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Effect of O_2 Concentration on Selective and Complete Oxidation of 1,3-Butadiene, Furan, and Maleic Anhydride over $MnMoO_4/MoO_3$ Catalysts

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Oxidation experiments of 1,3-butadiene, furan, and maleic anhydride have been performed over $MnMoO_4/MoO_3$ catalysts and their pure-phase constituents. The effect of oxygen concentration on catalytic activity and selectivity of these catalysts has been investigated. MoO_3 catalysts containing $MnMoO_4$ as a coexisting phase have been found to be active and selective for maleic anhydride formation for all feed materials and over a wide range of oxygen concentrations. The activity of the molybdenum trioxide catalyst has been found to be least affected by the concentration of gas-phase oxygen. Partial conversion of maleic anhydride to CO_2 has been observed over all three catalysts with $MnMoO_4$ showing the highest activity for complete oxidation.

1. INTRODUCTION

Maleic anhydride is among the most important partially oxidized hydrocarbon derivatives, particularly in the plastics industry. In recent years, the main feedstock for maleic anhydride production has switched to C_4 hydrocarbons from benzene, mainly due to the tighter emission controls and rising prices of benzene. Consequently, several studies have been performed dealing with the partial oxidation of C_4 hydrocarbons. Many studies have centered on vanadium–phosphorus–oxide (VPO) catalysts, similar to those used in benzene oxidation (*1–8*), while studies using molybdates and molybdenum oxides are fewer (*9, 10*). Ozkan and Schrader have reported on the catalytic behavior of $NiMoO_4$ and $CoMoO_4$ catalysts with excess MoO_3 for selective oxidation of C_4 hydrocarbons (*11–14*). The number of studies dealing with the oxidation of intermediates or products of the C_4 hydrocarbon oxidation reported in the literature is also very limited (*13, 15, 16*).

In an earlier paper, we have reported the synergy observed when the surfaces of MoO_3 were brought into contact with $MnMoO_4$ (*17*). The paper, which dealt with the comparison of the catalytic behavior of the two-phase catalyst ($MnMoO_4/MoO_3$) and its pure phase constituents in 1-butene oxidation, also presented detailed results from characterization studies performed over single-phase and two-phase catalysts.

This paper presents the results of studies of the effect of oxygen concentration on the selective oxidation of 1,3-butadiene and furan over both pure phases (MoO_3 and $MnMoO_4$) and the two-phase catalyst ($MnMoO_4/MoO_3$). These two C_4 hydrocarbons are intermediates that are generally accepted in the reaction scheme of 1-butene conversion to maleic anhydride. These studies provide some important clues about the role of oxygen in the synergistic mechanism. Results of the effect of oxygen concentration on the oxidation of maleic anhydride are also presented. These investigations provide evidence of maleic anhydride oxidation and show the effect of oxygen concentration on maleic anhydride disappearance.

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2. EXPERIMENTAL METHODS

2.A. Catalyst Preparation and Characterization

Pure phase $MnMoO_4$ catalyst was synthesized by a precipitation technique using aqueous solutions of ammonium heptamolybdate and manganese chloride as described previously (*17*). Pure phase MoO_3 was used as supplied (Aldrich). The two-phase catalyst was prepared by a stepwise, wet impregnation technique. Catalyst samples were pressed into pellets under a pressure of 15,000 psi. The catalyst particle size used in the reactor was 2–3 mm. All three catalysts were extensively characterized using BET surface area measurement, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, laser Raman spectroscopy, and Raman microprobe techniques. Details of the characterization studies have been reported previously (*17*).

2.B. Oxidation Experiments to Assess the Effect of O_2 Concentration

Steady-state selective oxidation of 1,3-butadiene, furan, and maleic anhydride was studied using the fixed-bed, integral reactor system described previously (*17*). The composition of the gas feed mixture was maintained using Tylan mass flow controllers. Introduction of furan and maleic anhydride to the system was achieved by means of a saturator system consisting of a sealed stainless-steel cylinder with inlet and outlet gas streams. Nitrogen was bubbled through the saturator, which was maintained at 0°C for furan feed, and 60°C for maleic anhydride feed. Hydrocarbon concentration was calculated using Raoult's Law, and saturation of the stream was checked by lowering the nitrogen flow rate and measuring the hydrocarbon concentration to ensure that the concentration did not change due to a change in the flow rate and that the N_2 stream was saturated at the calculated level. A second nitrogen stream was used to dilute the mixture to the desired concentration and to achieve the desired flow rate. The reactor was kept at 480°C for all experiments by immersion in a fluidized sand bath, and the temperature was checked at five points along the reactor by use of thermocouples. Compositional analysis of the feed and product gas streams was performed using on-line gas chromatography. The reactor pressure was 5 psig. The catalyst particles were mixed uniformly with SiC particles of equal size to provide dilution of the catalyst with an inert solid. The catalyst particles accounted for less than 10% of the total volume of solids present in the reactor. The total catalyst surface area in the reactor was kept constant at 30 m^2 for all runs.

