JOURNAL OF CATALYSIS 95, 137–146 (1985)

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

II. Selective Oxidation of 1-Butene

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Received September 25, 1984; revised April 4, 1985

The selective oxidation of 1-butene to maleic anhydride over $NiMoO_4$ catalysts containing "excess" MoO_3 was studied using a fixed-bed, integral reactor system. Activity and selectivity measurements were performed using catalysts which had been prepared by precipitation, impregnation, or solid-state reaction and which had previously undergone extensive characterization. The most selective component of the catalyst for maleic anhydride production was determined to be a MoO_3 phase which possessed a surface covering of $NiMoO_4$. Postreaction characterization by laser Raman spectroscopy. Raman microprobe spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy revealed that the catalyst was stable for prolonged reaction times. © 1985 Academic Press, Inc.

1. INTRODUCTION

Until recently maleic anhydride production has relied strongly on benzene feedstocks (*1, 2*), but the use of C_4 hydrocarbons is desirable for economic and environmental reasons. Most of the previous investigations of butane and butene conversion have used vanadium–phosphorus–oxygen catalysts (*3–7*) or V_2O_5–MoO_3 catalysts (*8–10*); molybdate catalysts have been the subject of far fewer investigations. Pasquon *et al.* (*11*) have investigated the oxidation of butenes to maleic anhydride on iron molybdate catalysts and have attributed the formation of maleic anhydride to the presence of adsorbed oxygen on tetrahedrally coordinated molybdenum(V) ions. The same argument was forwarded by Trifirò *et al.* (*12, 13*) for the oxidation of butenes to maleic anhydride on manganese, iron, cobalt, and cadmium molybdates. In their study of oxidation of butene over $CdMoO_4$, Forzatti *et al.* (*14*) reported formation of only butadiene and carbon oxides. Investigations of the selective oxidation of butenes over bismuth molybdate catalysts have been restricted to the oxidative dehydrogenation step (*15–20*).

There have been several reports in the literature indicating that pronounced changes in the catalytic behavior of simple molybdates occur due to the incorporation of excess MoO_3 (*21–28*). The number of investigations specifically regarding C_4 hydrocarbon oxidation to maleic anhydride is very limited, however. Mazzocchia *et al.* (*29*) reported the oxidation of 1-butene to maleic anhydride using catalysts which were obtained from precursors with the general formula $x\mathrm{NiO} \cdot y\mathrm{MoO_3} \cdot n\mathrm{H_2O} \cdot m\mathrm{NH_3}$; active and selective catalysts had a composition of $y/x > 1$.

In our previous papers, we have reported the preparation of $NiMoO_4$ catalysts with excess MoO_3 (*30*) and the results of extensive characterization.

2. EXPERIMENTAL METHODS

2.A. Catalyst Preparation

Pure $NiMoO_4$ was synthesized by precip-

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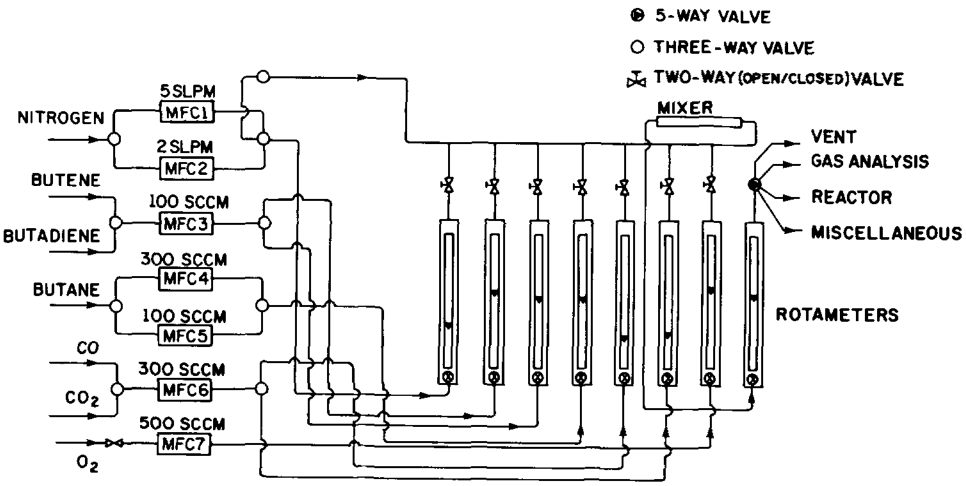


FIG. 1. Gas feed system.

itation using the procedure outlined previously (*30*). Catalysts containing excess MoO_3 were prepared by precipitation, solid-state reaction, and impregnation techniques, as described by Ozkan and Schrader (*31*).

