

Improved Olefin Disproportionation Selectivity by Olefin Pretreating a $\text{MoO}_3/\text{Al}_2\text{O}_3$ Catalyst

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Olefin treatment of molybdena-alumina at 200°C results in the deposition of a residue which is tenaciously held to the surface and gives a very selective catalyst for olefin disproportionation. Molybdena promotes the deposition of residue since only a small quantity of residue is deposited on alumina under comparable conditions. Upon olefin treatment, molybdena is reduced giving rise to an ESR signal attributed to Mo(V). No correlation was found between this signal and disproportionation activity or selectivity. It is proposed that the residue deposited on molybdena-alumina is analogous to the surface complex formed by heating to 200°C the butene-like polymeric species deposited on silica-alumina at room temperature. It is also proposed that this residue enhances olefin disproportionation selectivity by a similar mechanism proposed for the same enhancement which can be obtained by adding large polarizable cations such as K, Cs, Rb, and Tl, to molybdena-alumina.

INTRODUCTION

Olefin disproportionation has been a subject of considerable interest in recent years. A particularly important feature has been the control of the reaction so that a high selectivity to a single higher molecular weight olefin and ethylene can be obtained. The major source of low selectivity is isomerization of both reactant and products, all of which can undergo disproportionation leading to a wide spectrum of products. To minimize olefin isomerization, low concentrations of Groups Ia and IIa (1) metal oxides and oxides of silver (2) and thallium (3, 4) have been added to molybdena-alumina, resulting in high disproportionation selectivity. It has also been reported that pretreating molybdena and tungsten disproportionation catalysts with various compounds can result in improved conversion and selectivity values. In most cases hydrogen or carbon monoxide have been used to pretreat the catalysts to give the desired benefits (1, 5, 6). Patents by Reussen (7) and Heckelsberg (8) cite pre-

treatments of catalysts with hydrogen, carbon monoxide, gaseous olefin hydrocarbons, or gaseous paraffinic hydrocarbons or with nitric oxide which lead to improved catalyst selectivity and higher conversions. However, no examples are given demonstrating the effects of olefin pretreatment. In recent reports (9, 10), examples of the beneficial effects on conversion and selectivity for propylene disproportionation over a $\text{WO}_2\text{-SiO}_2$ catalyst were given, stemming from pretreatment of the catalyst with HCl, vinyl chloride, hydrogen, and hydrocarbons. No details were presented about the type of hydrocarbons used for pretreating. Thus, it is worthy to report details of the effect of pretreating molybdena-alumina catalysts with various olefins to enhance the selective disproportionation of 1-octene.

EXPERIMENTAL

The 10% molybdenum-alumina was prepared by impregnating Ketjen alumina

(227 m²/g) with a solution of ammonium paramolybdate of the desired concentration. The impregnated catalyst was then oven dried at 125°C and calcined in air at 540°C for 16 hr. This catalyst had a surface area of 191 m²/g.

The method for conducting catalyst evaluation was the same as previously described (3). The only difference was that provisions were made to introduce gaseous pretreating agents prior to the 1-octene disproportionation experiments. All reaction products were analyzed using a F & M model gas chromatograph with a 3/16-inch o.d. column, 20 ft long, packed with 5% OV-1 silicone oil and gas-chrom Q supplied by Applied Science Laboratories. Gaseous and liquid products were collected and analyzed separately with the total volume of the gaseous products also being determined. The data points given in Tables 1 and 2 and Figs. 1 and 2 represent lined-out values which were constant after the system was equilibrated for 1 hr before samples were taken for analysis.

A Cahn electrobalance was used to monitor weight gains attending butene pre-

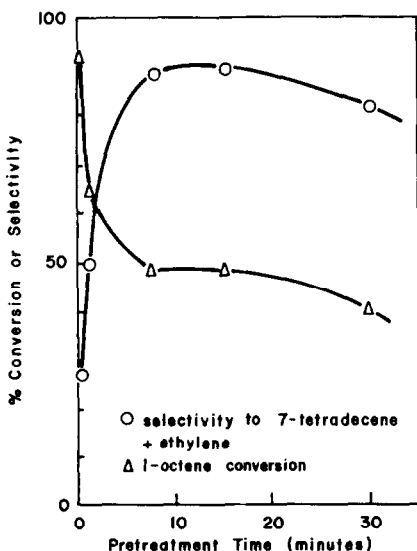


FIG. 1. 1-Octene disproportionation conversion and selectivity as a function of 1-butene pretreatment time. Reaction conditions: 100°C, 3 LHSV; pretreatment conditions: 200°C, 500 GHSV.