For the 1,3-butadiene oxidation studies, operating conditions were: 1,3-butadiene concentration (mole percent) 2.40%; volumetric flow rate of hydrocarbon, 738 cm^3 (STP)/h; total molar flow rate, 1.37 gmol/h. For furan and maleic anhydride oxidation studies, operating conditions were: furan concentration (mole percent), 1.94%; volumetric flow rate of furan, 593 cm^3 (STP)/h; total molar flow rate, 1.37 gmol/h; maleic anhydride concentration (mole percent), 0.1%. Maleic anhydride concentrations were kept at lower values than those of 1,3-butadiene and furan so that they would represent more closely the actual amounts found in the product stream.

The percentage conversion of feed hydrocarbon is defined as

$$\frac{\text{moles of hydrocarbon consumed}}{\text{moles of hydrocarbon in feed}} \times 100\%.$$

The yield of product A is defined as

$$\frac{\text{moles of } A \text{ produced}}{\text{moles of hydrocarbon in feed}} \times \frac{1}{\gamma} \times 100\%,$$

where γ is the ratio of the number of carbon atoms in feed hydrocarbon to the number of carbon atoms in the product.

The percentage selectivity to product A is defined as

$$\frac{\text{moles of } A \text{ produced}}{\text{moles of hydrocarbon consumed}} \times \frac{1}{\gamma} \times 100\%.$$

The effect of oxygen concentration on the selective and complete oxidation of the three hydrocarbon feeds was studied by performing steady-state reaction experiments at oxygen-deficient and oxygen-abundant levels over each of the three catalysts with each of the three feeds. The oxygen concentration was varied from 3.9 to 23.4%, while the total molar flow rate was held constant by varying the flow rate of the second N_2 stream to compensate for the changing O_2 flow. The maleic anhydride oxidation experiments were repeated at a lower oxygen concentration level which ranged from 0.2 to 1.3%. The hydrocarbon flow rate was also maintained at the levels given above.

3.RESULTS

3.A. *Catalyst Characterization Studies*

The compositional analysis of the Mn MoO_4 catalyst, obtained by energy dispersive X-ray analysis technique, showed a 1 : 1 ratio of Mn : Mo, indicating stoichiometric composition. The two-phase catalyst used in this study had $MnMoO_4$ to MoO_3 ratio of 0.15. The BET technique gave specific surface area measurements of 0.7, 1.9, and 2.1 m^2/g for MoO_3, $MnMoO_4$, and Mn MoO_4/MoO_3 catalysts, respectively. The X-ray diffraction patterns obtained from the pure phases showed close agreement with those previously reported in the literature (*18*). The two-phase catalyst gave an X-ray diffraction pattern identical to that of pure MoO_3. It was not possible to identify the *d*-spacings that correspond to $MnMoO_4$. The laser Raman spectroscopy, however, clearly showed the presence of both MoO_3 and $MnMoO_4$ in the two-phase catalyst. The scanning electron microscopy technique verified the two-phase nature of the $MnMo_4/MoO_3$ catalysts by revealing the intimate contact between MoO_3 and $MnMoO_4$.

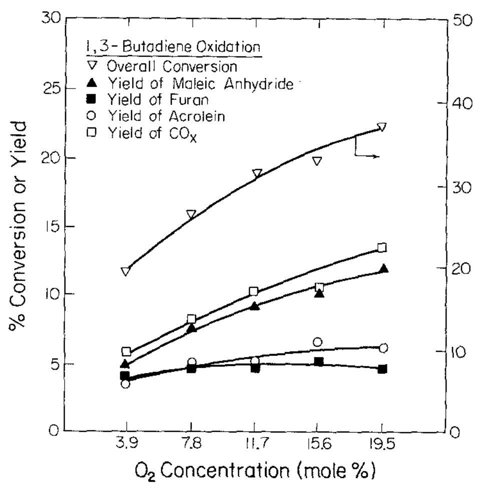

FIG. 1. Variation of conversion and yield with O_2 concentration in 1,3-butadiene oxidation over pure MoO_3 catalyst.

