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PROPYLENE CONVERSION REACTIONS; METATHESIS, CYCLIZATION AND HYDROGENOLYSIS CATALYZED BY Mo(100) AND OXYGEN-COVERED Mo(100)

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Analysis of the products formed in the Mo(100) single crystal-catalyzed decomposition of propylene using an isolatable high-pressure reactor shows that this surface simultaneously catalyzes metathesis, hydrogenolysis and also methylcyclopropane formation. The activation energy for olefin metathesis on Mo(100) is measured to be 65 ± 1 kcal/mole, and the reaction is first order in propylene pressure. These results are consistent with the reaction proceeding via a carbene mechanism on Mo(100) since hydrogenolysis indicates that carbon-carbon bonds can cleave selectively, and methylcyclopropane formation suggests that a metallacycle has formed. The observed first-order reaction kinetics are also in accord with this view. Pre-dosing the Mo(100) surface with a monolayer of oxygen reduces the catalytic activity by a factor of ~17. This implies that the four-fold hollow site is active for propylene metathesis on Mo(100) since atomic oxygen adsorbs at this site.

1. Introduction

Heterogeneously-catalyzed olefin metathesis has received a considerable amount of attention in the literature since its discovery by Banks and Bailey in 1964 [1]. Subsequently, a range of very heterogeneous catalysts were identified. Most of the investigations into this reaction have been aimed at identifying the reaction pathway. Since olefin metathesis is symmetry forbidden in the gas phase, the catalyzed reaction has received some theoretical scrutiny which suggested that the role of the catalyst was to lower the symmetry sufficiently so that it was no longer forbidden. This work spawned the quasi-cyclobutane mechanism which suggested that the reaction proceeds via the formation of a surface cyclobutane intermediate [2]. A similar mechanism involving the formation of a metalla-

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pentacycle was also proposed [3]. Finally, the "carbene" mechanism was suggested, which holds that initially catalytically-active carbenes ($CH_{2(ads)}$) are formed which can subsequently react with an alkene forming a metallacyclobutane. This can then decompose to form metathesis products [4]. The carbene mechanism is now the most commonly-accepted, particularly for homogeneously-catalyzed reactions where the most compelling supportive evidence comes from isolation of reaction intermediates [5] and by analyzing the first-formed products [6].

The reaction is most commonly catalyzed in heterogeneous phase by reduced MoO_3 [7]. It is shown, however, in the following that it can also be catalyzed by a Mo(100) single crystal, although with turnover frequencies considerably lower than for the supported oxide catalyst. The product distribution for the Mo(100)-catalyzed reaction is also consistent with results obtained by Burwell et al. who have studied hydrocarbon reactions catalyzed by metallic molybdenum. In this case, supported Mo(0) is formed either by decomposition of $Mo(CO)_6$ [8,9] or by the direct reduction of MoO_3 at high temperature [10]. Both preparation procedures lead to catalysts with identical properties [11,12], providing good hydrogenolysis catalysts [12–14] but exhibiting minimal metathesis activity [15,16]. Several pieces of experimental evidence suggest that the reaction also proceeds via the carbene mechanism in heterogeneous phase on supported oxides. Firstly, carbene species have been identified on the surface of an active metathesis catalyst [17], and grafting CH_2 species onto an MoO_3 surface by CH_2I_2 decomposition renders it extremely active [18]. In addition, it has been possible to link olefin metathesis and CO hydrogenation reactions via a common CH_2 intermediate [19].

The results presented below for Mo(100)-catalyzed propylene metathesis support the carbene mechanism on metallic molybdenum. In addition, it is shown that a monolayer of oxygen significantly diminishes the activity of the surface, suggesting that the active site for metathesis on Mo(100) is the four-fold hollow site.

2. Experimental

The apparatus used for these experiments has been described in detail in previous publications [20]. The main feature of the apparatus, for the purposes of the results presented here, is the inclusion of an isolatable high-pressure reactor in the UHV chamber. The bakeable stainless-steel chamber is pumped by a liquid-nitrogen-trapped diffusion pump, and operates at a base pressure of 2×10^{-10} Torr following bakeout. It contains an RFA for LEED measurements and for Auger analysis of the sample, and a quadrupole mass spectrometer for residual gas analysis and temperature programmed desorption. In addition, it incorporates an X-ray source and rotatable hemispherical analyzer for XPS.

The sample is mounted to the end of a co-axial sample manipulator and can either be resistively heated to 2000 K or cooled to 80 K by thermal contact to a liquid nitrogen filled reservoir. The sample temperature is measured by means of a W-5% Re/W-26% Re spot-welded to the sample. Both an oriented Mo(100) single crystal and polycrystalline foil were used for these experiments. The thermocouple was spot-welded to the edge of the crystal and on one face of the foil. The thermocouple calibration was checked, particularly in the case of the foil, by means of an infrared pyrometer.