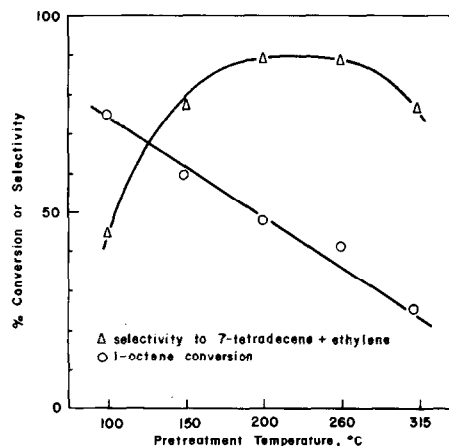


FIG. 2. 1-Octene disproportionation conversion and selectivity as a function of 1-butene pretreatment temperature. Reaction conditions: 100°C, 3 LHSV; pretreatment conditions: 1-butene time = 15 min, 500 GHSV.

TABLE 1
DISPROPORTIONATION OF OCTENE-1 USING
TREATED AND UNTREATED MOLYBDENA-
ALUMINA CATALYSTS^a

	Treated with butene-1	No treat- ment
Octene-1 conversion (mole %)	48.1	98.8
Product distribution (mole %)		
C ₂	40.21	11.44
C ₃	1.10	6.13
C ₄	0.07	1.30
C ₅	0.03	1.00
C ₆	0.09	2.07
C ₇	0.52	6.24
C ₈	1.31	9.28
C ₁₀	0.05	4.35
C ₁₁	0.09	5.74
C ₁₂	0.75	9.22
C ₁₃	2.13	8.48
C ₁₄	49.60	16.76
C ₁₅	1.28	9.38
C ₁₆	0.70	4.02
C ₁₇	0.42	1.56
C ₁₈	0.51	0.63
Higher olefins	1.13	2.38
C ₂ + C ₁₄ (mole %)	89.81	28.20

^a 10 Wt % molybdenum-Al₂O₃. Reaction conditions: Temperature, 100°C; LHSV, 3. Treatment conditions: Butene-1 flow rate, 500 GHSV; temperature, 200°C; time, 15 min.

TABLE 2
EFFECT OF TREATING 10 WEIGHT %
MOLYBDENUM-ALUMINA WITH
VARIOUS MATERIALS^a

Treating agent	Octene-1 conversion (mole %)	Selectivity to tetradecene and ethylene (mole %)
None	90.8	28.2
Ethylene	70.3	42.7
Propylene	67.8	72.0
1-Butene	48.1	89.8
Isobutylene	26.3	91.2
Octene-1	49.8	87.4
Propane	87.3	29.5
Butane	88.2	30.1
Hydrogen	83.2	41.6
Carbon monoxide	83.0	47.2

^a Reaction conditions: temperature, 100°C; octene-1 flow rate, 3 LHSV; 20 cc of catalyst; time, 1-4 hr. Treatment conditions: temperature, 200°C; flow rate of treating agent, 500 GHSV; (5 LHSV in case of octene-1); time, 15 min.

treatments. In all cases a 1-g sample was used. A DuPont moisture analyzer was used to measure the water released from the catalysts during treatment in the Cahn balance.

Extraction experiments were made in a Soxhlet extractor using 30 g of pretreated catalyst. After treatment for 16 hr with refluxing hexane or toluene, the catalysts were transferred to a vacuum oven where they were dried for 16 hr at 50°C and 30 psig vacuum.

The 10% molybdenum-alumina butene-treated catalyst was transferred in nitrogen to Pyrex glass tubes and sealed. The spin resonance spectra were obtained on a Varian V 4500 spectrometer operating at 9.5 kHz. The magnetic field was modulated by 100 kHz, and the first derivative of the spectrum was recorded. The sample tubes were filled with the sample to a height greater than the depth of the resonant cavity. The integrated intensities were taken to be proportional to the product of the signal amplitude and the square of the peak to peak width.

