CATALYST SECTION

Catalytic Oxidation of 1-Butene—Effect of Oxygen Pressure

Ferruccio Trifirò,* Gianpiero Caputo, and Pio Forzatti

Istituto di Chimica Industriale, Politecnico di Milano, 20133 Milan, Italy

Oxidation runs of 1-butene have been carried out in a Carberry-type gradientless reactor at different concentrations of oxygen using a series of molybdenum-based catalysts such as $MnMoO_4$, β-$FeMoO_4$, a-$CoMoO_4$, and $CdMoO_4$. By varying the partial pressure of oxygen from 1% to 20%, strong modifications in selectivity were observed. By lowering the concentration of oxygen it was possible to obtain successively CO–CO_2, maleic anhydride, butadiene, isomers. The data have been explained on the hypothesis of the formation of adsorbed forms of oxygen. The production of maleic anhydride has been related to the presence of molecular adsorbed oxygen and to low coverage of the catalyst surface, while high coverage and/or dissociative absorption were suggested to be responsible for CO and CO_2 formation. Therefore, the partial pressure of oxygen is a key for modifying the selectivity of the investigated catalysts.

Introduction

In designing a hydrocarbon oxidation process of the vapor phase catalytic type, a general problem faced is whether to use air, enriched air, or pure oxygen. The choice has usually been based on considerations such as the cost of pure oxygen, the facility of separating products, the amount of heat produced by the reaction, and the necessity of recycling the reagents. However, great consideration has not been given to the influence that the partial pressure of oxygen has on the catalysts' selectivity in oxidation reactions.

As reported in a previous paper, Trifirò, *et al.* (1973), the distribution of the products in the oxidation of 1-butene on $MnMoO_4$ based catalyst depends on the oxygen level in the gaseous phase. As $MnMoO_4$ shows close analogies in structural properties to β-$FeMoO_4$, a-$CoMoO_4$, and $CdMoO_4$, (Trifirò, *et al.*, 1974), the catalytic activity of all these compounds has been investigated under a wide range of experimental conditions mainly to clarify the role of oxygen in the oxidation of 1-butene.

Experimental Section

(A) Preparation of the Catalysts. The preparation of $MnMoO_4$ and β-$FeMoO_4$ was according to the method described respectively by Trifirò, *et al.*, (1973) and Pasquon, *et al.* (1973).

$CdMoO_4$ and a-$CoMoO_4$ were prepared as follows. $CdMoO_4$: A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 g in 300 ml of distilled water) at pH 5.5, at 80°C, was added to a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (17.6 g in 300 ml of distilled water) at pH 5.5, at 85°C. After filtering, the precipitate was dried for 2 hr at 450°C. The amounts were regulated in order to have a Cd/Mo ratio of 1:1.

$CoMoO_4$: Equimolar solutions of $Co(NO_3)_2 \cdot 6H_2O$ (53.04 g/l.) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (32.16 g/l.) were mixed at pH 5.5. The resulting solution heated to 85°C gave a violet colored precipitate which, after filtering, was dried at 120°C for 2 hr and calcined at 500°C for 2 hr. The catalyst always became olive-green when ground in a mortar after activation at $T > 250°C$. This olive-green color changed back to violet when heating was prolonged to $T > 410°C$.

Cylindrical pellets 2.5 mm in diameter and 5 mm high have been used for oxidation runs carried out in the stirred tank reactor, while the pulse microreactor has been filled with catalyst powdered to 30–50 mesh. The surface areas of the investigated catalysts are β-$FeMoO_4$, 2.5 m^2/g; $MnMoO_4$, 3.5 m^2/g; $CdMoO_4$, 3 m^2/g; $CoMoO_4$, 9 m^2/g.

(B) Reagents. 1-Butene of 99.9% purity was used, the impurities being isomers and propylene. Chromatographic air, helium, and nitrogen were also used.

