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$NiMoO_4$ Selective Oxidation Catalysts Containing Excess MoO_3 for the Conversion of C_4 Hydrocarbons to Maleic Anhydride

III. Selective Oxidation of 1,3-Butadiene and Furan

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The selective oxidation of 1,3-butadiene and furan to maleic anhydride over $NiMoO_4$ catalysts containing excess MoO_3 was investigated. Activity and selectivity measurements were performed using a fixed-bed, integral reactor system. The results were compared with those obtained for 1-butene oxidation which indicated the most selective component of the catalyst for maleic anhydride formation was a MoO_3 phase having a surface covering of $NiMoO_4$; similar results were found to be applicable for 1,3-butadiene and furan oxidation. $NiMoO_4$ was determined to be the catalyst component responsible for oxidative dehydrogenation of 1-butene; this phase also selectively blocked complete oxidation sites on MoO_3, thereby changing the selectivity in favor of maleic anhydride.

1. INTRODUCTION

The catalytic selective oxidation of C_4 hydrocarbons has been reported widely in the literature. Vanadium oxide catalysts (usually with phosphorus present) and molybdenum oxide catalysts (incorporating other transition metals to form simple molybdates) have been frequently employed in these studies (*1–7*). Among the C_4 hydrocarbon reactants which have been used are 1-butene, 1,3-butadiene, and furan. A commercially important product potentially resulting from such oxidation processes is maleic anhydride.

One of the earliest investigations of a C_4 hydrocarbon oxidation to maleic anhydride was reported by Moldavskii and Kernos (*8*). For Mo–Co, V–P, and Mo–P catalysts, a much higher yield of maleic anhydride was obtained when butadiene rather than butene was used as the reactant feedstock. Akimoto and Echigoya (*9, 10*) examined the oxidation of 1-butene and 1,3-butadiene using molybdena–titania catalysts; maleic anhydride was believed to be formed from butadiene adsorbed on Mo^{5+} sites, in contrast to CO_2 formation resulting form butadiene adsorbed on Ti^{4+} sites. Brkić and Trifirò (*6*) studied the reaction of 1-butene and 1,3-butadiene over V–P–O catalysts and have proposed a reaction pathway involving conversion of 1-butene to 1,3-butadiene by a redox mechanism utilizing lattice oxygen. Subsequent conversion of butadiene to maleic anhydride was believed to occur on another site involving an adsorbed oxygen species. The role of the partial pressure of oxygen in the oxidation of 1-butene and butadiene to maleic anhydride for V–P–O catalysts has been examined by Cavani *et al.* (*11*). Their model for the reaction pathway involves butadiene and furan as intermediate products. Ai (*12*) proposed the same reaction scheme for butene, butadiene, and furan oxidation over V_2O_5 and V_2O_5–P_2O_5 catalysts. He also indicated the formation of side products (mainly CO_x and some polymers) for each step and concluded that each intermediate step had different rates for the conversion to partially oxygenated products as compared to the conversion to

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side products. Ai and Suzuki (*13*) discussed the same reaction pathway involving the consecutive steps

$$C_4H_8 \rightarrow C_4H_8(\text{ads}) \rightarrow C_4H_6(\text{ads}) \rightarrow C_4H_4O(\text{ads}) \rightarrow \begin{matrix}\text{maleic}\\ \text{anhydride}\end{matrix}$$

for their studies of butene, butadiene, and furan oxidation over MoO_3–P_2O_5 catalysts containing Bi_2O_3.

These studies of C_4 hydrocarbon oxidation generally indicate that the following reaction pathway should be considered:

$$\begin{tikzcd}
\text{butene} \arrow[r] \arrow[d] & \text{butadiene} \arrow[r] \arrow[d] & {} \\
\text{side products} & \text{side products} & \\
& \text{furan} \arrow[r] \arrow[d] & \begin{matrix}\text{maleic}\\ \text{anhydride}\end{matrix} \\
& \text{side products} &
\end{tikzcd}$$

Detailed kinetic investigations of the mechanisms of these reactions have yet to be performed, but useful information about the performance of a catalyst for maleic anhydride synthesis can be obtained by using these various C_4 hydrocarbons which are capable of being converted to maleic anhydride. Previously, we have reported the conversion of 1-butene to maleic anhydride using nickel molybdate catalysts containing excess MoO_3; substantial amounts of butadiene and furan are formed in this conversion. In this paper we report the results of using butadiene and furan as feedstocks.