2.B. Catalytic Activity and Selectivity Measurements

Selective oxidation reaction experiments were performed using a continuous-flow, fixed-bed reactor system. The reactor was operated in an integral mode. The composition and flow rate of the gas feed mixture were measured and controlled using Tylan mass flow controllers (Model FC260) which were calibrated for each of the specific gases. Figure 1 shows the flowchart of the gas feed unit. The cylindrical reactor was constructed of 316 stainless steel with an inner diameter of $\frac{1}{2}$ in. and an outer diameter of 1 in. (Fig. 2). The length of the reactor was 15 in.; the actual length of the catalyst bed was 9 in. since the top and bottom 3-in. sections of the reactor were packed with an inert material (SiC). The reactor was equipped with 13 subminiature thermocouple probe assemblies (Omega Engineering) for monitoring the temperature in the reactor radially and axially. The reactor was also divided into seven individual heating zones, and each zone was equipped with an independently controlled resistance element. The entire reactor and the feed mixture preheater coil were imbedded in a fluidized sand bath for additional heating.

A four-column gas chromatograph (Antek 300) was employed for compositional analysis of feed and product mixtures (Fig. 3). The chromatograph was equipped with two flame ionization detectors, one thermal conductivity detector, and three heated sampling valves. All the exit lines from the

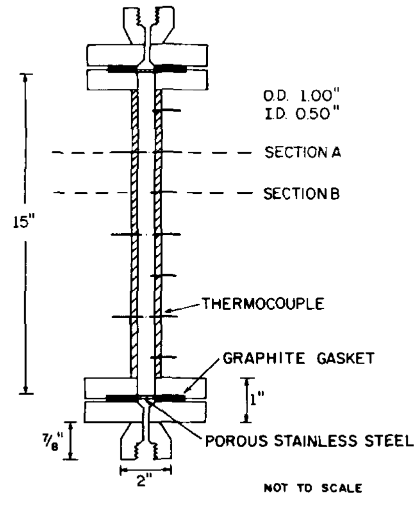
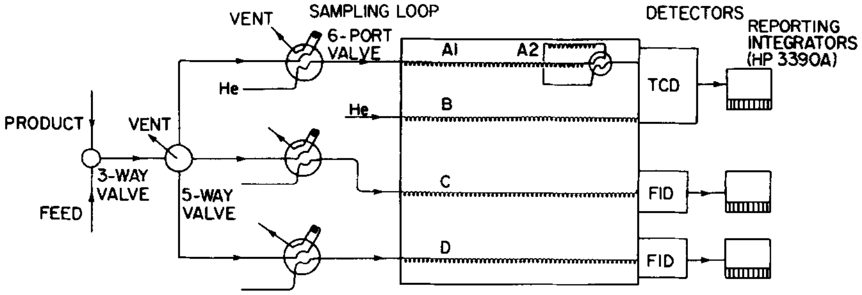


FIG. 2. Fixed-bed integral reactor.



COLUMNS

A1	**PORAPAK Q 50/80 MESH 5′ x 1/8″**
A2	**MOLECULAR SIEVE 5A 60/80 MESH 12′ x 1/8″**
B	**CHROMOSORB PAW SE 30 80/100 MESH 5′ x 1/8″**
C	**CARBOPACK B/5% CARBOWAX 20M 60/80 MESH 12′ x 1/8″**
D	**CARBOPACK C/0.19% PICRIC ACID 80/100 MESH 18′ x 1/8″**

FIG. 3. Analytical system.

reactor were heated to 130°C to prevent product condensation.

