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MoO_3 Catalysts Promoted by $MnMoO_4$

II. Effect of O_2 Concentration and Temperature in Selective Oxidation of 1-Butene to Maleic Anhydride

Stimulated by the rapid shift from benzene to C_4 hydrocarbons as feedstock for maleic anhydride production, several studies have been reported dealing with selective oxidation of C_4 hydrocarbons. Most of the previous investigations have used V–P–O (*1–5*) or V–Mo–O catalysts (*6*); studies on molybdates or molybdenum oxides are far fewer (*7–10*). In a previous paper, we have reported the results of a study where we focused our attention on catalytic activity and selectivity of pure MoO_3 and attempted to modify its catalytic behavior by bringing its surfaces into close contact with $MnMoO_4$ (*11*). While our characterization experiments revealed the two-phase nature of the $MnMoO_4/MoO_3$ catalyst, the activity studies showed a pronounced "promoter" effect in selective oxidation of both 1-butene and 1,3-butadiene to maleic anhydride, suggesting a possible synergy between the two phases. This note presents the results of our selective oxidation studies where the effect of temperature and oxygen partial pressure on catalytic behavior of the pure phases (MoO_3 and $MnMoO_4$) as well as the two-phase catalyst ($MnMoO_4/MoO_3$) has been investigated in conversion of 1-butene to maleic anhydride.

Pure $MnMoO_4$ catalysts were synthesized by precipitation as described previously (*11*). The two-phase catalysts were prepared by mixing MoO_3 powder with a slurry of $MnMoO_4$ and evaporating the water. All samples were calcined under a flow of O_2 at 500°C. All catalysts were characterized in detail using BET surface area measurement, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, laser Raman spectroscopy and Raman microprobe techniques. The surface areas of MoO_3, $MnMoO_4$, and the two-phase catalysts ($MnMoO_4/MoO_3$, mole ratio = 0.15) used in this study were 2.1, 1.7, and 2.4 m^2, respectively. The characterization studies clearly showed the coexistence of the two phases, but did not reveal any new phases or compounds formed, as reported previously (*11*).

Steady-state selective oxidation of 1-butene was studied using a fixed-bed, integral reactor system described previously (*11*). The total surface area of the catalyst present in the reactor was kept constant at 30 m^2 for all experiments reported in this article. The operating conditions were as follows: reactor pressure, 5 psig (34,473.7 N/m^2); 1-butene concentration (by volume) in the feed mixture, 2.40%; volumetric flow rate of hydrocarbon, 738 cm^3(STP)/h; total molar flow rate, 1.37 mol/h.

The yield of product *A* is defined as

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

where γ is the ratio of number of C atoms in the reactant to the number of C atoms in the product.

To assess the effect of temperature on conversion and yield, butene oxidation experiments were performed where all the reaction parameters except temperature were kept constant. For these experiments, O_2 and N_2 concentrations were maintained at 19.52 and 78.08%, respectively. Reaction temperature was varied in the range from 390°C (663 K) to 510°C (783 K).

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Effect of oxygen concentration was also investigated by varying the feed composition from oxygen-deficient conditions to excess oxygen conditions. For these experiments, the reaction temperature was maintained at 480°C (753 K). The total molar flow rate and the hydrocarbon concentration were kept constant while the nitrogen concentration was varied to compensate for the changing oxygen concentration. The ranges for the oxygen and nitrogen concentrations were 3.9 to 23.4% and 74.2 to 93.7%, respectively.

Figures 1a, 1b, and 1c show the effect of temperature on the catalytic behavior of pure MoO_3, pure $MnMoO_4$, and the two-phase catalyst, respectively. 1,3-Butadiene and carbon dioxide are the major reaction products over MoO_3. Small quantities of maleic anhydride, furan, acrolein, and some cracking products are also observed in the product stream. The fractional conversion of 1-butene, which does not include the isomerization reactions, increases with temperature, and the shape of the curve suggests an exponential relationship. The yields of 1,3-butadiene, maleic anhydride, and furan also increase with temperature, although the functional dependency of 1,3-butadiene yield on temperature seems to be stronger than those of maleic anhydride and furan yields. It is also noted that maleic anhydride does not form at temperatures below 420°C. The major reaction product over $MnMoO_4$ is CO_2. Other reaction products are 1,3-butadiene, furan, and acrolein. No maleic anhydride is detected over this catalyst in the temperature range from 390 to 510°C. The conversion of 1-butene increases with a constant slope as the reaction temperature increases. The yield of CO_2 increases with almost the same slope. Over the two-phase catalyst, the conversion of 1-butene levels off after a sharp increase with increasing temperature. Maleic anhydride is the major reaction product over this catalyst throughout the temperature range used in this study. At temperatures above 500°C, however, the yield of CO_2 surpasses that of maleic anhydride. The acrolein data, which are not included in the figure, indicate that the acrolein yield increases over all three catalysts with temperature; however, the highest yield is observed over the two-phase catalyst. Although not included in the figure, substantial isomerization is also observed over all three catalysts. Over the MoO_3 catalyst, the yield of *cis*-2-butene is consistently higher than that of *trans*-2-butene. Over the $MnMoO_4$ and $MnMoO_4/MoO_3$ catalysts, on the other hand, it is *trans*-2-butene which is favored over *cis*-2-butene. It is also noted that isomerization reaction seems to increase with temperature over pure MoO_3, but steadily decreases over both $MnMoO_4$ and $MnMoO_4/MoO_3$ catalysts.

