-state reaction and following the changes in the amount of oxygenated product that contained ^{18}O ions has provided information about the depth of participating lattice oxygen atoms in the catalysts studied. Weng *et al.* (*20*) studied the oxidation of propylene over a two-phase catalyst (MoO_3–Sb_2O_4) by labeling the Sb_2O_4 phase with $^{18}O_2$ and observing the mass distribution of the products. Through this study they were able to provide evidence of oxygen spillover from the Sb_2O_4 phase to the MoO_3 phase.

Our previous studies over the two-phase $MnMoO_4/MoO_3$ catalysts showed a strong synergy effect between the two phases in the partial oxidation of C_4 hydrocarbons to maleic anhydride (*13, 21*). Catalyst characterization studies and activity measurements have indicated that an intimate contact between the molybdenum trioxide and the molybdate phase caused a pronounced increase in activity of the catalyst as well as a substantial change in the product distribution in favor of maleic anhydride. In this study, the role of lattice and gas-phase oxygen has been investigated through use of isotopically labeled oxygen in the gas phase in the partial oxidation of 1,3-butadiene to maleic anhydride. The studies have been performed over the two-phase $MnMoO_4/MoO_3$ catalyst and its pure-phase constituents using a pulse reactor system coupled with an on-line gas chromatograph–mass spectrometer. Pulse reaction experiments have been conducted using both oxygen-abundant and oxygen-free feed mixtures to differentiate between the sources of oxygen incorporated into partial and complete oxidation products under transient conditions. High-temperature oxygen uptake measurements have also been performed over fresh catalysts and catalysts reduced with hydrogen to compare the oxygen uptake capacities of the two-phase catalyst and its single-phase components, as well as the degree of reduction achieved. The results from these studies have been combined with the evidence provided by our previous studies to elucidate the catalytic job distribution among the different components of the Mn MoO_4/MoO_3 catalysts.

EXPERIMENTAL

Catalyst Preparation

The pure manganese molybdate catalyst used in these studies was prepared from aqueous solutions of ammonium heptamolybdate and manganese chloride using a precipitation technique outlined previously (*13*). The two-phase $MnMoO_4/MoO_3$ catalyst was prepared by mixing molybdenum trioxide powder with a slurry of manganese molybdate and evaporating the water. The two-phase catalyst used in this study had a $MnMoO_4$-to-MoO_3 mole ratio of 0.15. Both preparation techniques included a calcination step at 500°C under a steady flow of oxygen.

Catalyst Characterization

The two-phase catalyst and its pure-phase constituents were characterized using BET surface area measurement, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, laser Raman spectroscopy, Raman microprobe, and X-ray photoelectron spectroscopy techniques. Results of these characterization studies have been reported previously (*13, 21*).

Transient Response Studies Using Isotopic Labeling Technique

The transient response reaction experiments were performed using a pulse microreactor, made from 316 stainless-steel tubing with an outer diameter of $\frac{1}{4}$ in. and a length of 6 in (Fig. 1). The catalyst sample was placed in the middle of the tube and the length of the catalyst bed was less than $\frac{1}{8}$ in. The reactor was heated by a Nichrome resistance element and the temperature was monitored through a thermocouple posi-

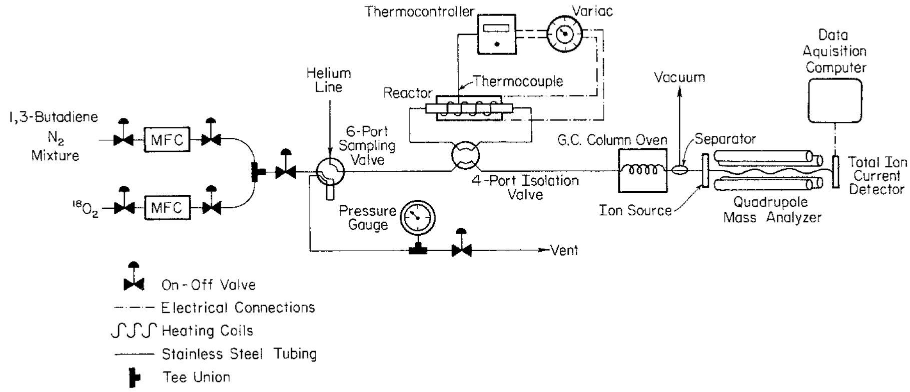

FIG. 1. Flow diagram of the feed, reactor, and analytical systems used for isotopic labeling studies.