The reactor was packed with the catalyst and with silicon carbide which served as a diluent. The catalyst bed consisted of 2 g of catalyst and 40 g of SiC mixed homogeneously. Both the catalyst and SiC particles were in the 2-mm size range. The reactor conditions which were kept constant for all runs were as follows: oxygen partial pressure—0.176 atm; 1-butene partial pressure—0.017 atm; nitrogen partial pressure–0.807 atm; reaction temperature—480°C; volumetric flow rate of 1-butene—1200 cm^3 (STP)/h; total molar flow rate—3.15 g-mol/h.

The percentage conversion for these studies is defined as

$$\frac{\text{moles of butene consumed}}{\text{moles of butene in feed}} \times 100\%,$$

where isomerization products are not included in the conversion.

The percentage selectivity to product A is defined as

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

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

The yield of product A is defined as

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

The rate of disappearance of butene is based on the initial surface area of the catalyst.

2.C. *Postreaction Characterization Techniques*

Postreaction characterization investigations were conducted using laser Raman spectroscopy, Raman microprobe spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. Raman spectra were obtained using a Spex 1403 laser Raman spectrometer. Raman microprobe experiments were conducted using a Spex 1482 Micromate illuminator. SEM investigations were performed with a JEOL Model JSM-U3 scanning electron microscope. The X-ray photoelectron spectra of the catalysts were obtained using an AIE 200B spectrometer. Detailed descriptions of the techniques and data acquisition parameters were reported previously (*31*).

3. EXPERIMENTAL RESULTS

3.A. *Selectivity and Activity Measurements for 1-Butene Oxidation*

3.A.1. Selectivity of precipitated $NiMoO_4$ catalysts. Selectivity measurements for pure $NiMoO_4$ and MoO_3 indicated that both

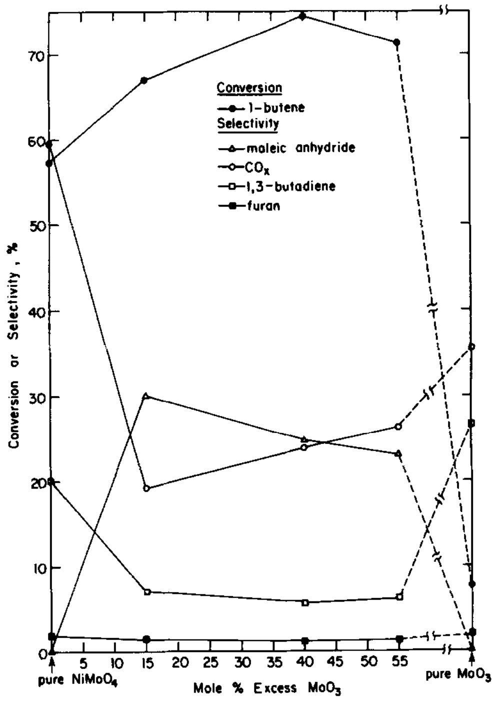


FIG. 4. Selective oxidation of 1-butene over precipitated $NiMoO_4$ catalysts as a function of excess MoO_3 concentration.

compounds were completely nonselective for maleic anhydride formation; but, the incorporation of excess MoO_3 into $NiMoO_4$ caused a dramatic change in catalytic performance. Figure 4 shows the change in the selectivity for various reaction products as a function of the excess MoO_3 concentration. The $NiMoO_4$ samples with varying MoO_3 concentrations were obtained by precipitation at various pHs (*30*). The selectivity for maleic anhydride production goes through a maximum with increasing percentages of excess MoO_3—the maximum occurring at 15% excess MoO_3. The selectivities for 1,3-butadiene and furan production go through minima with increasing percentages of excess MoO_3. The selectivity for carbon oxides, also, goes through a minimum; the minimum coincides with the maximum for maleic anhydride selectivity.

Table 1 provides yields for these catalysts, based on equal weights of catalysts present in the reactor. Included are the rates of disappearance of butene for precipitated $NiMoO_4$ catalysts and for MoO_3. The highest yield of maleic anhydride is again achieved using the $NiMoO_4$ catalyst containing 15% excess MoO_3. The rate of disappearance of butene shows an increase with increasing percentages of excess MoO_3; a decrease is observed for pure MoO_3. A comparison of the rates of the two pure compounds shows that MoO_3 is more active than is $NiMoO_4$, based on unit surface area.