Figures 1d, 1e, and 1f show the effect of gas-phase oxygen concentration on product yield over the three catalyst samples. Over MoO_3, the conversion of 1-butene and the yields of various reaction products appear quite insensitive to oxygen concentration, showing a slight increase with increasing O_2 concentration. The largest reaction product over the entire concentration range is 1,3-butadiene followed by CO_2. Maleic anhydride and furan are produced in very small quantities. The conversion of 1-butene shows a much stronger dependency on O_2 concentration over pure $MnMoO_4$ catalyst, increasing linearly from oxygen-deficient conditions to excess oxygen conditions. The yield of CO_2 increases linearly whereas the yield of 1,3-butadiene decreases with increasing oxygen concentration. Furan and acrolein are produced in small quantities and no maleic anhydride is detected in the product stream at any O_2 concentration. It is also noted that oxygen-deficient conditions favor 1,3-butadiene formation whereas presence of excess oxygen seems to promote complete oxidation, with CO_2 becoming the major reaction product at O_2 concentrations above 7.8%. Over the two-phase catalyst, the conversion of 1-butene and the yield of maleic anhydride increase

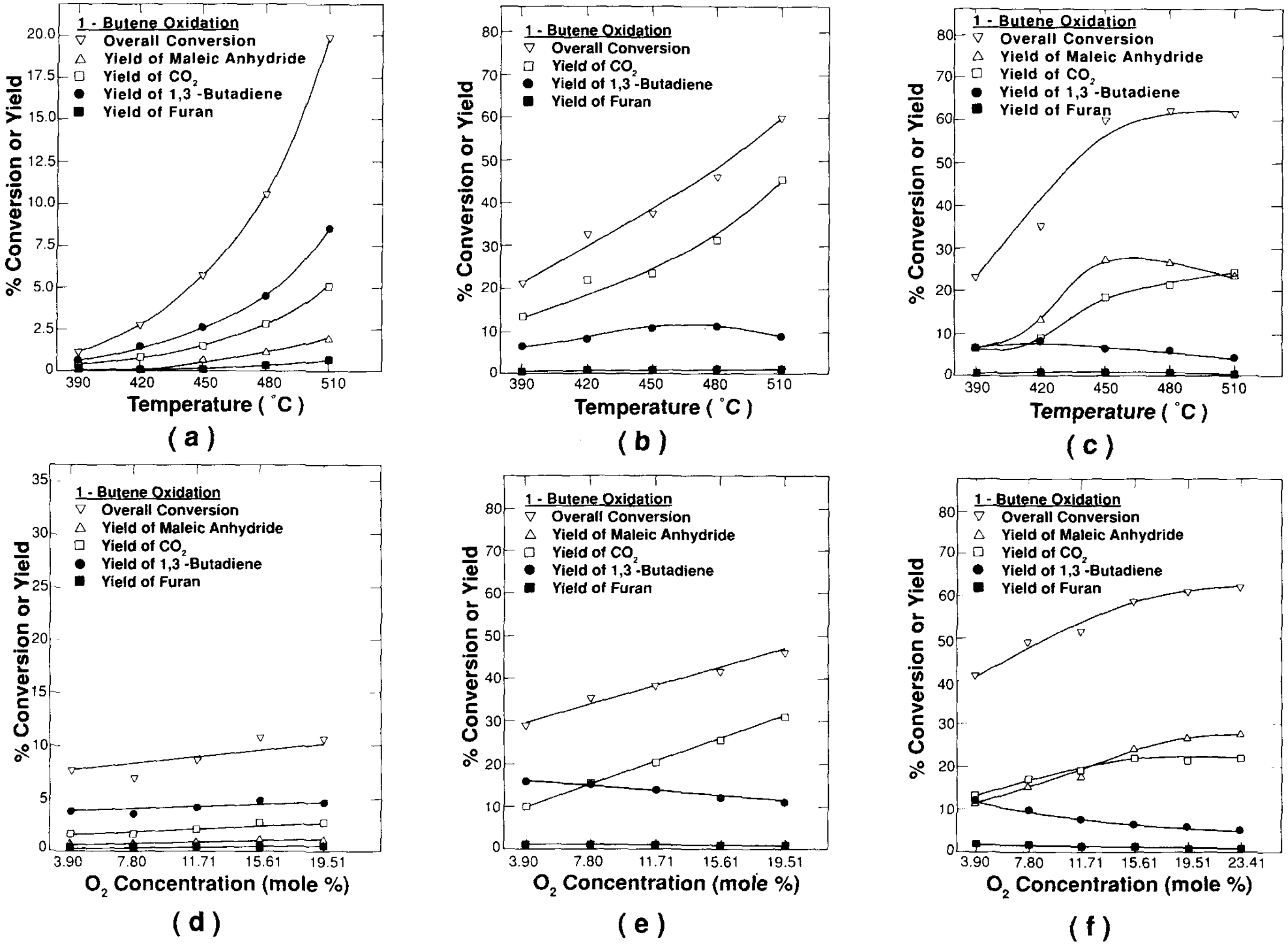

FIG. 1. Effect of temperature and oxygen concentration in 1-butene oxidation. (a) MoO_3, (b) $MnMoO_4$, (c) $MnMoO_4/MoO_3$, (d) MoO_3, (e) $MnMoO_4$, (f) $MnMoO_4/MoO_3$.

steadily whereas yield of 1,3-butadiene decreases with increasing gas-phase O_2 concentration. The yield of CO_2 shows an increase, then levels off at higher O_2 concentrations, leaving maleic anhydride as the major product. The yield of acrolein, which increases with oxygen concentration, is higher over this catalyst than it is over the pure phases.

1-Butene oxidation experiments performed over $MnMoO_4/MoO_3$ catalyst and its pure phase constituents showed a strong synergy, which was in effect over a wide range of temperatures and O_2 concentrations. The two-phase catalyst not only showed a higher activity than its pure phase components, but gave a higher selectivity toward partial oxidation products, especially maleic anhydride.

$MnMoO_4/MoO_3$ exhibited the highest sensitivity to temperature, increasing its activity very rapidly in the low-temperature region. At conversion levels above 60%, however, the activity remained essentially the same, suggesting a possible inhibition effect by the reaction products. Another possible explanation for this leveling off could be deactivation of the catalyst at elevated temperatures. However, postreaction characterization and steady-state experiments performed over prolonged reaction times did not show any indication of decay. Reproducibility studies performed using fresh catalysts at elevated temperatures also showed that the leveling off in the activity was not due to catalyst deactivation.