(C) Measurements of Activity. The activity data were obtained using a stirred tank gradientless reactor of the "Carberry" type described by Trifirò, *et al.* (1973), but with a cruciform catalyst basket and provided with four vertical baffles placed on the inner wall, as reported by Tajbl, *et al.* (1966), which gave an improvement of the mixing characteristics of the reactor. With this modification in the basket we were able to reach the asymptotic region in the plot of conversion *vs.* rotation speed at 1500 rpm, thus preventing the breaking into fragments of the catalyst and any weight loss even for not very hard catalysts. A reactor of this type was chosen so as to assure the absence of heat and mass gradients.

Each run was carried out with a procedure identical with that reported by Trifirò, *et al.* (1973). Some runs were carried out to determine the existence of homogeneous reactions at different temperatures and flow rates without catalyst. These runs have excluded the presence of substantial noncatalytic gas-phase oxidation of 1-butene, as only traces of butadiene at temperatures higher than 400°C have been observed. When butadiene was used as reagent only traces of furan were detected. Homogeneous gas-phase oxidation of maleic anhydride or of any other possible intermediate oxidation products was not checked.

(D) Analyses. Chromatographic analyses were carried out by means of a 6.5-m dimethylsulfulane column at room temperature and a 2-m dinonyl phthalate column at 140°C. Ir spectra were recorded with a Perkin-Elmer

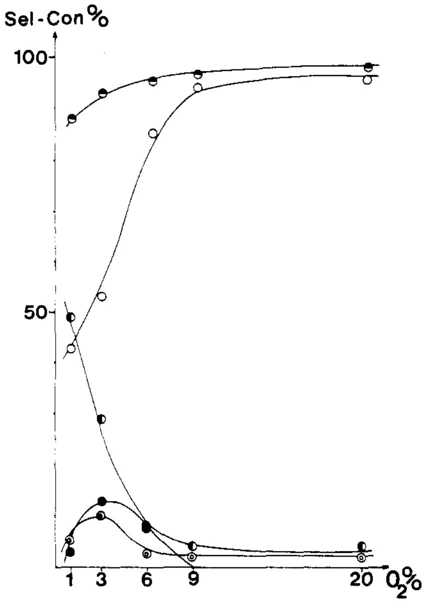

Figure 1. Selectivity (as (product)/(1-butene reacted)) and conversion (as (1-butene, reacted)/(1-butene, inlet)) *vs.* oxygen present in oxidation runs of 1-butene with a stirred tank reactor for $Fe_2(MoO_3)_4MoO_3$ catalyst; T = 390°C; F = 140 cc/min; 1-butene = 1%; catalyst g = 4.3; contact time = 3.07×10^{-2} g/cc min. ◓, conversion of 1-butene; ◐ selectivity of isomers (2-butene, cis and trans); ●, selectivity to maleic anhydride; ⊚, selectivity to 1,3-butadiene; ○, selectivity to CO and CO_2/4.

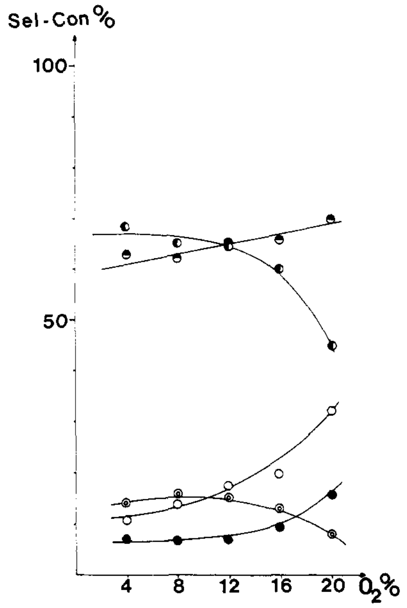

Figure 2. Selectivity and conversion *vs.* oxygen per cent in oxidation runs of 1-butene with a stirred tank reactor for $MnMoO_4$ catalyst: T = 390°C; F = 120 cc/min; catalyst, g = 1.73; 1-butene = 1%; contact time = 1.44×10^{-2} g/cc min. Symbols as in Figure 1.