3.A.2. Selectivity of impregnated Ni MoO_4. Pure $NiMoO_4$ samples were impregnated with an ammonium heptamolybdate solution to obtain various levels of excess MoO_3 (2–55%). Figure 5 shows the selectivities for the important reaction products as a function of excess MoO_3 concentration. Similar to precipitated samples, the selectivity for maleic anhydride production

TABLE 1

Comparison of Yields and Rates of Disappearance of Butene for Precipitated $NiMoO_4$ Catalysts and Pure MoO_3

	Yield (%)				
	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
1,3-Butadiene	11.50	4.68	4.19	4.37	2.03
Furan	1.13	1.03	0.92	0.94	0.14
Maleic anhydride	0.00	20.09	18.42	16.40	0.00
Carbon oxides	33.66	12.83	17.73	18.75	2.71
Rate of disappearance of butene (g-mol/min-m^2)	6.91×10^{-6}	9.06×10^{-6}	1.28×10^{-5}	1.59×10^{-5}	1.13×10^{-5}

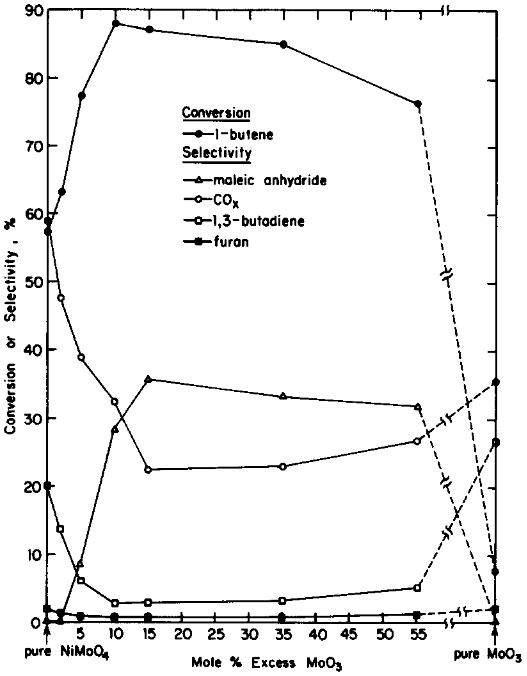


FIG. 5. Selective oxidation of 1-butene over impregnated $NiMoO_4$ catalysts as a function of excess MoO_3 concentration.

goes through a maximum (occurring at 15% excess MoO_3 concentration). The maximum selectivity is 35.6%. Since the impregnation technique permits much better control over the amount of excess MoO_3 incorporated, it is possible to synthesize samples with low excess MoO_3 concentrations. One interesting feature of the results is that the $NiMoO_4$ catalyst containing only 2% excess MoO_3 produces no maleic anhydride.

The selectivity for carbon oxides also passes through a minimum, which occurs at 15% excess MoO_3. The selectivities for furan and butadiene production go through minima similar to the ones observed for the precipitated catalysts.

3.A.3. Selectivity of impregnated MoO_3. Selectivity measurements were conducted on impregnated MoO_3 samples which were prepared as described previously (*31*). Table 2 shows a comparison of the selectivities for pure MoO_3 and for impregnated MoO_3. Results clearly demonstrate the sudden rise in selectivity for maleic anhydride production for impregnated MoO_3. There is simultaneously a pronounced decrease in selectivity for carbon oxides.

TABLE 2

Comparison of Selectivities for Pure MoO_3 and Impregnated MoO_3 (15% Excess $NiMoO_4$)

	Pure MoO_3	Impregnated MoO_3
1,3-Butadiene	26.64	19.29
Furan	1.84	2.19
Maleic anhydride	0.0	22.10
Carbon oxides	35.56	19.95
% Conversion	7.62	22.81

3.A.4. Selectivity of $NiMoO_4$ catalysts prepared by solid-state reaction. Reactor experiments conducted using catalysts prepared by solid-state technique showed that this technique also is an effective method for incorporating excess MoO_3 into $NiMoO_4$. Table 3 shows comparison of catalysts prepared by three different techniques. All catalysts contain 15% excess MoO_3. It is seen that impregnation of $NiMoO_4$ gives the highest selectivity for maleic anhydride.