tioned at the center of the catalyst bed and connected to an OMEGA proportional controller. The reactor system had a four-port and a six-port Valco valve used for isolating and pulsing the reactor, respectively.

The feed gas mixture composition and flow rates were controlled by two mass flow controllers (Tylan Model FC280) calibrated for each of the specific gases. The feed gas consisted of 1.6% 1,3-butadiene and 16% isotopically labeled oxygen (>99% $^{18}O_2$, Cambridge Isotope) by volume. Nitrogen, inert to the system, comprised the remainder of the gas feed.

The reactor was connected directly to the carrier gas line of a gas chromatograph–mass spectrometer system (Finnigan 4000) for separating the species present in the feed and the product streams and quantifying them with respect to their mass/charge (*m*/*e*) ratios.

Prior to each experiment, catalyst samples were degassed at 400°C for 5 h under vacuum (<0.0005 mm Hg), cleaning the surfaces of any adsorbed gases. After degassing, the catalyst bed was completely isolated to prevent contamination from atmospheric oxygen. The total catalyst surface area present in the reactor was kept constant at 0.25 m^2 for each reaction run.

The feed gas composition was analyzed both before and after the reaction with the reactor in the bypass/isolation mode. The reactor temperature was kept constant at 450°C and the helium flow rate was maintained at 26 cc/min. The pulses of the reactant gas mixture were introduced using the six-port Valco valve through a 1-cc sample loop at 2 psig and 24°C. The catalyst bed was pulsed at approximately 45-min intervals. The exit lines from the reactor were heated to prevent condensation of the reaction products.

The percentage conversion of the feed hydrocarbon (1,3-butadiene) is defined as

$$\frac{\begin{array}{c}\text{moles of 1,3-}\\ \text{butadiene consumed}\end{array}}{\begin{array}{c}\text{moles of 1,3-}\\ \text{butadiene in feed}\end{array}} \times 100\%.$$

The percentage of labeled and unlabeled species was calculated by dividing the peak area corresponding to each *m*/*e* value by the sum of the peak areas corresponding to all possible *m*/*e* values for the species being analyzed.

The percentage normalized oxygen conversion was defined as

$$\frac{\text{moles of oxygen consumed}}{\begin{array}{c}\text{moles of oxygen in feed} \times\\ \%\ \text{conversion of 1,3-butadiene}\end{array}} \times 100\%.$$

Oxygen Uptake Measurements

Oxygen uptake measurements were performed over the two-phase catalyst (Mn

MoO_4/MoO_3) and its pure-phase constituents using a static adsorption system equipped with high-temperature chemisorption furnaces (Micromeritics Accusorb 2100E). The fresh catalyst samples were degassed at 400°C for 5 h prior to oxygen chemisorption experiments. Two consecutive adsorption isotherms were obtained by evacuating the sample between two isotherms to differentiate between reversibly and irreversibly adsorbed oxygen.

Oxygen uptake experiments were repeated after reducing the catalyst samples with hydrogen using the Micromeritics 2100E Accusorb system. To achieve reduction, samples were brought into contact with hydrogen at 400°C and 760 mm Hg. Approximately every 20 min, the spent hydrogen and reduction products were evacuated and replaced with fresh hydrogen for a total of 4.6 h. The catalyst samples were then evacuated for 2 h at the same temperature before the chemisorption experiments were begun. For both fresh and reduced samples, the isotherms were continued until no more oxygen adsorption took place.