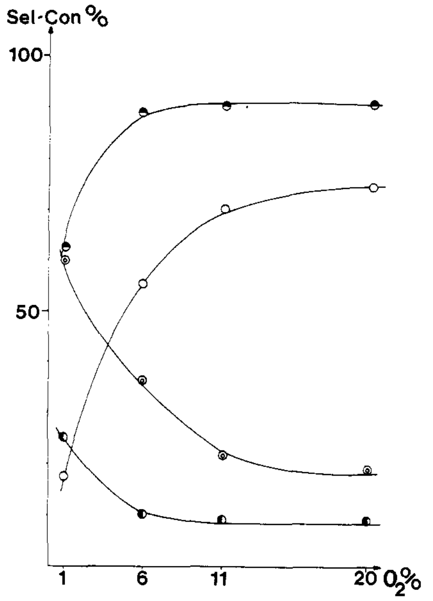

Figure 3. Selectivity and conversion *vs.* oxygen per cent in oxidation runs of 1-butene with a stirred tank reactor for $CdMoO_4$ catalyst: T = 425°C; F = 160 cc/min; catalyst g = 3.3; 1-butene = 1.5%, contact time = 2.06×10^{-2} g/cc min. Symbols as in Figure 1.

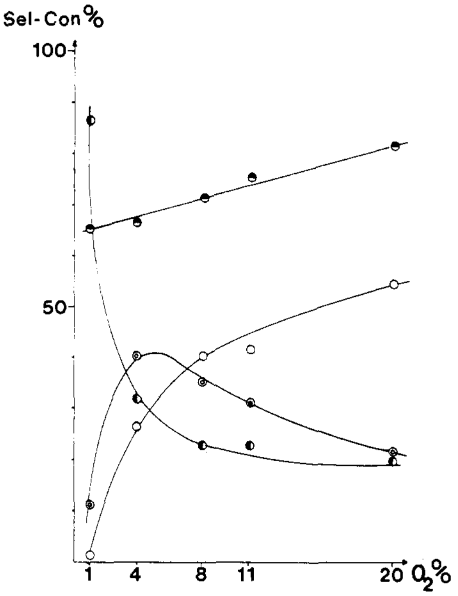

Figure 4. Selectivity and conversion *vs.* oxygen per cent in oxidation runs of 1-butene with a stirred tank reactor for $CoMoO_4$ catalyst: T = 435°C; F = 160 cc/min; catalyst g = 4.5; 1-butene = 1.5%; contact time = 2.81×10^{-2} g/cc min. Symbols as in Figure 1.

Model 257 instrument using the KBr tablet technique. Model ATR spectra were recorded by adapting ATR attachment RIIK TR 25 to the same spectrophotometer. X-Ray spectra were recorded with a Geiger Counter Philips spectrogoniometer using both Cu Kα and Mo radiation.

Results and Discussion

1. Catalytic Behavior. In Figures 1, 2, 3, and 4 we report the conversion of 1-butene and the selectivity to butadiene, isomers, carbon oxides, and maleic anhydride for the investigated catalysts in oxidation runs carried out in a flow reactor of the stirred tank gradientless type at different levels of oxygen.

All the molybdates tested showed high selectivity to butadiene and isomers at low partial pressure of oxygen, while as we increased the oxygen level in the gaseous feed, CO, CO_2, and maleic anhydride (the latter only for $MnMoO_4$ and β-$FeMoO_4$) were the main products, and the conversion did not practically change with the exception of $CdMoO_4$ (at very low levels).

Actually, in the case of iron molybdates, we tested a $Fe_2O_3 \cdot MoO_3$ sample prepared, as reported, by Pasquon, *et al.* (1973). Its activity rapidly decreases at oxygen partial pressure below 10%, when by spectroscopic measurements (ir and X-ray techniques) we realized that β-

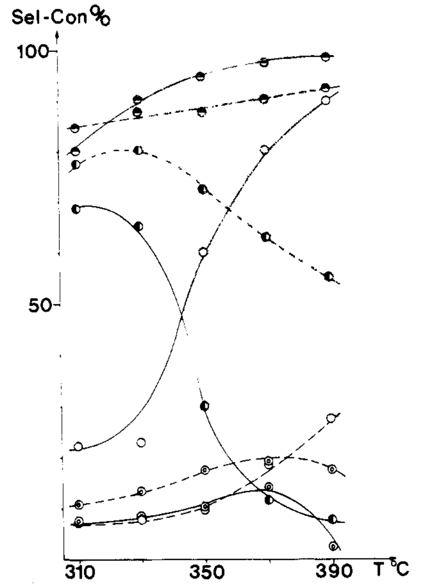

Figure 5. Selectivity and conversion *vs.* temperature in oxidation runs of 1-butene with a pulse micrordactor for $CdMoO_4$ catalyst: F of carrier gas = 33 cc/min; catalyst g = 1; 1-butene = 1.5%, Symbols as in Figure 1; ——, runs with air; - - -, runs without air with 1-butene diluted in helium.