RESULTS

Reaction Studies

Treatment of a 10 wt % molybdenum-alumina catalyst with butene-1 at temperatures somewhat above reaction temperature results in a marked increase in octene-1 disproportionation selectivity. This is shown by the data given in Table 1 which give selectivities to various products for treated and untreated catalysts. The desired disproportionation products from octene-1 are 7-tetradecene and ethylene, which are formed at 89.8% selectivity with the treated catalyst and only 28.2% with the untreated catalyst. Conversion is decreased considerably with the treated catalyst which also occurs when various Group Ia metal oxides, silver or thallium oxides are added in low concentrations to molybdena-alumina catalysts to enhance selectivity. The butene treatment time and temperature used to obtain the data in Table 1 were determined from data shown in Figs. 1 and 2, respectively. Treatment at reaction temperature results in a selectivity increase from about 28% to 43%; however, treating around 195°-235°C results in a selectivity value of approximately 90%. Treating at temperatures beyond 260°C results in lower selectivity values as well as continually lower conversions. As shown in Fig. 1, a butene treatment time of only 7 min is required at 200°C and GHSV of 500 to give near 90% selectivity to 7-tetradecene. The treatment time can be increased to about 20 min without any deleterious effects; however, prolonging the treatment results in declining conversion and selectivity values. Table 2 gives the results of using various pretreating molecules. Paraffinic hydrocarbons essentially had no effect. Hydrogen and carbon monoxide resulted in significant selectivity increases while still maintaining high conversion levels. However, selectivity values of 41.6 and 47.2 are still too low when maximum single pass 7-tetradecene yield is desired. Ethylene treatment results in a decrease in conversion with a significant increase in selectivity. Comparison of

the results obtained by treating with propylene to those obtained using ethylene shows that the conversion levels are approximately the same. However, with propylene the selectivity increases to 72% compared to only 42.7% when ethylene is used. Increasing the olefin size to 1-butene further reduces the conversion level with a marked selectivity increase. Pretreating the catalyst with 1-octene gave similar results as treating with 1-butene. The results obtained using isobutylene show that the conversion level is decreased to 26% with a selectivity greater than 91%. Thus, the type of pretreating olefin has a pronounced effect on conversion and selectivity levels for the disproportionation of octene-1. During pretreatment with propylene, butenes, isobutylene, and octene-1 liquid as well as gaseous products were formed ranging from ethylene through C_{26} products. A quantitative evaluation of these products was not made.

The butene treatment to give enhanced selectivity is not a temporary phenomenon. This was verified from bench-scale experiments where constant conversion-selectivity values were obtained using long reaction cycles. Thus, the hydrocarbon residue deposited on the catalyst by olefin pretreatment is not readily removed during reaction, if at all.

Catalyst Studies

Several techniques were employed to obtain information about what happens to molybdena-alumina catalysts upon treating with butene. Treatment of alumina at room temperature with butene for 15 min, followed by drying in a vacuum oven for 16 hr at 50°C resulted in 0.21 wt % carbon retained. Treatment at 200°C for the same time with the same subsequent drying resulted in 0.41 wt % carbon on the catalyst. Treating the 10 wt % molybdenum-alumina catalyst the same way resulted in 2.0 wt % carbon retained.

This carbonaceous residue is tenaciously held to the molybdena catalyst. A butene-treated 10 wt % molybdenum catalyst was removed from the reactor after the butene treatment and subjected to a 10^{-7} mm Hg

vacuum at 200°C. A few droplets of yellow residue were obtained in the cold trap. This material analyzed to be a mixture of olefins ranging from C_6 through C_{26} , which most likely resulted from both disproportionation and polymerization of butene and disproportionation of products. The amount of carbon retained after removal of this small amount of material was 2.1 wt %. Another butene-treated sample of 10% molybdenum was transferred from the reactor in a blanket of nitrogen to a Soxhlet extractor where it was treated with refluxing hexane for 16 hr. After this treatment, the sample was dried in a vacuum oven for 16 hr at 50°C. This sample analyzed to contain 2.2 wt % carbon, indicating that no carbonaceous residue was removed with refluxing hexane. Another sample was treated with refluxing toluene using the same procedure. Analysis of the toluene solution by gas chromatography and high resolution mass spectrometry showed that no high molecular weight material was removed.