3.B. *Oxidation of 1,3-Butadiene*

The effect of oxygen concentration in the oxidation of 1,3-butadiene over pure MoO_3 catalyst is shown in Fig. 1. It is seen that carbon oxides are the major products at all O_2 concentration levels. Yields of maleic anhydride and acrolein increase throughout the O_2 concentration range studied, while the yield of furan begins to decrease at higher O_2 levels. While the yield of CO_x is always greater than that of maleic anhydride, the difference between the two grows at higher O_2 concentrations. When selectivities are calculated, the selectivity to acrolein is seen to go through a broad maximum, as does selectivity to maleic anhydride, while the selectivity to CO_x shows an increasing trend. Selectivity to furan steadily decreases.

The results of oxidation of 1,3-butadiene over pure $MnMoO_4$ catalyst are shown in Fig. 2. $MnMoO_4$ is seen to be a much more active catalyst than MoO_3 for 1,3-butadiene oxidation. Overall conversion levels of 1,3-butadiene over $MnMoO_4$ reached 72%, while the highest conversion level over MoO_3 was only 38%. The other striking difference between these two pure phases is

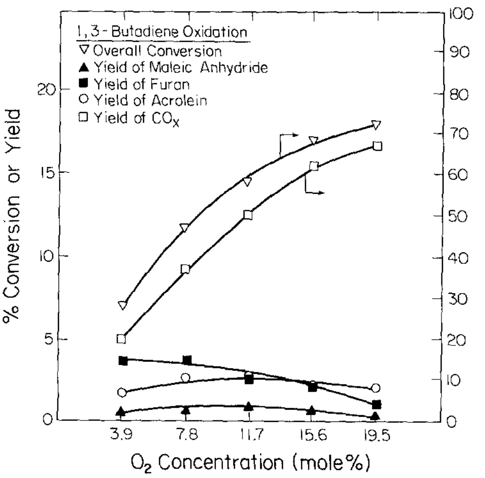

FIG. 2. Variation of conversion and yield with O_2 concentration in 1,3-butadiene oxidation over pure $MnMoO_4$ catalyst.

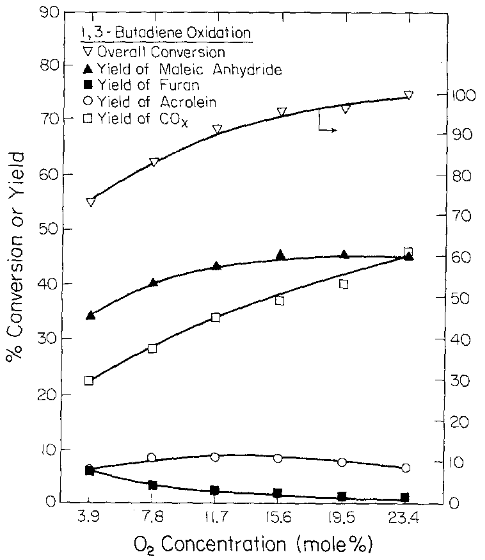

FIG. 3. Variation of conversion and yield with O_2 concentration in 1,3-butadiene oxidation over MoO_3 catalyst promoted with $MnMoO_4$.

their sensitivity to oxygen concentration. Pure $MnMoO_4$ appears to be much more sensitive to changes in oxygen concentration, becoming much more active for CO_2 at higher O_2 concentrations. As in oxidation runs over MoO_3, both overall conversion and yield of CO_x show an increasing trend with O_2 concentration, and CO_x is once again the major product. Yields of all partial oxidation products are low (less than 5%) and decrease over the increasing O_2 range, with furan showing the fastest decrease.