RESULTS

Catalyst Characterization

The results of characterization studies over $MnMoO_4/MoO_3$, $MnMoO_4$, and MoO_3 catalysts have been reported previously (*13*). The characterization studies clearly indicated the two-phase nature of the Mn MoO_4/MoO_3 catalysts where the two phases appeared in intimate contact with each other and ruled out the formation of a new compound or a new phase being formed when the molybdenum oxide and the simple molybdate phases were brought in close contact. The surface areas for the MoO_3, $MnMoO_4$, and the $MnMoO_4/MoO_3$ catalysts used in this study were 0.540, 2.049, and 1.771 m^2/g, respectively.

Catalysts were characterized following the degassing process using BET surface area measurement, laser Raman spectroscopy, and X-ray photoelectron spectroscopy. No changes were observed in the surface areas, the Raman bands or the binding energies of the catalysts as a result of the degassing treatment.

Isotopic Labeling Studies

Isotopic labeling studies have been used to examine the involvement of lattice oxygen in selective and complete oxidation reactions over the two-phase $MnMoO_4/MoO_3$ catalyst and its pure-phase components. Figure 2 shows the distribution of furan isotopes over the three catalyst samples in transient oxidation of 1,3-butadiene with $^{18}O_2$ in the gas phase. It is seen that the MoO_3 catalyst utilized almost exclusively lattice oxygen in the formation of furan since molecular weight of 68 represents $C_4H_4{}^{16}O$ whereas molecular weight of 70 indicates that oxygen atom in the furan molecule is oxygen-18 ($C_4H_4{}^{18}O$). The involvement of the lattice oxygen does not show a rapid decline with the pulse number. In contrast to the MoO_3 catalyst, the gas-phase oxygen is seen to be incorporated into the hydrocarbon molecule more readily over the $MnMoO_4$ catalyst. In the first pulse about 25% of all the oxygen incorporated into furan is derived from the gas phase. The contribution of the gas-phase oxygen rises to about 35% by the fifth pulse. The two-phase catalyst $MnMoO_4/MoO_3$ is closer to MoO_3 in the utilization of lattice oxygen with 93% of furan being unlabeled in the first pulse.

In transient response experiments, Mn MoO_4/MoO_3 was the only catalyst to yield substantial quantities of maleic anhydride. Figure 3 shows the relative amounts of maleic anhydride formed containing zero ($C_4H_2{}^{16}O_3$), one ($C_4H_2{}^{18}O^{16}O_2$), or two ($C_4H_2{}^{18}O_2{}^{16}O$) isotopically labeled oxygen atoms. No maleic anhydride was detected with all three oxygen atoms labeled. It is seen that in the first pulse, the relative percentages of maleic anhydride isotopes with molecular weight of 98, 100, and 102 are 65, 31, and 4% respectively. For the fifth pulse, these percentages are 61, 34, and 5%.