The adsorption-desorption behavior of 1-butene on the 10 wt % molybdenum catalyst and alumina support was studied in a microbalance flow reactor and complemented by analysis of water evolved during treatment using an on-stream moisture analyzer. Composite Fig. 3 shows how the weight of molybdena-alumina and alumina increased when butene-1 was adsorbed at 178°C along with the corresponding formation of water. Initially, there was a rapid buildup of deposit followed by a more gradual weight gain. After 1 hr exposure to butene, the catalyst and support were purged with nitrogen resulting in some weight decrease. The weight of deposit retained by the catalyst in this experiment corresponds closely to the weight of carbon obtained by carbon analysis. During the nitrogen purge step, the desorbed material from the catalyst was collected in a liquid nitrogen trap and analyzed by gas chromatography. Besides the traces of C_2 and C_3 olefins, a small amount of liquid collected contained a mixture of C_6 to C_{26} olefins.

The formation of water during the pre-

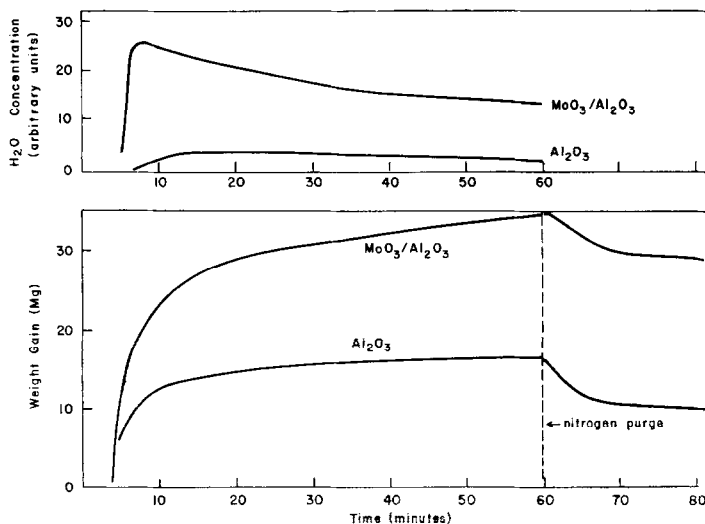


Fig. 3. Catalyst weight gain and water formation with time on contact with butene-1 at 178°C.

treatment step was monitored only qualitatively using a DuPont moisture analyzer. The curve in Fig. 3 shows the water evolved in arbitrary units as observed directly from the instrument. It is evident that the amount of water produced over molybdena-alumina is higher than for pure alumina during the pretreatment step with 1-butene.

After the nitrogen purge at 178°C, the catalyst was heated to 530°C in nitrogen followed by slow programmed heating in air to 530°C. Analysis of the evolved CO₂ and H₂O indicated that the "coke-like" material had a carbon-to-hydrogen ratio of 0.6. The formation of CO₂ was detected initially at 350°C which is in the temperature region for the existence of a low temperature "coke" species. Reintroduction of butene at 200°C to the catalyst after air regeneration at 530°C resulted in a retrace of the adsorption plot indicating that no major change in surface properties of the molybdena-alumina resulted from the air oxidation treatment.

The water evolved during butene treatment results from the reduction of Mo(VI). Calcined molybdena-alumina contains molybdenum only in this state. The catalyst after butene treatment exhibits an ESR signal having a g value of 1.931, which has been assigned to Mo(V)

(11). The width and shape of the signal are characteristic of Mo(V) on Al₂O₃ and indicate that the Mo(V) is in an environment of axial symmetry. All characteristics of this signal are comparable with those observed for a hydrogen-reduced molybdena-alumina catalyst (12). As will be mentioned later, the Mo(V) observed could come from hydrogen released during the butene treatment. No free radical-type signal was observed in this sample.

A pretreated sample was transferred under nitrogen and heated at 500°C in vacuum for 2 hr and then again examined by ESR. In addition to the Mo(V) signal, which was not changed in any way (Fig. 4b) a narrow signal with a free spin g value of 2.0022 was observed which can be assigned to a carbon radical. The concentration of Mo(V) observed after treating the 10 wt % molybdenum-alumina catalyst with butene at 200°C for 15 min was 2.36×10^{19} spins/g, which corresponds to 3.7% of the total molybdenum present.