Results of oxidation of 1,3-butadiene over the promoted catalyst are presented in Fig. 3. The most striking result is that yields of maleic anhydride have now risen above those of CO_x for all oxygen concentrations except the highest, 23.4%, where the two curves meet. Yield of maleic anhydride increases, then levels off at O_2 concentrations above 10%, while yield of CO_x appears to increase steadily. It is also seen that the promoted catalyst ($MnMoO_4/MoO_3$) shows the highest activity among the three catalysts tested at every oxygen concentration level, with activity increasing at higher oxygen concentrations. Yields of other partial oxidation products are again relatively low (less than 10%). Yield of acrolein shows a broad maximum at 15.6% O_2, while furan yield decreases over the entire range.

3.C. *Oxidation of Furan*

The results of furan oxidation over pure MoO_3 are shown in Fig. 4. The overall con-

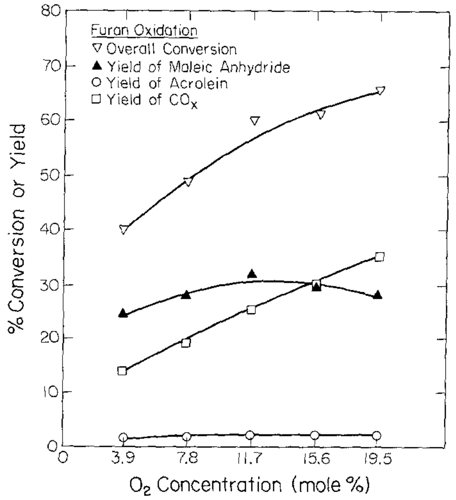

FIG. 4. Variation of conversion and yield with O_2 concentration in furan oxidation over pure MoO_3 catalyst.

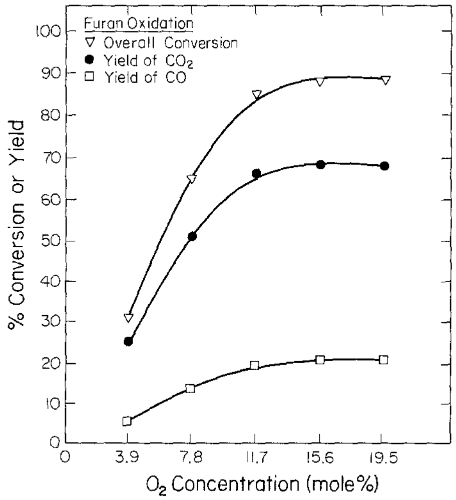

FIG. 5. Variation of conversion and yield with O_2 concentration in furan oxidation over pure $MnMoO_4$ catalyst.

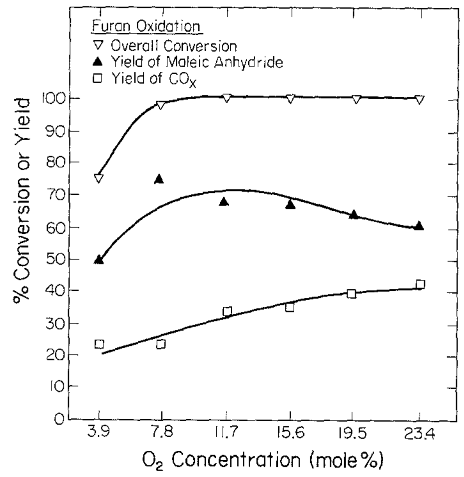

FIG. 6. Variation of conversion and yield with O_2 concentration in furan oxidation over MoO_3 catalyst promoted with $MnMoO_4$.

version rises gradually with increasing O_2 concentration. It is also noted that maleic anhydride yield is greater than that of CO_x, although the maleic anhydride yield does begin to decrease at an oxygen concentration of 12%, while CO_x yield increases linearly with O_2 concentration. Acrolein yields are very low, around 2%.

The effect of oxygen concentration on furan oxidation over the pure $MnMoO_4$ catalyst is shown in Fig. 5. A rapid increase in activity is observed as oxygen concentration is increased from oxygen-deficient conditions to excess oxygen conditions. In contrast with the data of Fig. 4, no maleic anhydride is formed over this catalyst; CO_2 and CO are the only detectable products. Figure 5 shows the yields of both CO and CO_2 increasing with oxygen concentration, while CO_2 yield increases more sharply with increasing oxygen concentration than that of CO.