3.B. Stability of Catalysts

In order to test the stability of the catalysts, experiments were conducted using $NiMoO_4$ samples with excess MoO_3 where the reaction run was continued for 200 h. Upon reaching steady state (typically after 8 h), no change was observed in the activity of the catalyst or in the product distribution.

TABLE 3

Comparison of Selectivities for Catalysts Prepared by Different Techniques (15% Excess MoO_3)

	Precipitation	Impregnation of $NiMoO_4$	Solid state
1,3-Butadiene	6.99	2.84	4.19
Furan	1.54	0.72	0.96
Maleic anhydride	30.00	35.63	29.41
Carbon oxides	19.16	22.44	31.52
% Conversion	66.96	86.88	79.60

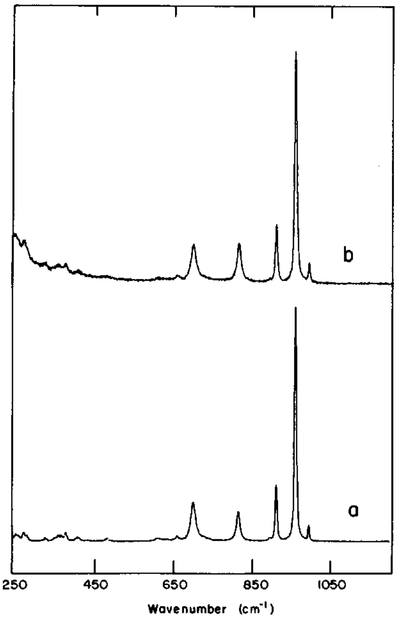


FIG. 6. Raman spectra of precipitated $NiMoO_4$ (15% excess MoO_3): (a) before reaction and (b) after reaction.

3.C. *Characterization of Used Catalysts*

Following reaction catalysts were cooled to room temperature while the feed gas mixture continued to flow through the reactor. Thus, they were not exposed to air until they were at room temperature. The color of the catalyst particles was dark grey after reaction, compared to the yellow color of the fresh catalyst. No attrition of the catalyst particles was observed.

3.C.1. Raman spectroscopy. Catalysts were characterized using Raman spectroscopy after being crushed into powder. Figure 6 shows a comparison of the Raman spectra obtained from a 15% excess precipitated catalyst before (a) and after being used in the reactor (b). The spectra indicate that no change occurred in the band positions after the reaction. Another important spectral feature is that the relative intensities of the MoO_3 bands and the $NiMoO_4$ bands remain the same.

3.C.2. Raman microprobe spectroscopy. Raman microprobe studies indicated that the catalyst structural features revealed in our previous characterization studies (*31*) remain unchanged after reaction. Used catalysts—similar to the fresh ones—exhibited a separate particle identity in that the separate MoO_3 and $NiMoO_4$ crystallites were apparent. It was also observed that a $NiMoO_4$ structure "decorated" the surfaces of MoO_3 crystallites; this phenomenon was clearly established during characterization of the fresh catalysts. Figure 7 shows two postreaction microprobe spectra obtained from a catalyst prepared by precipitation containing 15% excess MoO_3. The bottom spectrum (b) was obtained by focusing the laser beam on a particle which has the general appearance of a $NiMoO_4$ particle. It has no indication of the presence of any MoO_3. Figure 7a is the spectrum taken on a particle which had the typical MoO_3 crystalline shape. The spectrum exhibits Raman bands corresponding to both MoO_3 and $NiMoO_4$.

3.C.3. Scanning electron microscopy. Following reaction catalysts were also

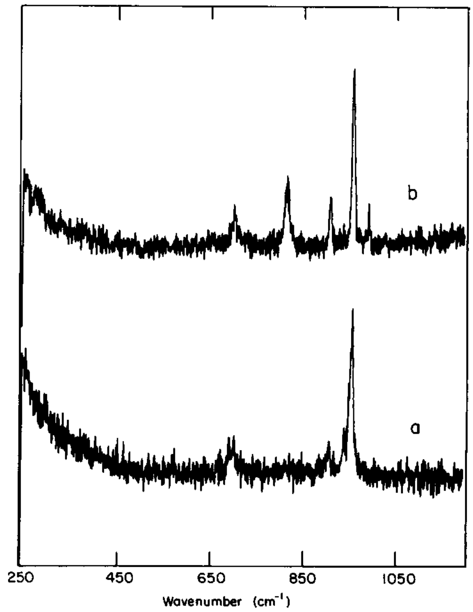


FIG. 7. Raman microprobe spectra of used catalyst (precipitation, 15% excess MoO_3). (a) $NiMoO_4$ particle and (b) MoO_3 particle.