In another ESR experiment, a sample of 10 wt % molybdenum, which was treated in dry air at 550°C for 16 hr, was transferred to an ESR tube under a nitrogen blanket and then octene-1 was added to the catalyst particles to the point of incipient wetness. The catalyst particles immediately started to darken and a

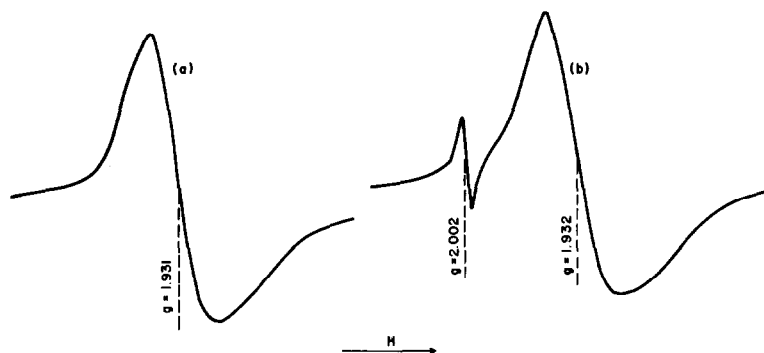


FIG. 4. ESR spectrum of (a) 10 wt % molybdenum-alumina treated with 1-butene at 200°C and (b) after heating the treated sample for 2 hr at 500°C in vacuum.

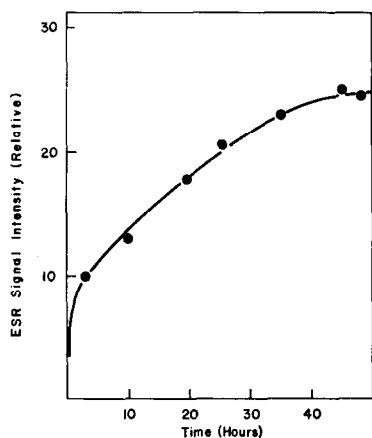


FIG. 5. Variation of Mo(V) ESR signal intensity with time from a 10 wt % molybdenum-alumina, octene-1 sample.

resonance signal was observed, the same as given in Fig. 4a. The signal intensity was observed over a 45-hr period, giving the curve shown in Fig. 5. The amount of Mo(V) detected after 45 hr was about the same as that observed when the sample was treated with butene at 200°C for 15 min.

The butene-treated 10% molybdenum catalyst was also examined by infrared spectroscopy. No bands attributable to hydrocarbon could be observed, evidently the concentration was too low.

DISCUSSION

The deposition of residues from olefins on alumina and silica-alumina catalysts

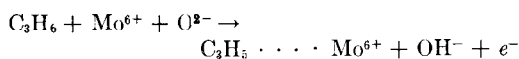
has been extensively studied (13-18) in the past. We found that very little residue is deposited on alumina, which is in agreement with a previous report (18). However, on treatment of silica-alumina with butenes (and several other types of olefins) a very rapid formation of polymer residue occurs at room temperature. This residue is further dehydrogenated on heating and transforms to what Webb (13) called a charge-transfer complex. Hall (19) took issue with this assignment and it now appears that this species is a multiply unsaturated carbonaceous residue in between the butene-like complex, which is deposited at room temperature, and "coke."

The hydrocarbon residue deposited on silica-alumina at low temperature is easily removed by washing with pentane (14) and catalyzes olefin isomerization. It has been suggested that this olefinic residue consists of polymeric olefins which periodically form the corresponding carbonium ions by reacting with Bronsted sites. However, when the residue is heated to 200°C, it becomes more difficult to remove and its activity for butene isomerization is decreased. The data presented show that addition of molybdena to alumina increases the amount of hydrocarbon residue formed when the catalyst is treated with butenes (and other olefins) at temperatures around 200°C. This residue is tenaciously held and results in a significant improvement of olefin disproportionation selectivity. We feel that the residue deposited on molyb-

dena-alumina is similar to that deposited on silica-alumina after the latter has been heated to about 200°C. ESR and micro-balance results confirmed that this residue is not "coke" but does transform to a "coke-like" material upon heating to higher temperatures.