In the first two papers of this series, detailed preparation and characterization studies of $NiMoO_4$ catalysts containing excess MoO_3 were reported (*14, 15*). In the third paper (*16*), the results of the oxidation of 1-butene to maleic anhydride over these catalysts were presented, together with postreaction catalyst characterization. Our investigations have shown that the structural requirement for high maleic anhydride selectivity is the presence of a surface layer of $NiMoO_4$ adhering to MoO_3 crystallites. It was also indicated that the components of the selective catalyst have different roles in butene oxidation to maleic anhydride. In the present paper, we report the results of a similar investigation for the oxidation of 1,3-butadiene and furan. Emphasis is placed on the catalytic function of the catalyst phases in the complex reaction pathway previously reported in the literature for C_4 hydrocarbon oxidation.

2. EXPERIMENTAL METHODS

2.A. *Catalyst Preparation*

Pure $NiMoO_4$ was synthesized by precipitation using the procedure outlined in the first paper of this series (*14*). Catalysts containing excess MoO_3 were prepared by precipitation, impregnation, and solid-state reaction, also as described previously (*15*).

2.B. *Catalytic Activity and Selectivity Measurements*

Selective oxidation reaction experiments were performed using a continuous integral fixed-bed reactor system (*16*). The composition and flow rate of the gas feed mixture, consisting of oxygen, nitrogen, and 1,3-butadiene, were maintained using Tylan mass flow controllers. For furan oxidation experiments, a syringe pump (Sage Instruments, Model 341A) was used to introduce furan into the feed stream followed by evaporation in a heating chamber. For activity measurements, a reactor was used which had an inner diameter of 0.5 in. and a length of 15 in.; the catalyst bed was 9 in. long. The reactor was designed to permit zone heating with the use of several heating elements. The temperature in the reactor could be monitored radially and axially. Compositional analysis of the feed and product gas mixtures was performed using gas chromatography as described previously (*16*).

For butadiene studies, the following reactor parameters were maintained: oxygen partial pressure—0.176 atm; 1,3-butadiene partial pressure—0.017 atm; nitrogen partial pressure—0.807 atm; total molar flow rate 3.15 g-mol/h; volumetric flow rate of

1,3-butadiene—1200 cm^3(STP)/h; reaction temperature—480°C. For furan oxidation, a lower hydrocarbon concentration was used; the following parameters were constant: oxygen partial pressure—0.178 atm; furan partial pressure—0.008 atm; nitrogen partial pressure—0.814 atm; total molar flow rate—3.12 g-mol/hr; volumetric flow rate of furan—559 cm^3(STP)/h; reaction temperature—480°C.

Conversion and selectivity measurements were taken after steady state was reached, which in most cases was 8 h.

The percentage conversion for feed hydrocarbon HC is defined as

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

The percentage selectivity of product A is defined as

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

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

The percentage yield of product A is defined as

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

The rates of disappearance of the hydrocarbons are based on the unit surface area of the catalyst.

3. EXPERIMENTAL RESULTS

3.A. Activity and Selectivity Measurements for 1,3-Butadiene Oxidation

Similar to the 1-butene oxidation experiments, the results of the oxidation of butadiene by $NiMoO_4$ and MoO_3 show that the pure form of these catalysts produce the highest yields of carbon oxides. It was also noted that $NiMoO_4$ yielded no maleic anhydride; for MoO_3, maleic anhydride was produced, but in smaller quantities than all but the minor products. In contrast, $NiMoO_4$ catalysts containing excess MoO_3 possessed high maleic anhydride selectivity, while producing small amounts of CO_x.

Figure 1 shows the variation in the selectivities for the major reaction products as a function of the excess MoO_3 concentration (precipitated catalysts). The selectivity for maleic anhydride goes through a maximum as the percentage of excess MoO_3 is increased, with the maximum occurring at 15%. The selectivity for CO_x similarly goes through a minimum, coinciding at the same catalyst composition at the maximum for the maleic anhydride selectivity. Furan selectivity goes through a much broader minimum.