The yield of maleic anhydride was observed to go through a broad maximum with temperature over the two-phase catalyst. The yield of CO_2 increased and, at higher temperatures, caught up with the yield of maleic anhydride yield, suggesting complete oxidation of the reactants and possibly of the product itself. Our maleic anhydride oxidation studies have confirmed this possibility by showing considerable levels of maleic anhydride conversion at elevated temperatures (*12*).

When the three catalysts were compared for their sensitivity to gas-phase O_2 concentration, it was seen that MoO_3 was not much affected, with conversion and product yields increasing very little from the oxygen-deficient region to the excess oxygen region. Over pure $MnMoO_4$, the effect of O_2 concentration on activity was much more visible. However, it was observed that excess oxygen conditions favored complete oxidation over this catalyst. The two-phase catalyst also showed a high sensitivity to O_2 concentration, but the presence of excess O_2 seemed to favor the formation of maleic anhydride more than the formation of complete oxidation products.

Our recent studies using isotopic labeling and oxygen chemisorption techniques pointed out that pure MoO_3 used lattice oxygen almost exclusively for the formation of partial oxidation products, but had very low oxygen uptake (*13*). $MnMoO_4$, on the other hand, was not very efficient in utilizing lattice oxygen, but had a high oxygen uptake under reaction conditions. Butene oxidation experiments, when combined with the results of our isotopic labeling and oxygen chemisorption studies, indicate that MoO_3 does not make efficient use of gas-phase oxygen. Pure $MnMoO_4$ uses gas-phase oxygen much more readily, but almost all of the activity is for complete oxidation. A possible job distribution between the components of the two-phase catalyst could involve incorporation of oxygen from the crystal lattice of MoO_3 leaving it with reduced surface sites. The role of the $MnMoO_4$ could be that of providing oxygen to the MoO_3 component of the catalyst through an oxygen spill-over mechanism, hence making regeneration (reoxidation) of the oxygen insertion sites on MoO_3 surface possible.

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