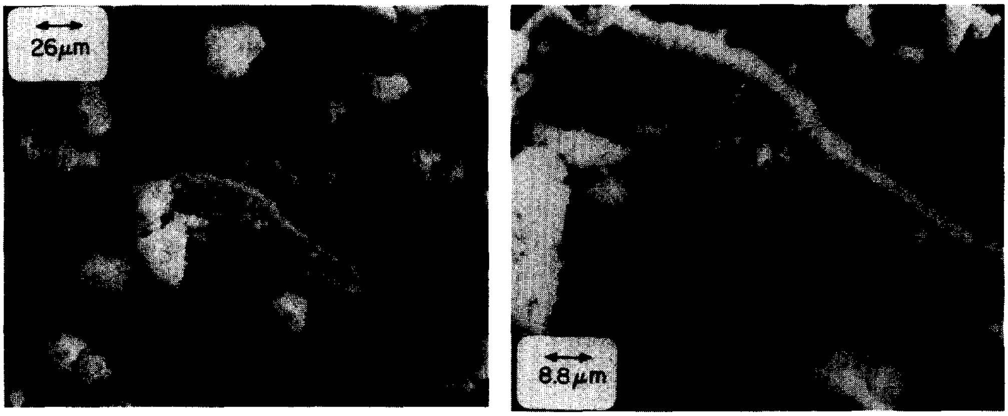


FIG. 8. Scanning electron micrographs of precipitated NiMoO$_4$ catalyst (15% excess MoO$_3$) after reaction. Magnification: (a) 385× and (b) 1134×.

characterized with scanning electron microscopy. The two-phase nature of the catalyst was apparent after the reaction as well. Figure 8a shows separate NiMoO$_4$ and MoO$_3$ particles distinctly. Figure 8b is a close-up of a MoO$_3$ particle which clearly shows the NiMoO$_4$ structure partially covering the surface.

3.C.4. X-Ray photoelectron spectroscopy. Catalysts were characterized by X-ray photoelectron spectroscopy following reaction, but no change in the oxidation states of Mo and Ni was observed. Table 4 lists the Mo 3*d* and Ni 2*p* binding energies for fresh and spent catalysts. Figures 9 and 10 provide the Mo 3*d* and Ni 2*p* X-ray photoelectron spectra, respectively, for fresh and spent catalysts.

4. DISCUSSION OF RESULTS

Reaction kinetics experiments with Ni MoO$_4$ catalysts containing excess MoO$_3$ have clearly shown that the presence of excess MoO$_3$ is the key factor in determining the selectivity for maleic anhydride. Studies with catalysts prepared by all three techniques (precipitation, solid-state reaction, and impregnation) have shown that the presence of MoO$_3$ is essential in order to achieve selectivity for maleic anhydride,

TABLE 4

Photoelectron Spectra Binding Energies for NiMoO$_4$ Catalysts Containing Excess MoO$_3$ before and after Reaction (eV)

	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Ni $2p_{3/2}$	Ni $2p_{1/2}$
Before reaction	232.7	235.9	855.7	873.4
After reaction	232.6	235.8	855.5	873.2

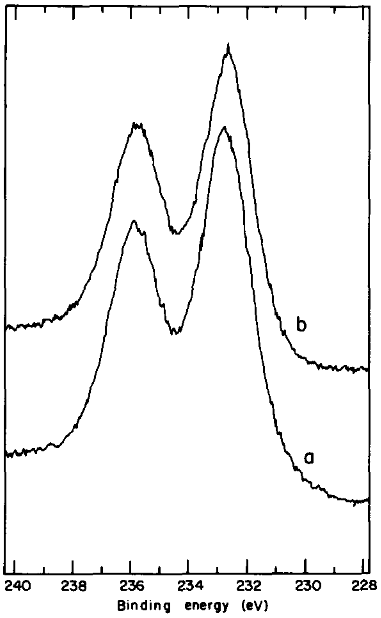


FIG. 9. Mo 3*d* photoelectron spectra of impregnated NiMoO$_4$ (35% excess MoO$_3$): (a) before reaction and (b) after reaction.