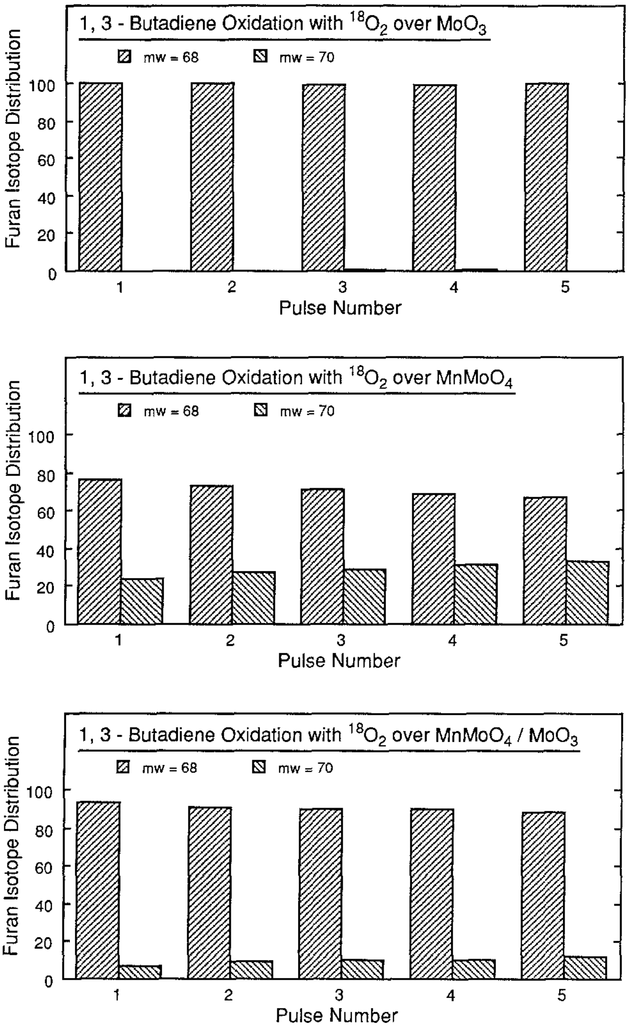

FIG. 2. Distribution of furan isotopes in transient oxidation of 1,3-butadiene.

These numbers indicate that close to 90% of all the oxygen incorporated into the hydrocarbon molecules to form maleic anhydride comes from the crystal lattice of the catalyst and the increase of the gas-phase oxygen contribution is very gradual.

In addition to furan and maleic anhydride, transient oxidation of 1,3-butadiene yielded substantial quantities of acrolein, a partially oxygenated C_3 hydrocarbon derivative. Figure 4 shows the distribution of acrolein isotopes over the MoO_3, Mn MoO_4, and $MnMoO_4/MoO_3$ catalysts. The

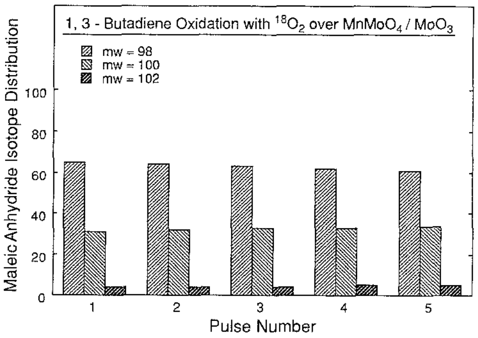

FIG. 3. Distribution of maleic anhydride isotopes in transient oxidation of 1,3-butadiene.