Table 1 provides the yields of reaction products (equal weights of catalyst being present in the reactor). Again, the highest yield of maleic anhydride results from using the catalyst containing 15% excess MoO_3.

Table 2 shows the rate of disappearance of 1,3-butadiene and the rate of formation

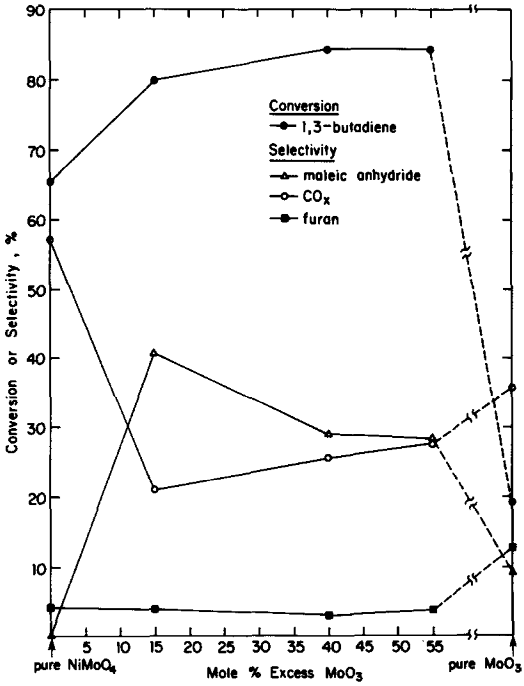

FIG. 1. Selective oxidation of 1,3-butadiene over precipitated $NiMoO_4$ catalysts as a function of excess MoO_3 concentration.

TABLE 1

Comparison of Yields for Precipitated $NiMoO_4$ Catalysts and Pure MoO_3 in 1,3-Butadiene Oxidation

	Yield (%)				
	Pure $NiMoO_4$	$NiMoO_4$ with 15% excess MoO_3	$NiMoO_4$ with 40% excess MoO_3	$NiMo_4$ with 55% excess MoO_3	Pure MoO_3
Furan	2.68	3.09	2.74	3.17	2.45
Maleic anhydride	0.00	32.47	25.48	23.86	1.74
CO_x	37.30	16.80	22.48	23.30	6.80

of CO_x for catalysts of various compositions. A comparison of the rates of disappearance of 1,3-butadiene shows that the activity increases with increasing percentages of excess MoO_3. Pure MoO_3 is the most active catalyst for butadiene oxidation, but it is apparent from the rates of formation of CO_x that the high activity of MoO_3 is an indication of its tendency to promote complete oxidation. The rate of formation of CO_x is observed to pass through a minimum as a function of excess MoO_3 concentration, indicating that pure compounds have the greatest tendency for complete combustion; intermediate catalyst compositions are more selective for partial oxidation products.

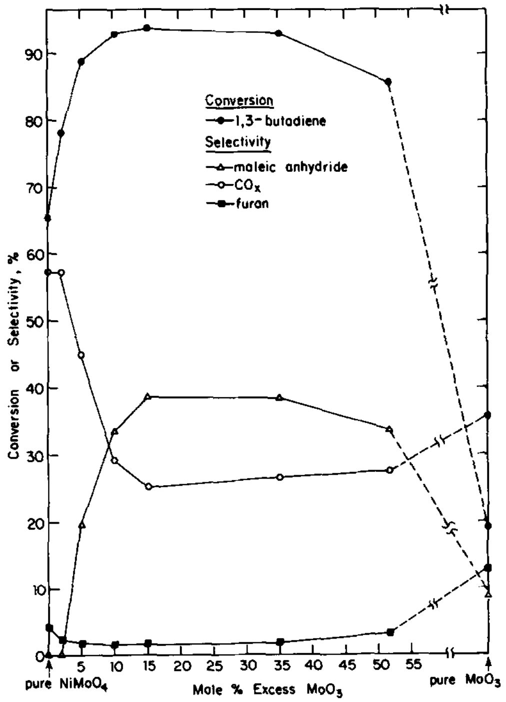

FIG. 2. Selective oxidation of 1,3-butadiene over impregnated $NiMoO_4$ catalysts as a function of excess MoO_3 concentration.