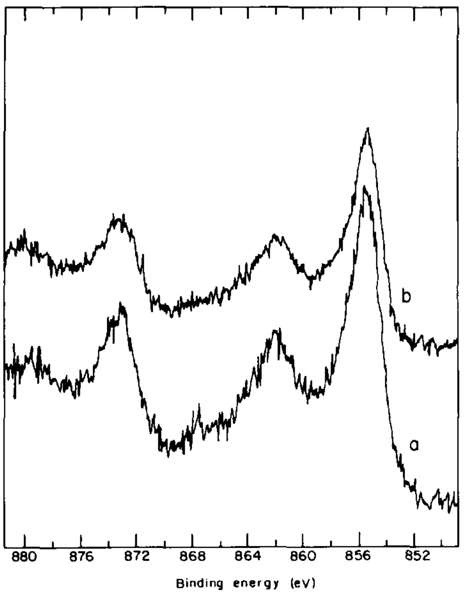


FIG. 10. Ni 2p photoelectron spectra of impregnated $NiMoO_4$ (35% excess MoO_3): (a) before reaction and (b) after reaction.

regardless of the technique used for incorporating the excess MoO_3.

However, the precise form of this excess MoO_3 is crucial. In order to rule out the possibility that the reason for the high maleic anhydride selectivity was merely the coexistence of $NiMoO_4$ and MoO_3 in the reactor bed, a set of experiments was conducted which involved packing the reactor with separate particles of $NiMoO_4$ and MoO_3. $NiMoO_4$ and MoO_3 particles were separated by SiC particles such that no contact was allowed between the two compounds. The overall concentration of each compound was adjusted to have a total of 15% excess MoO_3 present in the bed. Table 5 shows the selectivity measurements taken using this catalyst bed. Similar to pure $NiMoO_4$ and pure MoO_3, this packing provided no conversion to maleic anhydride. Clearly the cause of the dramatic change in selectivity was not the mere coexistence of the two compounds in the reactor.

When the results of the activity and selectivity experiments are combined with the synthesis and characterization investigations reported previously (*30, 31*) the true significance of the specific structural arrangement observed for these catalysts becomes more apparent. Our results indicate that the cause of the very pronounced change in selectivity by the incorporation of excess MoO_3 is the formation of a specific arrangement of the phases which provides a close contact between MoO_3 and $NiMoO_4$. Most clearly apparent is a $NiMoO_4$ structure covering or "decorating" the surfaces of MoO_3 crystallites. This structure was detected in all catalyst samples which showed selectivity for maleic anhydride production; no other structures (except for $NiMoO_4$ and MoO_3) were observed using the extensive array of spectroscopic characterization.

The reactor experiments conducted using impregnated catalysts indicated that no formation of maleic anhydride occurred with the use of a catalyst having a 2% excess MoO_3 concentration. Raman spectra of these samples have very weak bands corresponding to MoO_3; the concentration of this MoO_3 is so small, however, that its effect on catalytic behavior is insignificant. As the percentage of excess MoO_3 increases, more and more MoO_3 particles separate out with $NiMoO_4$ layers covering their surfaces. Therefore, the extent of the contact between the two phases increases dramatically, with a resulting increase in selectivity.