The variation in conversion and product yields in furan oxidation over the two-phase catalyst is shown in Fig. 6. Maleic anhydride is the major product throughout the oxygen concentration range studied. It is also seen that the conversion level of furan increases very sharply in the oxygen concentration range from 4 to 8% and reaches 100%. Maleic anhydride yield goes through a maximum at about 8% O_2 concentration level, while yields of CO_x continuously increase. Selectivity results are shown in Fig. 7. It is interesting that selectivity to maleic anhydride and CO_x mirror each other almost ex-

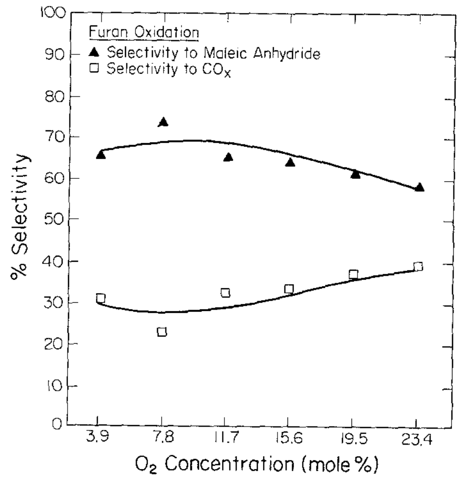

FIG. 7. Variation of selectivity with O_2 concentration in furan oxidation over MoO_3 catalyst promoted with $MnMoO_4$.

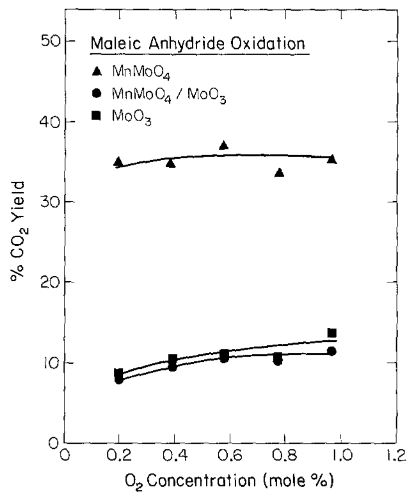

FIG. 8. Variation of CO_2 yield with O_2 concentration in maleic anhydride oxidation over MoO_3, $MnMoO_4$, and MoO_3 catalyst promoted with $MnMoO_4$.

actly: as maleic anhydride approaches its maximum, CO_x approaches its minimum; as selectivity to maleic anhydride begins to decrease, selectivity to CO_x begins to increase, and they both appear to level off as the oxygen concentration increases over 19.5%.

3.D. Oxidation of Maleic Anhydride

Carbon dioxide was the only detectable product in maleic anhydride oxidation experiments. The variation in carbon dioxide yield with oxygen concentration for all three catalysts is presented in Fig. 8. As in oxidation runs with the other hydrocarbon feeds, pure $MnMoO_4$ is shown to be the most active catalyst for complete oxidation, followed by molybdenum trioxide. This trend remained the same when similar experiments were performed using higher oxygen concentrations ranging from 3.9 to 23.4%. All three catalysts seem to be fairly insensitive to oxygen concentration for complete oxidation of maleic anhydride, showing only a slight increase in CO_2 yield with increasing oxygen concentration.

4. DISCUSSION

Oxidation experiments performed using 1-butene (*19*) and possible reaction intermediates 1,3-butadiene and furan over single-phase catalysts (MoO_3 and $MnMoO_4$) and the two-phase catalyst ($MnMoO_4/MoO_3$) showed that the synergism was present over the two-phase catalyst for every feed material and at every oxygen concentration ranging from oxygen-deficient conditions to excess oxygen conditions. The catalyst which contained both the molybdenum oxide and the simple molybdate phases together was clearly more active and more selective for partial oxidation products, especially for maleic anhydride.

In general, the activity of each catalyst increased as the feed was changed from 1-butene to 1,3-butadiene to furan. This increase in activity, however, was more pronounced over pure MoO_3 than it was over pure $MnMoO_4$ or over the two-phase catalyst ($MnMoO_4/MoO_3$). Considering that the theoretical oxygen requirement is the highest for oxidation of 1-butene and the lowest for oxidation of furan, this observation may suggest that the activity of MoO_3 is a stronger function of the theoretical oxygen requirement of the feed material than were the activities of the other two catalysts. This, in turn, may be closely related to the ineffectiveness of MoO_3 in utilizing gas-phase oxygen directly for either oxidizing the hydrocarbon or regeneration of its reduced surface sites.