Figure 2 shows the change in the selectivity of impregnated $NiMoO_4$ catalysts containing different amounts of excess MoO_3. The selectivity for maleic anhydride is zero for pure $NiMoO_4$, and it remains at zero up to a 2% excess MoO_3 concentration. With increasing MoO_3 concentrations, the selectivity rises to a maximum at 15% and then declines gradually. The conversion to CO_x, on the other hand, drops sharply until it reaches a minimum at 15% excess MoO_3 concentration; the amount of CO_x produced increases with the presence of more MoO_3.

TABLE 2

Comparison of Rates of Disappearance of 1,3-Butadiene and Rates of Formation of CO_x for Precipitated $NiMoO_4$ Catalysts and MoO_3 in 1,3-Butadiene Oxidation

	Pure $NiMoO_4$	$NiMoO_4$ with 15% excess MoO_3	$NiMoO_4$ with 40% excess MoO_3	$NiMoO_4$ with 55% excess MoO_3	Pure MoO_3
Rate of disappearance of 1,3-butadiene (g-mol/min-m^2)	7.88×10^{-6}	1.08×10^{-5}	1.51×10^{-5}	1.88×10^{-5}	2.84×10^{-5}
Rate of formation of CO (g-mol/min-m^2)	1.80×10^{-5}	9.08×10^{-6}	1.50×10^{-5}	2.08×10^{-5}	4.04×10^{-5}

TABLE 3

Comparison of Selectivities for Pure MoO_3 and Impregnated MoO_3 in 1,3-Butadiene Oxidation

	Pure MoO_3	Impregnated MoO_3
Furan	12.85	9.63
Maleic anhydride	9.12	34.44
CO_x	35.66	20.19

TABLE 4

Comparison of Selectivities for Catalysts Prepared by Different Techniques (15% Excess MoO_3) in 1,3-Butadiene Oxidation

	Precipitation	Impregnation	Solid-state reaction
Furan	3.87	1.53	3.21
Maleic anhydride	40.66	38.62	35.23
CO_x	21.04	25.12	28.06

The selectivity for furan exhibits a minimum similar to the one observed for precipitated catalysts.

Selectivity measurements were conducted on MoO_3 samples which were impregnated with $NiMoO_4$, prepared as described previously by Ozkan and Schrader (*16*). Table 3 shows a comparison of the selectivities for pure and impregnated MoO_3 samples. Impregnated MoO_3 samples have a much higher selectivity for maleic anhydride than pure MoO_3. It is also apparent that the tendency for complete oxidation exhibited by pure MoO_3 decreases decidedly when MoO_3 is impregnated with $NiMoO_4$.

Similar to the catalyst studies involving butene oxidation, it was possible to prepare $NiMoO_4$ catalysts by solid-state reaction which also had a high selectivity for 1,3-butadiene conversion to maleic anhydride. Table 4 presents a comparison of the selectivities of catalysts prepared by these different synthesis techniques. All three techniques produced catalysts having a selectivity for maleic anhydride greater than 35%, but catalysts prepared by precipitation and impregnation generally tended to have a slightly higher selectivity than those prepared by solid-state reaction.

3.B. Activity and Selectivity Measurements for Furan Oxidation

Furan has also been suggested as a possible reaction pathway intermediate for 1-butene oxidation, and therefore experiments were conducted using furan as the reactor feed. Table 5 shows product yields for pure $NiMoO_4$, pure MoO_3, and a precipitated $NiMoO_4$ sample containing 15% excess MoO_3. It is seen that both $NiMoO_4$ and MoO_3 produce only very small yields of maleic anhydride from furan. $NiMoO_4$ has a

TABLE 5

Comparison of Yields and Selectivities for Pure $NiMoO_4$, Pure MoO_3, and Precipitated $NiMoO_4$ Containing 15% Excess MoO_3 in Furan Oxidation