When samples with a high MoO_3 concen-

TABLE 5

Selectivity Measurements on a Catalyst Bed Consisting of Separate Particles of MoO_3 and $NiMoO_4$

Product	% Selectivity
1,3-Butadiene	19.21
Furan	1.48
Maleic anhydride	0.0
Carbon oxides	53.24
% Conversion	60.95

tration were characterized by scanning electron microscopy, it was found that separate MoO_3 clusters had formed. It was also noted that these clusters housed "free" MoO_3 particles which had no surface coverage of $NiMoO_4$ (*31*). This observation explained the graduate decline in selectivity with increasing percentages of excess MoO_3. The reason for the gradual decline is the fact that there are two competing effects being imposed on the system as the amount of excess MoO_3 is increased. One is an enhancement of the maleic anhydride selectivity due to the increased contact between the two phases. The other is an adverse effect resulting from an increased presence of MoO_3 clusters and "free" MoO_3 surfaces which are nonselective. The selectivity measurements conducted on impregnated MoO_3 samples provide further support for interpretation by showing that presence of $NiMoO_4$ on MoO_3 crystallites is essential for achieving selectivity for maleic anhydride.

Studies with $NiMoO_4$ catalysts prepared by the three different techniques have also provided some insight into the formation of the regions of contact between the two compounds. The fact that all three preparation techniques demonstrate a similar trend in selectivity eliminates the possibility that the cause of this sudden change in selectivity is a specific arrangement taking place during the precipitation stage. It is more likely that coverage of the MoO_3 surfaces by $NiMoO_4$ takes place during calcination, which is a preparation step common to all techniques.

The characterization of catalysts following reaction shows no indication of any significant chemical or structural change. The level of excess MoO_3 remains constant while the catalyst preserves its two-phase nature. The X-ray photoelectron spectra results indicated that carbon deposition occurred on the surface, which could partly account for the color change. No reduction of the surface was detected with any of the techniques used.

5. CONCLUSIONS

In our studies of $NiMoO_4$ catalysts containing excess MoO_3, it has been clearly established that the structural requirement for a selective maleic anhydride catalyst is the presence of $NiMoO_4$ adhering to the surface of MoO_3 crystallites. Complementary characterization techniques have revealed that precipitation, solid-state reaction, and impregnation techniques can be used to generate this structure. These techniques also reveal that the active catalyst is stable for reaction times up to 200 h.

The reactor experiments provide a better understanding of the reaction pathway, the reaction intermediates, and the role of different catalyst components. Our results indicate that the two major compounds produced—other than maleic anhydride and CO_x—are 1,3-butadiene and furan. Selectivity for both of these products passes through minima with increasing percentages of excess MoO_3, suggesting that 1,3-butadiene and furan are likely intermediates in the formation of maleic anhydride. The fact that the selectivity for maleic anhydride decreases as the amount of carbon oxides increases seems to indicate that the formation of maleic anhydride and the formation of carbon oxides are competing reactions; the selectivity for maleic anhydride is determined by these competing rates. The selectivity results show that carbon oxides (CO_x) are the major product for both $NiMoO_4$ and MoO_3 in their pure form, but MoO_3 has a higher activity than $NiMoO_4$. Therefore, MoO_3 is capable of oxidizing hydrocarbons more readily. It is possible that the presence of $NiMoO_4$ on MoO_3 can have a moderating effect on the complete oxidation reactions, and thereby significantly alter the catalytic behavior. If MoO_3 is capable of forming maleic anhydride from possible intermediates such as 1,3-butadiene or furan, then it would seem to suggest that the competing reactions—formation of CO_x and formation of maleic anhydride—take place on different catalytic sites on

MoO_3. The presence of $NiMoO_4$ on MoO_3 may alter the selectivity in favor of maleic anhydride by selectively blocking the complete oxidation sites. It is possible that Ni MoO_4 effectively acts as an inhibitor, since it is considerably less active than MoO_3. It would also seem likely that formation of 1,3-butadiene from 1-butene takes place on $NiMoO_4$, giving it a multifunctional role in the catalysis.

Although butene oxidation experiments provide valuable information about the catalytic behavior as well as the reaction scheme, they alone are not completely definitive. In the fourth article in this series (*32*), results of activity and selectivity measurements for the same catalytic system using 1,3-butadiene and furan as the feedstocks will be reported. More information concerning possible reaction networks, reaction intermediates, and catalytic functions for the components of the catalyst will be provided.

ACKNOWLEDGMENTS

This work was conducted through the Ames Laboratory which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. The X-ray photoelectron spectroscopy work by James W. Anderegg of the Ames Laboratory—USDOE is gratefully acknowledged.

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