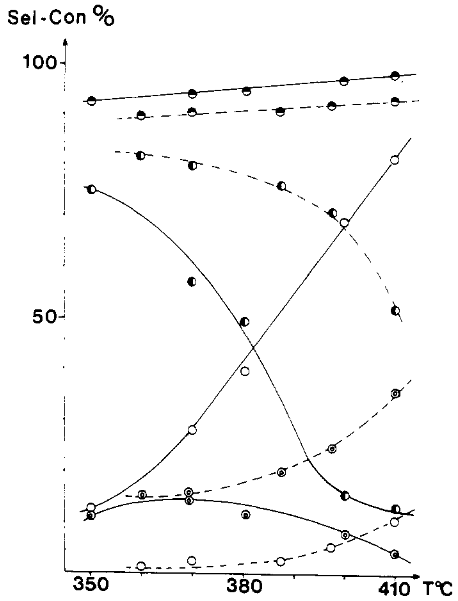

Figure 6. Selectivity and conversion *vs.* temperature in oxidation runs of 1-butene with a pulse microreactor for $MnMoO_4$ catalyst: F of carrier gas = 33 cc/min; catalyst g = 1; 1-butene = 1%. Symbols as in Figures 1 and 5.

$FeMoO_4$ is formed. Therefore, the observed changes at around 10% oxygen level are due to Fe(III) → Fe(II) reduction, while the catalytic behavior of β-$FeMoO_4$ (for oxygen below 10%) strongly depends on the concentration of oxygen. By increasing the oxygen partial pressure CO and CO_2 become the main products, the selectivity to isomers decreases, and the formation of butadiene and maleic anhydride (the latter at a not much higher oxygen level) reaches a maximum.

2. The Role of Lattice Oxygen. In order to clarify the mechanism whereby gaseous oxygen increases the complete oxidation of butadiene and 1-butene, runs were carried out in both the absence and presence of oxygen in a pulse microreactor. In Figures 5 and 6 the data for $CdMoO_4$ and $MnMoO_4$ are reported.

In the absence of oxygen high selectivity to butadiene was detected for Mn(II), violet Co(II), and Fe(II) molybdates while in the presence of oxygen the activity was almost the same but the selectivity was not. High amounts of CO and CO_2 were formed in this case. In the case of $CdMoO_4$ not much different behavior was observed. In the absence of oxygen mainly 2-butenes and a lower amount of butadiene were observed, while in the presence of oxygen, CO and CO_2 were the main products.

Therefore the selectivity to butadiene in the case of violet Co(II), Mn(II), Fe(II), and Cd(II) molybdates is due to lattice oxygen, while burning butadiene previously formed through interaction with the catalyst is due to adsorbed oxygen.

As previously reported by Trifirò and Pasquon (1968), and by Dewing (1970), and Weiss, *et al.* (1972), Mo═O groups are responsible in molybdates for the dehydrogenation of butenes to butadiene. According to Trifirò, *et al.* (1968), Mo═O bonds were also observed in Bi-molybdates which show high selectivity to butadiene.

Actually, Fe(II) (920 cm^{-1}), Mn(II) (925 cm^{-1}), and violet Co(II) (920 cm^{-1}) molybdates show absorption bands in the 910–940-cm^{-1} region of their infrared spectra, which are usually attributed to Mo terminal oxygen stretching vibration. Only $CdMoO_4$ has no band with an absorption maximum in the 800–1000-cm^{-1} region that *can* be attributed to Mo═O groups. However, shoulders, resolved in the ATR spectrum, are present at 940 and at 795 cm^{-1}. Actually, the absorption at 945 cm^{-1} might reveal the presence of Mo═O surface groups.