	$NiMoO_4$		MoO_3		$NiMoO_4$ with 15% excess MoO_3	
	% Yield	% Selectivity	% Yield	% Selectivity	% Yield	% Selectivity
Maleic anhydride	1.40	1.72	11.97	23.54	51.97	52.72
CO_x	55.33	68.17	38.87	76.45	37.42	37.96
Overall % conversion	81.16		50.84		98.58	

TABLE 6

Comparison of Rates of Disappearance of Furan and Rates of Formation of CO_x for $NiMoO_4$, MoO_3, and $NiMoO_4$ with 15% Excess MoO_3 in Furan Oxidation

	$NiMoO_4$	MoO_3	$NiMoO_4$ with 15% excess MoO_3
Rate of disappearance of furan (g-mol/min-m^2)	4.34×10^{-6}	3.65×10^{-5}	6.26×10^{-6}
Rate of formation of CO (g-mol/min-m^2)	1.18×10^{-5}	1.12×10^{-4}	9.52×10^{-6}

very low selectivity for maleic anhydride; a high conversion (combustion) of furan to CO_x is observed. Pure MoO_3 has a higher selectivity for maleic anhydride than does pure $NiMoO_4$, but its highest selectivity is still for CO_x. In comparison, the catalyst containing excess MoO_3 yields maleic anhydride as the major product; a much lower conversion to CO_x is observed.

In Table 6, a comparison is given involving the rate of disappearance of furan and the rate of formation of CO_x for pure Ni MoO_4, pure MoO_3, and $NiMoO_4$ with 15% excess MoO_3. Pure MoO_3 is much more active than pure $NiMoO_4$. It is also noted that pure MoO_3 has the highest rate of CO_x formation, indicating that it has a greater tendency for complete oxidation.

3.C. Reactivities of Butene, Butadiene, and Furan for Complete and Selective Oxidation

When the yields of CO_x for pure $NiMoO_4$ catalysts were compared for different hydrocarbon feeds (Table 7), the CO_x yield was observed to follow the order butene (*16*) < butadiene < furan. Although the same trend was observed for pure MoO_3, the increase was much more dramatic. Table 7 shows the ratio of the CO_x yield in butadiene oxidation to the CO_x yield in butene oxidation and also the ratio of CO_x yield in furan oxidation to the CO_x yield in butadiene oxidation. Table 8 shows the ratio of butadiene conversion to butene conversion and the ratio of furan conversion to butadiene conversion. The reactant conversion also increases in the order butene < butadiene < furan for both pure MoO_3 and $NiMoO_4$. Again the increase for MoO_3 is much sharper than for $NiMoO_4$. Another important observation revealed by the ratios given in Tables 7 and 8 is that the increase in conversion from butadiene to furan is close to three times for MoO_3 while the CO_x yield increases almost six times. This observation shows that the tendency of MoO_3 for complete oxidation increases much more rapidly than its overall activity for this series of reactants.

4. DISCUSSION OF RESULTS

Selective oxidation studies conducted with three different hydrocarbon feeds have shown that $NiMoO_4$ catalysts contain-

TABLE 7

Comparison of CO_x Yields in Butene, Butadiene, and Furan Oxidation for Pure MoO_3 and Pure $NiMoO_4$

	$\frac{\text{Yield of } CO_x \text{ in } C_4H_6 \text{ oxidation}}{\text{Yield of } CO_x \text{ in } C_4H_8 \text{ oxidation}}$	$\frac{\text{Yield of } CO_x \text{ in } C_4H_4O \text{ oxidation}}{\text{Yield of } CO_x \text{ in } C_4H_6 \text{ oxidation}}$
$NiMoO_4$	1.11	1.48
MoO_3	2.51	5.72

TABLE 8

Comparison of % Overall Conversions in Butene, Butadiene, and Furan Oxidation for Pure MoO_3 and Pure $NiMoO_4$

	% Conversion in C_4H_6 oxidation / % Conversion in C_4H_8 oxidation	% Conversion in C_4H_4O oxidation / % Conversion in C_4H_6 oxidation
$NiMoO_4$	1.14	1.24
MoO_3	2.50	2.66

ing excess MoO_3 have the highest selectivity for maleic anhydride regardless of the C_4 hydrocarbon reactant used. Pure compounds ($NiMoO_4$ and MoO_3) show either no conversion to maleic anhydride or very poor selectivity; catalysts with excess MoO_3 have shown a high selectivity for maleic anhydride using 1-butene, 1,3-butadiene, and furan.