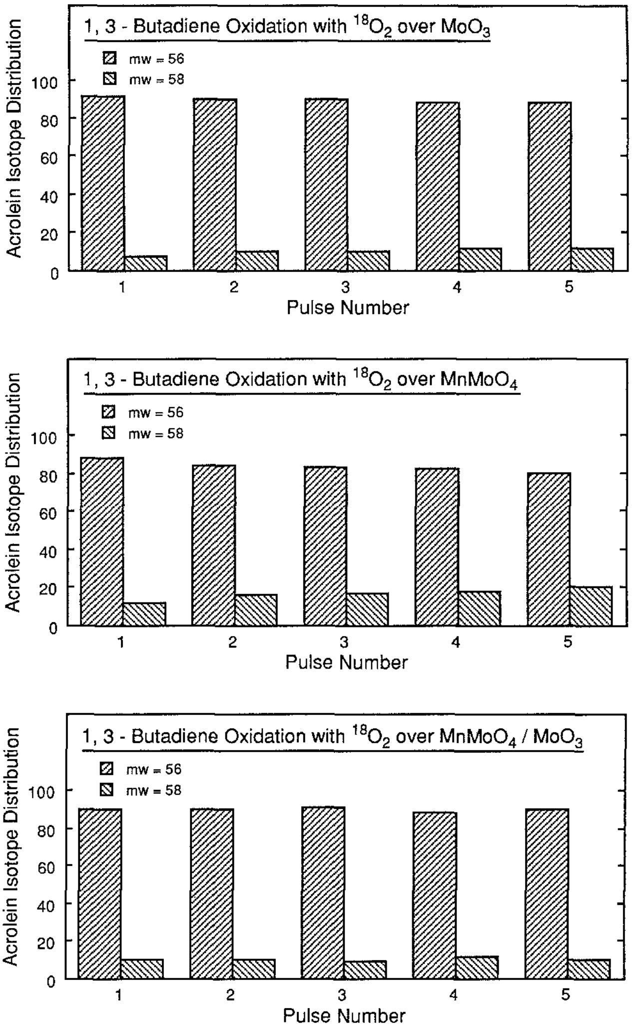

FIG. 4. Distribution of acrolein isotopes in transient oxidation of 1,3-butadiene.

percentage of unlabeled acrolein over the MoO_3 catalyst remains fairly constant with the pulse number, ranging from 92 to 89% from the first to the fifth pulse. Over the $MnMoO_4$ phase the contribution of the gas-phase oxygen builds up more rapidly, increasing from 12 to 20%. The two-phase catalyst appears to be closer to the molybdenum trioxide catalyst in behavior.

Figure 5 shows the distribution of carbon dioxide isotopes. Over pure MoO_3 no $C^{18}O_2$ was detected. However, the use of gas-phase oxygen was much more significant in the formation of CO_2 than it was in the formation of furan, with the relative amount of $C^{18}O^{16}O$ being around 30%. Over $MnMoO_4$, both $C^{18}O^{16}O$ and $C^{18}O_2$ relative percentages increased rapidly with the pulse number, ranging from 22 to 39% for $C^{18}O^{16}O$ and from 2 to 8% for $C^{18}O_2$. The two-phase catalyst ($MnMoO_4/MoO_3$) showed a smaller increase in the amount of $C^{18}O^{16}O$, up from 22 to 29%. The relative percentage of CO_2 with the molecular weight of 48 remained constant around 1%.

In order to further examine the role of

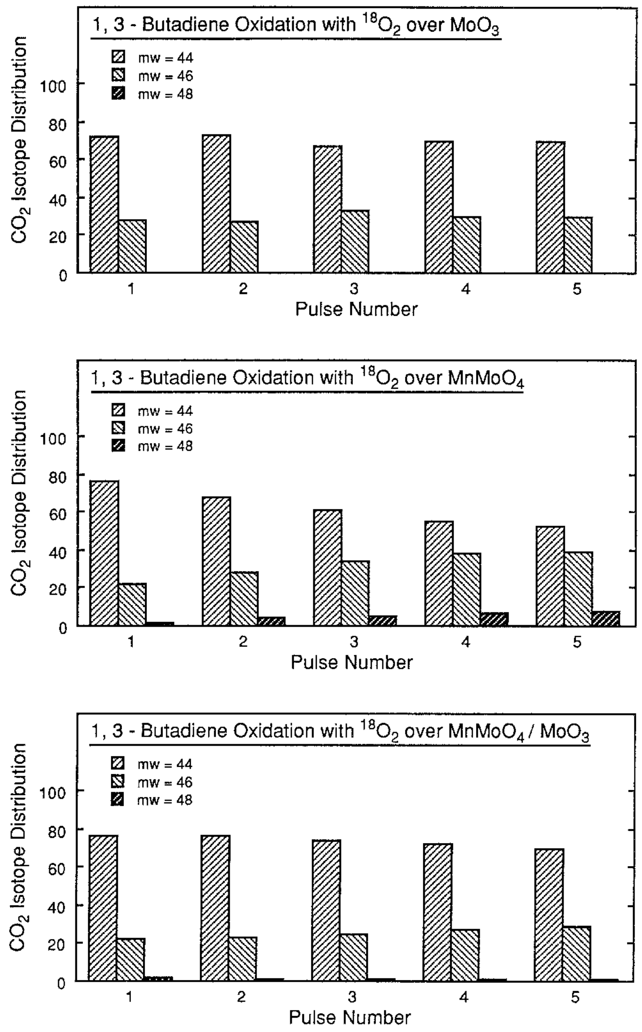

FIG. 5. Distribution of CO_2 isotopes in transient oxidation of 1,3-butadiene.