The conversion of 1-butene in the runs carried out in the pulse microreactor without oxygen in the gas phase decreased even after one pulse, while the activity was practically the same after three pulses for the other catalysts. This suggests that Mo═O groups are present in low ratio on the surface of $CdMoO_4$. These centers are regenerated by gaseous oxygen, as can be deduced by the high activity observed in the flow reactor.

This conclusion relates to the role of lattice oxygen. Figures 5 and 6 show that CO and CO_2 formed, though in small quantities, when the oxidation of 1-butene was accomplished in the pulse microreactor, in the absence of oxygen, even at relatively low temperatures. Therefore, we can conclude that lattice oxygen is also able to give a partial contribution to the formation of oxidized products.

3. The Role of Gaseous Oxygen. The differences observed between Bi-molybdates and the molybdates considered here, reveal (when the reaction is carried out in the presence of oxygen) that the role of gaseous oxygen differs. In fact, in the case of Bi-molybdates no difference in selectivity to butadiene was observed either in the presence or absence of oxygen as also shown by Keizer, *et al.* (1969), and by Pasquon, *et al.* (1967), for the ammonoxidation of propylene.

A two-center mechanism, given below, was proposed in the case of Bi-molybdates: Pasquon, *et al.* (1967), Matsura and Schuit (1972), and Peacock, *et al.* (1969), and in the case of Fe(III) molybdate, Trifirò, *et al.* (1969)

$$\mathrm{Mo^{VI}} + \text{hydrocarbon} \longrightarrow \mathrm{Mo^{V}} + \text{oxidized products} \qquad \text{(I)}$$

$$\mathrm{Mo^{V}} + \mathrm{Bi^{III}}\ (\text{or } \mathrm{Fe^{III}}) \longrightarrow \mathrm{Mo^{VI}} + \mathrm{Bi^{III}}\ \text{reduced (or } \mathrm{Fe^{II}}) \qquad \text{(II)}$$

$$\mathrm{Bi^{III}}\ \text{reduced (or } \mathrm{Fe^{II}}) + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Bi^{III}}\ (\text{or } \mathrm{Fe^{III}}) \qquad \text{(III)}$$

The first step is similar to the one we propose for

$MnMoO_4$, violet $CoMoO_4$, β-Fe(II)MoO_4, and also for $CdMoO_4$, as the selectivity to butadiene for these catalysts in a pulse reactor and in the absence of oxygen is close to that observed for Bi-molybdates, since butadiene was present in the highest quantity among oxidized products.

We believe that the second step cannot occur for the investigated catalysts since the second metal is in its lowest oxidation state and therefore cannot oxidize the reduced form of Mo^{VI}.

In addition, the oxidation of the second metal by gaseous oxygen to a higher oxidation state does not easily occur for Mn(II), Co(II), and Cd(II) while it has been demonstrated that it takes place for Fe(II) when the oxygen partial pressure is sufficiently high and β-$FeMoO_4$ changes into $Fe_2O_3 \cdot MoO_3$. In the latter case a two-center redox mechanism is again operating due to the presence of Fe(III).

In the case of the other catalysts and for β-$FeMoO_4$ at low oxygen level, we think that in the reoxidation step of Mo^V gaseous oxygen must interact with Mo^V itself giving rise to Mo^V–O_2 adsorbed forms which are responsible for the formation of CO, CO_2, and maleic anhydride.

Concerning $CoMoO_4$, Mo has an octahedral coordination in phase b, while Courtine, *et al.* (1968) (through a comparative study of X-ray patterns) arrived at the conclusion that a-$CoMoO_4$ has Mo in tetrahedral coordination.

As some of us have already shown in another paper, Trifirò, *et al.* (1974), the change of color from violet to green, which is noticed when samples are ground and which turns back to violet after prolonged heating at $T >$ 410°C, is connected to the superficial coordination that Mo assumes, *i.e.*, to the presence at the surface of phase a or b.