In comparing the sensitivity of the three catalysts to changes in gas-phase oxygen concentration, MoO_3 appeared to be least affected, while $MnMoO_4$ exhibited the strongest sensitivity to changes in oxygen concentration, becoming more active as oxygen concentration increased. The dependency on oxygen concentration became stronger as feed was changed from 1-butene to 1,3-butadiene to furan.

When dependency of the product distribution on oxygen concentration over the catalysts that yielded maleic anhydride was examined, it was seen that increasing oxygen concentration favored maleic anhydride formation, but that CO_x formation was favored more srongly. This observation became more apparent when selectivities were compared at different oxygen concentrations. Selectivity to maleic anhydride appeared to either stay constant or decline with increasing oxygen concentration whereas selectivity to CO_x increased steadily. This enhanced selectivity to CO_x may be the result of either increased total oxidation of the feed and the intermediates, or the oxidation of the product (maleic anhydride) itself. However, furan oxidation over these catalysts gave high yields to maleic anhydride, and furan was the only feed material which gave maleic anhydride as the major product over pure MoO_3. This evidence points to furan converting preferentially to maleic anhydride rather than directly to CO_x over MoO_3. Therefore, the enhanced yield of CO_x at higher oxygen concentrations over these catalysts is probably due to oxidation of the maleic anhydride itself.

The $MnMoO_4$ catalyst was the most active oxidizing catalyst, with CO_x being the major product over the entire oxygen concentration range studied with each feed. The only exception occurred in 1-butene oxidation (*19*), where under oxygen deficient conditions, 1,3-butadiene was the major product. Thus, while pure MoO_3 does not appear to use gas-phase oxygen efficiently, Mn MoO_4 readily utilizes it for complete oxidation.

Oxidation experiments using maleic anhydride as feed material over each of the catalysts showed that the pure phase Mn MoO_4 catalyst yielded large amounts of CO_2 in comparison to the pure MoO_3 and the two-phase catalyst ($MnMoO_4/MoO_3$). While $MnMoO_4/MoO_3$ catalyst gave the lowest CO_2 yield, it was very close to that of the pure phase MoO_3 catalyst. Thus, it appears that the synergistic effect is not one of simply preventing further oxidation of maleic anhydride over MoO_3, but rather one of actually increasing the rate of formation of the partial oxidation products as evidenced by very pronounced increases observed both in overall conversion and in selectivity levels when the two phases were combined. Also, the studies performed using maleic anhydride as feed indicate that the lack of maleic anhydride formation over $MnMoO_4$ cannot be explained by complete oxidation of maleic anhydride since the conversion of maleic anhydride to CO_2 observed over $MnMoO_4$ was far from complete.

For all reaction runs, the catalyst particles constituted only a small fraction of the solids present in the reactor (about 10% by volume) since catalyst particles were uniformly mixed with SiC particles of equal size to dilute the catalyst and ensure a constant residence time in the gas phase. The differences in the performances of the three catalysts cannot be explained by a change in residence time or a change in total catalyst surface area since these parameters were kept constant for each run. Blank reactor runs were also performed to see the contribution of homogeneous reactions both by using a completely empty reactor and by packing the reactor with inert SiC particles. Neither set of experiments gave a substantial conversion of the hydrocarbon feed, leading us to conclude that the role of any homogeneous reaction under the conditions we used in these studies was negligible. The experiments performed to check the reproducibility of the data showed the data points were reproducible within 5%.

The results of the studies performed using three different feed materials (1-butene, 1,3-butadiene, furan) to examine the effect of gas-phase oxygen concentration on catalytic behavior of single-phase catalysts (MoO_3, $MnMoO_4$) and the two-phase catalyst which contains both phases in intimate contact suggest that the key to the synergism lies in the ability of each of the pure phases to utilize gas-phase oxygen, either for direct oxidation of the hydrocarbon molecule or for regeneration of the reduced oxidation sites. The results obtained in this study suggest that a possible job distribution between the two components of the two-phase catalyst may involve use of lattice oxygen from the MoO_3 phase followed by reoxidation of the reduced surface sites through an oxygen spillover mechanism where gas-phase oxygen chemisorbed by the $MnMoO_4$ phase migrates to the MoO_3 surface in an activated form. The studies we performed using isotopic labeling and high-temperature oxygen chemisorption techniques provide further evidence of the catalytic job distribution suggested in this paper (*20*).

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