lattice and gas-phase oxygen in the manifestation of the synergy effect that is observed between the two phases of the Mn MoO_4/MoO_3 catalyst, the activity of the two-phase catalyst and its pure phase constituents were compared for conversion of 1,3-butadiene in the absence as well as in the presence of gas-phase oxygen. Catalyst samples were degassed for the oxygen-free runs using the same procedure described above. Table 1 shows the conversion of 1,3-butadiene using oxygen-abundant and oxygen-free feed gas mixtures. The most striking feature of these results is the drastic change that took place in the activity of the pure-phase catalysts MoO_3 and $MnMoO_4$ when the feed was switched from a mixture containing excess oxygen to an oxygen-free mixture. The changes in the activity of the two single-phase catalysts were completely opposite of each other. The molybdenum trioxide catalyst was seen to be much more active in the absence of gas-phase oxygen whereas the manganese molybdate catalyst proved to be strongly dependent on the presence of gas-phase oxygen to maintain

TABLE 1

Percentage Conversion of 1,3-Butadiene with Oxygen-Abundant and Oxygen-Free Feed Mixtures

Pulse number	With oxygen-abundant feed			With oxygen-free feed		
	MoO_3	$MnMoO_4$	$MnMoO_4/MoO_3$	MoO_3	$MnMoO_4$	$MnMoO_4/MoO_3$
1	16	31	83	43	7	28
2	15	31	84	39	4	33
3	15	31	85	33	4	32
4	14	31	86	28	4	32
5	16	31	86	20	4	33

its activity, as indicated by the sharp drop in the conversion level when the feed mixture was completely depleted of gas-phase oxygen. The activity level for the two-phase catalyst fell between those of the single-phase catalysts with oxygen-free feed mixtures. The conversion level with the excess-oxygen mixtures over this catalyst, however, was well above those observed over both the MoO_3 and the $MnMoO_4$ catalysts.

Oxygen Uptake Measurements

Table 2 summarizes the results of oxygen uptake measurements performed over fresh and reduced catalysts at 400°C. When fresh catalyst samples are used, MoO_3 is seen to chemisorb the smallest amount of oxygen. $MnMoO_4$, on the other hand, appears to be much more adsorbent toward oxygen, adsorbing close to five times more oxygen per unit surface area than does pure MoO_3. The amount of oxygen adsorbed over the two-phase catalyst is between the amounts adsorbed over the single-phase catalysts, but closer to the amount adsorbed over molybdenum trioxide.

Oxygen uptake measurements were repeated on catalyst samples which were reduced with hydrogen at 400°C. Since part of the oxygen taken up by each catalyst is used to reoxidize the reduced sites, the oxygen uptake value is a function of the degree of reduction of the catalyst. The variation in the oxygen uptake values among catalyst samples appears to be quite different over the reduced catalysts than it is over fresh samples. After reduction, MoO_3 is seen to take up 3.3 times more oxygen than does $MnMoO_4$, indicating a larger degree of reduction than that of $MnMoO_4$. Following reduction, the manganese molybdate catalyst is seen to take up the least amount of oxygen among the three catalyst samples, indicating a low degree of reduction with hydrogen. The oxygen uptake over the two-phase catalyst is seen to be slightly higher than that of MoO_3.

TABLE 2

Oxygen Uptake over Fresh and Reduced Catalysts[a]

Catalyst	Fresh sample	Reduced sample
MoO_3	0.0075	0.980
$MnMoO_4$	0.0320	0.298
$MnMoO_4/MoO_3$	0.0080	1.001

[a] cm^3(STP)/m^2.