These samples can be used for high-pressure catalytic reactions since they can be enclosed in a co-axial, isolatable, high-pressure reactor. In this case, the sample manipulator is retracted to seat on an "anvil", and the high pressure cell brought up from the bottom of the chamber to enclose the sample. In order to minimize opening and closing times, the cell is motor driven. The cell is sealed by means of a thick, annealed copper gasket, and once sealed the UHV portion of the apparatus can be maintained at 5×10^{-10} Torr with the cell pressurized to 1 atmosphere. The reaction cell is connected to a recirculation loop, equipped with a recirculating pump, capacitance manometer and sampling valve for diverting a portion of the reaction mixture for chromatographic analysis. Reactions were carried out for propylene pressures between 35 and 140 Torr, and in all cases the total pressure was made up to 800 Torr using nitrogen. The mixture was homogenized for 20 minutes using the recirculation pump prior to starting the reaction, following which the sample was heated to the desired reaction temperature. Reaction rates were measured by periodically analyzing the reaction mixture using a gas chromatogram equipped with a flame ionization detector, and product concentrations were normalized to the propylene signal. This resulted in a linear product accumulation curve which exhibited no induction period. Concentrations measured in this way are reproducible to within 5%. Reaction rates are measured from the slope of these curves for low ($< 1\%$) conversions. The reaction products were identified from their retention times by comparison with mixtures of gases of known compositions. Their identities are confirmed by measuring the retention times of each of the products individually, A 30-cm length Poropak-filled column was used to separate products which were detected using a flame ionization detector.

The samples were cleaned using a standard protocol [21], and were judged clean when no Auger signals were detected due to adsorbed contaminants (predominantly carbon and oxygen). The propylene (Union Carbide, Linde Division; 99.0%) was transferred from a cylinder to a glass bottle and purified by several bulb-to-bulb distillations by keeping only the middle portion of the distillate. The gas was stored in glass until use, and its purity checked mass-spectroscopically prior to each reaction.

3. Results

Fig. 1 displays a histogram showing a typical product distribution from the reaction of propylene over a Mo(100) single crystal obtained using the high-pressure reactor (in this case with a partial pressure of 70 Torr at a reaction temperature of 880 K). The product distribution indicates that several reactions are proceeding simultaneously. Firstly, C_4 compounds are formed indicating that this surface catalyzes metathesis. The proportion of the ethylene (C_2) associated with this reaction is shaded on the histogram. In addition, equimolar amounts of methane (C_1) and ethylene (in excess of that ascribed to metathesis) are also formed indicating that Mo(100) also catalyzes hydrogenolysis. The hydrogen required for this reaction likely derives from propylene decomposition [22]. Finally, methylcyclopropane (designated cyclo-C_4) is also detected in the reaction products. No other hydrocarbon products were detected, and a carbon mass balance was maintained throughout the reaction. Note that a carbonaceous film several monolayers thick is found on the Mo(100) surface using Auger spectroscopy following the reaction. This carbon, however, comprises a negligible proportion of the total hydrocarbon reacting at the surface. Reaction with

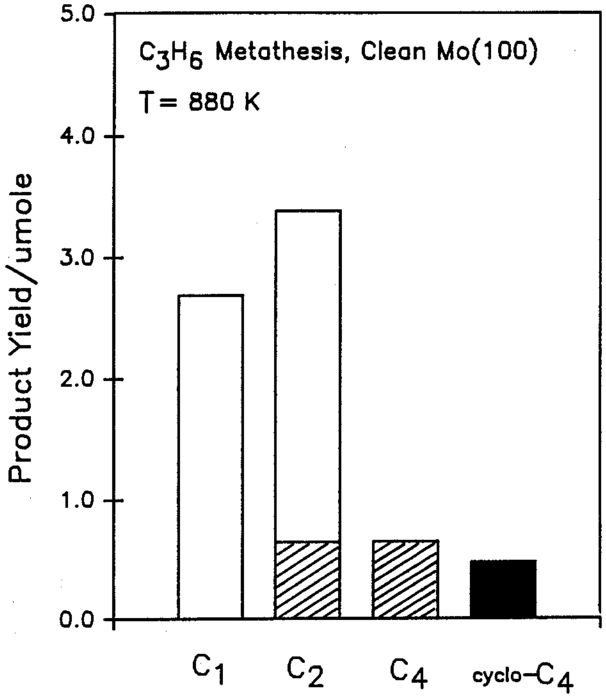

Fig. 1. A histogram showing a typical product distribution in this case obtained from the Mo(100)-catalyzed reaction of propylene at a reaction temperature of 880 K at a reactant pressure of 70 Torr. All reaction products are shown and include methane (C_1), ethylene (C_2) and butenes (C_4) as well as methylcyclopropane (cyclo-C_4).