In a previous paper (3) we reported that the addition of molybdena to alumina results in a marked increase in surface acidity as determined by ammonia adsorption. This increase in acidity most likely is a key factor for the significant increase in residue deposited on molybdena-alumina compared with that deposited on alumina.

Treatment of the molybdena-alumina catalyst with olefins results in the reduction of molybdena. The initial reduction of Mo(VI) probably occurs according to the reaction proposed by Peacock and co-workers (1) using propylene,



where a neighboring Mo(VI) ion is reduced to Mo(V) by the freed electron giving rise to the Mo(V) ESR signal. Besides this, after hydrocarbon deposition occurs, the molybdenum may catalyze further dehydrogenation of the deposit, giving a multi-unsaturated surface deposit, perhaps similar to a conjunct polymer, which becomes tenaciously bonded to the surface as it is dehydrogenated. The ability of molybdenum-alumina to function as a dehydrogenation catalyst is well known (20).

There is no correlation between the amount of Mo(V) observed by ESR and olefin disproportionation selectivity. Approximately the same amount of Mo(V) is observed when the catalyst is treated with butene at 200°C as that formed by treating with 1-octene at lower temperature for a longer time. However, disproportionation selectivity after the butene treatment at 200°C is much higher than that obtained by passing 1-octene over the catalyst at 100°C for a long time. The amount of Mo(V) is probably not a true indica-

tion of how extensive the reduction of molybdenum is since Mo(VI) can be reduced to Mo(IV) which would not be observed by ESR.

Seshadri and co-workers (12) demonstrated the uniqueness of molybdena-alumina compared with other molybdena-oxide combinations. The molybdena-alumina surface and its acidity is complex and not well understood. However, the surface properties of alumina have been studied extensively and considerable evidence exists indicating that its surface acid sites are not of the Bronsted type, at least at room temperature. The adsorption of butene-1 on alumina can proceed, as suggested by Haag and Pines (21) and by Hall (22) via allylic hydrogen abstraction. The butene-2 fraction formed during the disproportionation reaction over molybdena-alumina had a cis/trans ratio of approximately 3.0, which is close to that obtained by Hall (22) and much higher than that reported for the Bronsted-type surfaces (18). Kiviat and Petrakis (23) found that addition of molybdenum to alumina resulted in an increase in Bronsted surface acid sites. Hirshler (14) identified the residue on silica-alumina at room temperature as a polymeric carbonium ion (produced by and adsorbed on acidic OH groups) which could easily pass on the proton to the monomer leading to double bond isomerization in the latter. If the deposit on molybdena-alumina is a multiply unsaturated species, the probability of passing on a proton will be greatly reduced because a protonated multi-unsaturated hydrocarbon residue will be much more stable than a classical carbonium ion. Thus, the high cis/trans ratio over molybdena-alumina can be accounted for by the blocking of Bronsted surface sites and/or by the inability of the surface deposit to pass on a proton.

In the first paper (3) we presented on this subject it was stated that besides direct combination or blockage of surface sites, there is another effect dependent on the size of the added ion. By adding thallium or any group Ia metal, surface acidity and olefin isomerization activity

are reduced thus resulting in increased disproportionation selectivity. The reduced surface acidity with increasing cation size most likely corresponds to the increased polarizability associated with the increased cation size. As the surface is covered with large polarizable cations, areas of high surface charge density associated with the surface sites will be reduced in intensity. For example, it was found that the addition of 1.5×10^{-4} moles of thallium per gram of molybdena-alumina catalyst would only cover 5% of the surface sites, but was enough to almost totally inhibit olefin isomerization (8). Butene pretreatment results in 2.0 wt % carbon deposited, giving approximately 1.67×10^{-3} moles of carbon per gram of catalyst or 3.3×10^{14} carbon atoms/cm² of surface. Assuming that each polymeric species consists of 12 carbon atoms, then the surface coverage is equivalent to that obtained with 1.5×10^{-4} moles of thallium, and in both cases the same enhancement of olefin disproportionation is obtained. A multi-unsaturated polymeric residue on the molybdena surface would be expected to be highly polarizable and function in a similar way as thallium and other group Ia metals do. Admittedly, this like any proposed mechanism to date accounting for the enhanced disproportionation selectivity is speculative.

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