For violet $CoMoO_4$ we caution against the use of spectroscopic techniques (*e.g.*, ir) which require the grinding of the catalyst powder. By a careful analysis of X-ray patterns, ATR and uv spectra, it can be seen that both violet and green colors show the structure of a-$CoMoO_4$ in the bulk, with a low amount of b, while green $CoMoO_4$ has the structure of b-$CoMoO_4$ at the surface.

This is particularly interesting because green $CoMoO_4$, which has an octahedral coordination of Mo at the surface, is inactive, as also reported by Boutry, *et al.* (1968), while at around 410°C (temperature at which there is a change from green back into violet) there is a strong rise in activity.

The Role of Oxygen Partial Pressure. Based on what has previously been said, it would seem that, as oxygen partial pressure lowers in the gas phase, changes occur on the catalyst surface. Such modification may involve (i) the chemical nature of the catalyst or (ii) only the oxygen adsorbed species.

The first case is evident in the catalytic behavior of $Fe_2(MoO_4)_3 \cdot MoO_3$. At low levels of oxygen, in the presence of a reducing agent such as an olefin β-$FeMoO_4$ is formed, which is responsible for the different spectra of products and for the higher selectivity.

The second case might be that of $CdMoO_4$, β-$FeMoO_4$, a-$CoMoO_4$, and $MnMoO_4$. These catalysts at low oxygen partial pressure form products which are oxidized at a low degree (butadiene) and at higher oxygen partial pressure they form products which are oxidized at a higher degree (CO, CO_2, and maleic anhydride). The oxygen level in the gaseous feed should become a controlling factor in the reaction mechanism, as a redox mechanism (like the one proposed for Bi-molybdates) is ruled out by the fact that the second metal is in its lowest oxidation state as we also checked by spectroscopic means on catalysts taken out from the reactor.

At this point an attempt may be made to associate the nature of the products we obtained with the probability that a hydrocarbon molecule could find enough oxygen adsorbed species to be oxidized to a certain level (maleic anhydride, CO, CO_2).

A basic hypothesis is that, for the three classes of products (isomers, butadiene, and CO, CO_2, maleic anhydride) there must be present different sites responsible for their formation: acid sites for isomers, dehydrogenation sites for butadiene, and adsorbed oxygen species for CO, CO_2, and maleic anhydride.

Other authors have previously proposed that the nature of dehydrogenation sites may be connected to Mo=O groups and we hold the same opinion as they still exist in the absence of gaseous oxygen.

It is difficult to quantify the distribution of the active sites on the surface according to their nature and to deduce the probability of a hydrocarbon molecule reacting to a certain product. The problem may become even more difficult if we consider that also the adsorbed oxygen may undergo many transformations.

In fact, according to Schwets and Kazanski (1972), a chain reaction of this kind may occur on tetrahedral Mo(V)

$$O_{2\,\mathrm{gas}} \longrightarrow O_{2\,\mathrm{ads}} \longrightarrow O_2^{\cdot} \longrightarrow 2O^{\cdot} \longrightarrow 2O^{2\cdot}$$

in which the first stage is that of an excited molecule of gaseous oxygen, O^{2-} being an oxide species of the catalyst.

Attempts to quantify the problem have been made by Callahan and Grasselli (1963), but because of the simplicity of the reaction studied and the approximation given, we cannot apply the results to our case.

Actually, if the formation of maleic anhydride and carbon oxides would be exclusively due to the probability so that a butene or butadiene molecule could find enough oxygen adsorbed species, stoichiometrically required, to be oxidized to the desired level, the formation of maleic anhydride *vs.* oxygen level in the gaseous feed should reach a maximum. Such behavior has been observed only in the case of β-$FeMoO_4$ (below 10% oxygen level).

Concerning $MnMoO_4$, we found that both rates of production of maleic anhydride and carbon oxides are first order with respect to oxygen (as can be gained from Figure 2). The observed dependences on oxygen partial pressure reveal that the coverage of the catalyst surface is still low and, moreover, nondissociative adsorption is likely to occur. We think that molecular adsorbed species are formed.