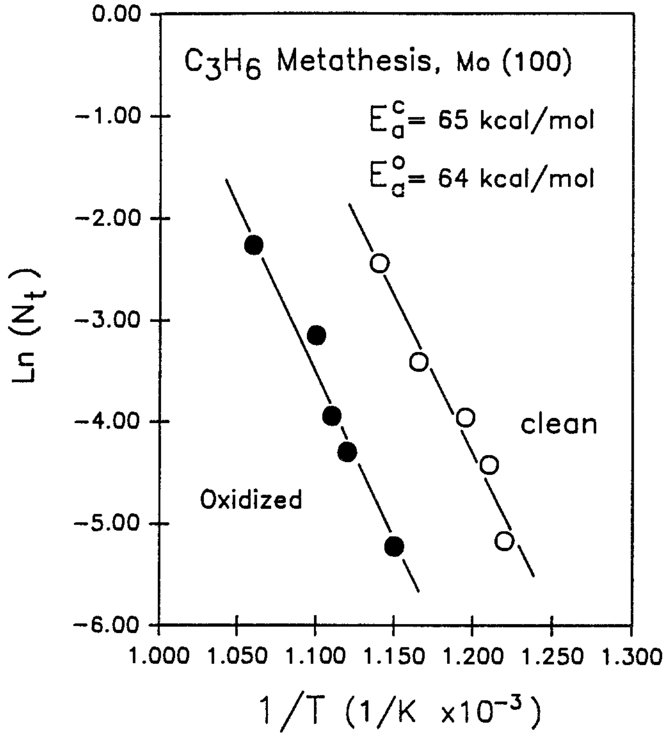

Fig. 2. Arrhenius plot for propylene metathesis catalyzed by Mo(100), (○), which yields a reaction activation energy, E_a^C, of 65 ± 1 kcal/mole, and catalyzed by oxygen-covered Mo(100) (●) which yields an activation energy, E_a^O, of 64 ± 1 kcal/mole. The propylene partial pressures used for these reactions was 70 Torr.

ethylene (100 Torr) using exactly identical conditions produced *no* C_4 products indicating that C_4 hydrocarbons are not produced by reaction of hydrogenolysis products (ethylene) with the catalyst.

Shown in fig. 2 are the temperature dependencies for metathesis plotted in Arrhenius form for the reaction catalyzed both by initially-clean Mo(100) (○), and by a Mo(100) single crystal covered by a monolayer of oxygen (●) [23]. The oxygen coverage was confirmed using Auger spectroscopy. The reaction activation energy (65 ± 1 kcal/mole) is identical both for clean and oxygen-covered Mo(100). This activation energy is, however, considerably higher than usually observed for supported oxide metathesis catalysts [24]. Note also that the reaction *rate* is approximately 17 times lower for the oxygen-covered Mo(100) single crystal than for the corresponding clean surface. The reaction has also been studied using a clean molybdenum foil, and yields exactly identical results to those shown in fig. 2. More importantly, the rate, normalized to the exposed areas of the samples, is identical for both model catalysts, confirming that the reaction is indeed catalyzed by the molybdenum. In addition, replacing the molybdenum sample by palladium completely suppresses any catalytic activity. Turnover

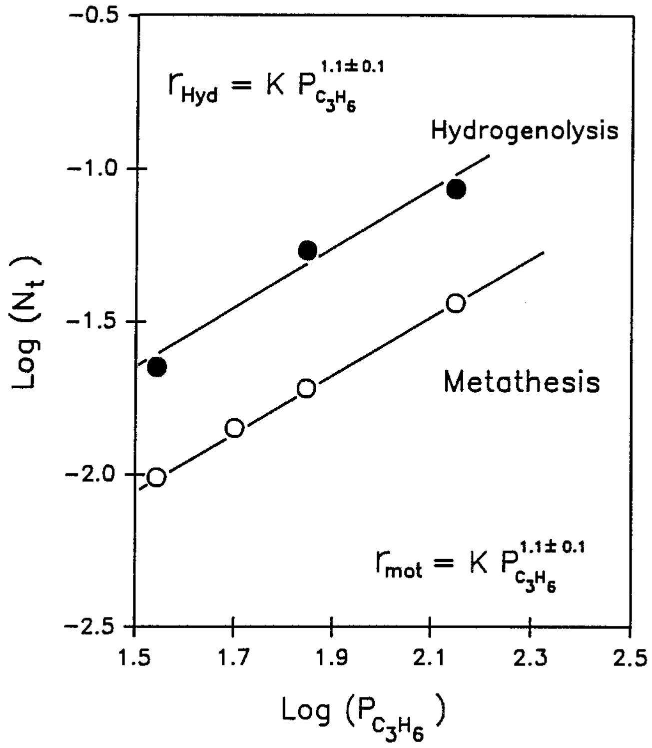

Fig. 3. Plot of log(reaction rate) (Log(N_t)) versus log(propylene pressure) (Log($P(C_3H_6)$)) for Mo(100)-catalyzed propylene metathesis (○) and hydrogenolysis (●) at a reaction temperature of 838 K. The gradient of the curve in both cases is 1.1 ± 0.1, and data were obtained for propylene pressures between 35 and 140 Torr.