DISCUSSION

Our previously reported studies have shown that the catalytic behavior of molybdenum trioxide catalysts in partial oxidation of C_4 hydrocarbons could be modified quite drastically by bringing them in contact with a simple molybdate phase (e.g., Mn MoO_4 (*13*), $CdMoO_4$ (*22*)). This resulted in a pronounced increase in the selectivity toward maleic anhydride accompanied by an increase in overall activity. Careful characterization of pure phases as well as the two-phase catalyst did not reveal the formation of a new phase or a new compound, but clearly showed the coexistence of the two phases in intimate contact with each other, suggesting a strong synergy effect.

In this study, we have investigated the role of oxygen in the synergy mechanism by using transient response isotopic labeling and high-temperature oxygen chemisorption techniques. The transient response studies have, one more time, verified the observed synergy effect, with the two-phase catalyst ($MnMoO_4/MoO_3$) being the only one with a substantial yield of maleic anhydride and showing a higher activity than either of the single-phase catalysts. When we compared the normalized conversion levels of oxygen over the three catalysts (Table 3), we saw that the two-phase catalyst had the lowest normalized oxygen conversion, indicating that it favored partial oxidation of the hydrocarbon more than the complete oxidation which would have resulted in a higher consumption of oxygen.

The isotopic labeling studies provide some important clues about the role of oxygen in the synergy mechanism. The results show that pure molybdenum trioxide could utilize lattice oxygen much more readily than its counterpart, manganese molybdate. In the formation of furan, it is almost 100% lattice oxygen which is incorporated into the hydrocarbon molecule over MoO_3. The use of gas-phase oxygen is much more visible over $MnMoO_4$. When pure molybdenum trioxide uses gas-phase oxygen, it results mostly in complete oxidation products. These results seem to suggest that selectivity of the two-phase catalyst for partial oxidation products, especially for furan and maleic anhydride, is closely related to the use of lattice oxygen from its molybdenum trioxide component. In fact, it appears that a partially reduced lattice may be more effective in formation of partial oxidation products since selectivity toward partial oxidation products is seen to increase with the pulse number in oxygen-free transient response experiments (*21*). When the percentage of unlabeled oxygen incorporated into maleic anhydride is calculated, we see that about 90% of all oxygen present in maleic anhydride is derived from the catalyst lattice. This result is quite significant since chemisorbed oxygen was previously hypothesized to be essential for the formation of maleic anhydride (*8*).

TABLE 3

Percentage Normalized Conversion of Gas-Phase Oxygen

Pulse number	MoO_3	$MnMoO_4$	$MnMoO_4/MoO_3$
1	93	77	35
2	82	71	30
3	56	61	28
4	68	58	29
5	53	52	28

The catalysts used in the isotopic labeling experiments were degassed in vacuum to clean the surfaces of any adsorbed gases prior to reaction experiments and were completely isolated from the atmosphere to prevent contamination with atmospheric oxygen. Characterization experiments performed over these catalysts using laser Raman spectroscopy, BET surface area measurements, and X-ray photoelectron spectroscopy techniques showed no change in these samples due to evacuation at high temperature. In order to ensure that the source of unlabeled oxygen (^{16}O) was indeed the crystal lattice of the catalyst, a series of oxygen exchange experiments was performed where catalyst samples were pulsed with pure $^{18}O_2$ using the same parameters that were used in the transient response experiments and the concentration of labeled and unlabeled oxygen was monitored using the gas chromatograph–mass spectrometer system. These experiments showed that there was no oxygen exchange between the catalyst lattice and the gas phase under the conditions of the transient response experiments.