In the case of $CdMoO_4$ and a-$CoMoO_4$, only traces of maleic anhydride have been detected, and the rate of production of carbon oxides, which were the main products, increases markedly even from low oxygen levels, thus revealing high coverage of the catalyst surface and/or dissociative oxygen adsorption.

In the case of $Fe_3(MoO_4)_2$ we observe that from β-$FeMoO_4$ at oxygen level over 10% the rate of production of carbon oxides does not depend on the oxygen partial pressure, thus revealing a very high coverage of the catalyst surface. In such a situation, the catalyst burns almost exclusively to CO and CO_2.

Conclusions

A series of molybdates, such as $MnMoO_4$, β-$FeMoO_4$, a-$CoMoO_4$, and $CdMoO_4$, highly selective in the oxidative dehydrogenation of butenes to butadiene at low oxygen partial pressure but unselective when air was used, has been investigated. The following points concerning their catalytic behavior have been stressed: (1) Lattice oxygen is responsible for selective oxidation to butadiene. (2) Adsorbed forms of oxygen are responsible for substantial production of CO, CO_2, and maleic anhydride. (3) The production of maleic anhydride seems to require low coverage of the catalyst surface and, we think, the presence of molecular adsorbed oxygen species. (4) The partial pressure of oxygen is a key to modify the selectivity to the desired products (carbon oxides, maleic anhydride, or butadiene).

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Catalytic Reduction of Nitric Oxide on Ruthenium

Richard L. Klimisch and Kathleen C. Taylor*

Physical Chemistry Department. General Motors Research Laboratories
General Motors Technical Center. Warren. Michigan 48090

The details of nitric oxide catalytic reduction by carbon monoxide and hydrogen over a supported ruthenium catalyst have been investigated. The feed stream used in these studies resembled automotive exhaust. The effect of space velocity and various reactant concentrations on the ammonia/nitrogen product distribution were studied along with the effect of these various parameters on the rate of nitric oxide removal. The pertinent chemical reactions in this system and the limitations imposed by an exhaust gas feed stream are discussed.

Introduction

Recent studies have shown that ruthenium catalysts selectively convert NO to N_2 in feed streams resembling automotive exhaust (Klimisch and Taylor, 1973; Taylor and Klimisch, 1973; Shelef and Gandhi, 1972). The problem of ammonia formation, which has plagued other catalysts, is minimized with ruthenium. It was noted by Klimisch and Taylor (1973) that ruthenium catalysts exhibit two states which differ in activity characteristics. One state can be obtained by treating the catalyst with oxygen at low temperature and the other is obtained when the catalyst is treated with a reducing feed stream at high temperature (>650°C). These transformations are reversible since they have been repeated a number of times for an individual catalyst sample. The phenomenon was only eliminated when the catalyst was exposed to sulfur containing materials (Taylor and Klimisch, 1973). The application of physical methods of surface examination to characterize the two states of the catalyst gave no evidence that the so-called oxidized form of the catalyst is an oxide under the reaction conditions for NO reduction (Taylor, *et al.*, 1974).

A recent publication from this laboratory described how various reactant parameters influence the product distribution for NO reduction over a reduced ruthenium catalyst supported on silica-alumina (Taylor and Klimisch, 1973). A complementary study of the oxidized form of a ruthenium on alumina catalyst is the subject of the present work. Specifically, this study will examine product distribution as a function of reactant concentration and will also examine the question of ammonia intermediacy in the reduction of NO to N_2.

Experimental Section

The ruthenium catalyst was prepared by impregnation of ⅛-in. alumina spheres (Kaiser KC/SAF) with an aqueous solution of ruthenium trichloride ($RuCl_3 \cdot 1\text{-}3H_2O$, Alfa Inorganics). The catalyst was dried in air at 25°C and then calcined in air at 500°C for 4 hr (gas hourly space velocity = 500). The catalyst was made up to contain 0.1 wt % ruthenium. The total ruthenium content determined by X-ray fluorescence was 0.081 wt %.

The catalytic reactor and gas analysis techniques have been described before (Klimisch and Barnes, 1972). The gas hourly space velocity (GHSV) was 38,000 for most experiments. The feed stream referred to as the standard feed stream contained 0.10% NO, 1.0% CO, 0.3% H_2, 10%