Our previous characterization investigations of these catalysts (*15*) have shown that they exhibit a two-phase nature. The most striking structural characteristic is the coverage of MoO_3 crystallite surfaces by $NiMoO_4$. The activity and selectivity studies with these three different feed materials have shown that MoO_3 surfaces which are "decorated" with $NiMoO_4$ are essential for achieving maleic anhydride selectivity.

Having established the existence of a similar catalyst structural feature for the selective oxidation of this series of C_4 hydrocarbons, there remains the crucial question of how this structural arrangement achieves the dramatic change in the catalytic behavior. The reactor studies indicate that this question should be approached from a consideration of the job distribution between various components of the catalyst. Our results have shown that oxidative dehydrogenation of 1-butene to 1,3-butadiene does occur on pure $NiMoO_4$ (*16*). There are several examples of allylic oxidation of butenes to butadiene on simple molybdates reported in the literature (*17–19*). The results also indicate that pure MoO_3 is capable of forming maleic anhydride from 1,3-butadiene (although in small amount); $NiMoO_4$ produces no maleic anhydride from butadiene. The fact that MoO_3 gives some conversion to maleic anhydride from 1,3-butadiene and from furan (although the major product is CO_x) indicates that formation of both maleic anhydride and CO_x takes place on MoO_3. Our results also clearly reveal that CO_x is the major product for both compounds in their pure state—regardless of the feed being used; but, MoO_3 has a considerably higher activity than $NiMoO_4$. All this evidence suggests that the selectivity for maleic anhydride is determined by competing rates for CO_x formation and for maleic anhydride formation, which take place on different catalytic sites on MoO_3. The crucial role of the specific structural arrangement (namely MoO_3 surfaces "decorated" by $NiMoO_4$) is that $NiMoO_4$ selectively blocks the complete oxidation sites on MoO_3 and thereby alters the selectivity in favor of maleic anhydride. $NiMoO_4$ acts as an inhibitor for complete oxidation since it is less active than MoO_3. (This is in addition to its role in the oxidative dehydrogenation of butene.) Due to our previous extensive characterization work (*15*), we can conclude that the selectivity for maleic anhydride is more strongly affected by the relative amounts of "decorated" and "free" MoO_3 surfaces than it is affected by the relative amounts of $NiMoO_4$ and MoO_3.

The results for the three different feed materials show that regardless of the catalysts, furan is more reactive than butadiene which in turn is more reactive than butene toward oxidation. This increase in reactivity is much more pronounced for pure MoO_3 than for pure $NiMoO_4$. Similarly, the tendency for complete oxidation increases progressively from butene to butadiene to furan; but the increase is much more pronounced for MoO_3 than for $NiMoO_4$. In fact, the increase in CO_x yield as the feed is changed from butadiene to furan is much larger than that can be accounted for by the increase in overall activity. It is also noted that the yield of furan obtained for pure MoO_3 increases about 18 times as the feed material is changed from butene to butadiene. This information indicates that MoO_3 is incapable of forming butadiene from butene in large quantities, and therefore the furan yields in butene oxidation are extremely low; when butadiene is the feed material, the furan yield increases sharply. It is also clear that CO_x is always the major reaction product for MoO_3 regardless of the feed material. The selectivity changes when the $NiMoO_4$ structure covers MoO_3 surfaces; this not only promotes the oxidative dehydrogenation step for 1,3-butadiene formation, but also blocks the complete oxidation sites on MoO_3.

Industrial selective oxidation catalysts typically consist of a complex mixture of metal oxides. The nature of the interactions between the phases which possibly exist for these catalysts has not been widely discussed. The work presented in this series of papers (*14–16*) provides valuable clues for acquiring a better understanding of highly active and selective catalysts for vapor-phase oxidations.

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