When the activities of catalysts are compared in the presence and in the absence of oxygen, the job distribution between the two components of the two-phase catalysts becomes clearer. The comparison of the activities shows that when there is excess oxygen in the gas phase, manganese molybdate is more active in 1,3-butadiene conversion than MoO_3. When the gas phase is completely depleted of gas-phase oxygen, however, the catalytic activity of the two pure phases becomes completely reversed, with molybdenum trioxide becoming much more active than $MnMoO_4$. This result clearly shows that manganese molybdate is strongly dependent on the presence of gas-phase oxygen whereas molybdenum trioxide is quite efficient in utilizing the oxygen in its crystal lattice. These results are in agreement with our steady-state oxidation experiments where the effect of oxygen partial pressure on the activity and selectivity of the same catalysts was investigated using a large range of oxygen concentrations varying from oxygen-deficient conditions to excess-oxygen conditions (*23*). In that study, $MnMoO_4$ was shown to be much more sensitive to the gas-phase oxygen concentration whereas molybdenum trioxide appeared not to be effected much by this parameter, indicating both its effectiveness in utilizing lattice oxygen and its inability to make efficient use of the gas-phase oxygen.

The high-temperature oxygen uptake measurements provide further evidence about the catalytic job distribution of the components of the two-phase catalyst. These studies show that manganese molybdate has a higher oxygen uptake than MoO_3—a result which is in agreement with the findings of Bielanski and Haber (*24*), who reported a study on oxygen adsorption over transition metal oxides and correlated the oxygen adsorption with the ionization potential of the cation. This result, once again, shows that the molybdenum trioxide phase of the selective catalyst is not very effective in chemisorbing oxygen although it is seen to incorporate its lattice oxygen quite readily into the hydrocarbon molecule. The manganese molybdate phase, on the other hand, with its high oxygen uptake, can use gas-phase oxygen as indicated by the transient response and steady-state oxidation experiments. When similar measurements are performed following a reduction procedure over the same catalysts, the MoO_3 phase exhibits much higher oxygen uptake than the $MnMoO_4$ phase. This, in turn, indicates a higher degree of reduction of the MoO_3 phase since the difference between the amounts of oxygen taken up over the fresh and the reduced catalyst is due to the consumption of oxygen to reoxidize the reduced surface sites. This finding is, again, indicative of the lattice oxygen of MoO_3 being much more readily available to oxidize the hydrocarbon molecule than the lattice oxygen of the $MnMoO_4$ phase.

The results obtained in this study, when combined with our previous findings over the same catalytic system, lead us to consider a catalytic job distribution in which the molybdenum trioxide phase has the active sites for partial oxidation through insertion of oxygen from its lattice. It does not, however, seem to be readily capable of reoxidizing the surface sites with oxygen from the gas phase. This is where the synergy (for which intimate contact between the two phases appears to be the key) comes into effect. The manganese molybdate phase, which is shown to depend much more strongly on the presence of gas-phase oxygen for its activity, provides oxygen to the MoO_3 component through an oxygen-spillover mechanism. The fact that the two-phase catalyst exhibits a much higher activity than either of its pure-phase constituents in the presence of oxygen, although its activity falls between those of the pure phases when there is no oxygen in the feed stream, is consistent with the spillover hypothesis.

Molybdenum trioxide is seen to be more active in the absence of gas-phase oxygen than in its presence. This finding seems to suggest a competition between oxygen and the hydrocarbon for the same catalytic site over MoO_3 surfaces. If this is the case, then the synergy effect may be operating through an oxygen spillover process where an active form of oxygen for reoxidizing the catalytic sites on MoO_3 is provided by the $MnMoO_4$ phase. One possible form of oxygen is the nucleophilic oxygen (O^{2-}) as suggested by Delmon and co-workers (*25*, *26*) for a Sb_2O_4/MoO_3 system. This form of oxygen has also been suggested by Bielanski and Haber (*24*) for filling up the oxygen vacancies created in the lattice of oxidation catalysts due to reduction with the hydrocarbon. In our case, it is possible that manganese molybdate not only chemisorbs gas-phase oxygen more readily than molybdenum trioxide, but also allows it to migrate to the surface of MoO_3 in an activated form as nucleophilic oxygen (O^{2-}) which is, in turn, used for regeneration of the active sites reduced by the partial oxidation reactions on the molybdenum trioxide phase.

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