frequencies of 10^{-1} to 10^{-2} (normalized to the number of unit cells on Mo(100); $1 \times 10^{15}/\text{cm}^2$) for the reaction are typical. However, the reaction was allowed to proceed sufficiently long that several hundred to thousands of turnovers had accumulated. No diminution of the reaction rate was observed indicating that the reaction is catalytic.

Fig. 3 shows a plot of log(reaction rate) (log(N_t)) versus log(propylene pressure) (log $P(C_3H_6)$), for Mo(100)-catalyzed propylene metathesis for reactions at constant temperature (838 K). In this case the reaction rates were all measured for low ($< 1\%$) conversions. The slope of this curve is 1.1 ± 0.1, indicating that the reaction is first order in propylene over the pressure range (35 to 140 Torr) used for these experiments. These results also show that the hydrogenolysis reaction is also first order in propylene pressure.

Finally, it should be pointed out that *significant* amounts of carbon (several monolayers) were detected following reaction on the Mo(100) surface using Auger spectroscopy. It appears that metathesis proceeds in the presence of this carbon, since "restart" reactions (without any intervening surface treatment) proceed at exactly identical rates. This observation will be discussed in greater detail elsewhere [22].

4. Discussion

Although Mo(O) is not commonly thought of as an active metathesis catalyst [15,16], these results indicate that it *does* catalyze this reaction, albeit at a low rate. The product distribution furthermore indicates that it simultaneously catalyzes hydrogenolysis [12–14] (since equimolar amounts of methane and ethylene are detected), and methylcyclopropane formation. This latter reaction has been observed previously, particularly on low-valent catalyst [25,26].

Several pieces of evidence are consistent with the view that the reaction proceeds via a carbene mechanism on Mo(100). The observation of hydrogenolysis products indicates that carbon-carbon bonds are cleaved on the metal surface. The observed reaction is in accord with the view that these products are formed via propylene dissociation. Indeed, the preponderance of hydrogenolysis products suggests that carbon-carbon bond cleavage is facile. This conclusion is in accord with surface analysis experiments on ethylene on Mo(100) [27] which shows that heating an ethylene precovered surface to ~ 300 K leads to carbon-carbon bond cleavage and the formation of surface CH_x species. Secondly, the formation of methylcyclopropane suggests that metallacycles *have* formed since these are likely to arise via reductive elimination of the metallacycle [25,26]. Finally, the first-order pressure dependence is in accord with such a mechanism. That is, both the quasi-cyclobutane and the metallapentacycle mechanisms would lead to second-order kinetics in propylene partial pressure since they involve an associative reaction between two adsorbed propylene molecules. In contrast, the carbene mechanism implies a first-order pressure dependence irrespective of whether carbene or metallacycle formation are rate-limiting.

Finally, the activity of the Mo(100) model catalyst is significantly diminished (by a factor of ~ 17) by the presence of a monolayer of chemisorbed oxygen. Since the crystal was pre-dosed in UHV, this result further demonstrates that the reaction is indeed catalyzed by the single crystal surface. This confirms the conclusions arrived at by substituting palladium and molybdenum foils for the single crystal. Oxygen adsorbs dissociatively on Mo(100) and occupies the four-fold hollow site [28]. The diminution in activity of the oxygen-covered Mo(100) surface therefore suggests that the four-fold hollow provides the active site for olefin metathesis on Mo(100). This conclusion is in accord with the proposed chemisorption site for ethylene on Mo(100) [27]. It should be noted, however, that part of this effect may be due to electronic modification of the surface by the presence of a co-adsorbed electronegative adsorbate and may not be due exclusively to geometrical effects.

5. Conclusions

Metallic molybdenum (in the form of a Mo(100) single crystal or polycrystalline foil) catalyzes propylene metathesis, hydrogenolysis and methylcyclopropane formation. Comparison of the rate of product formation using a Mo(100) single crystal with a polycrystalline foil, oxygen-covered Mo(100) single crystal and a palladium foil indicates that the reaction *is* catalyzed by metallic molybdenum. The activation energy for propylene metathesis is 65 ± 1 kcal/mole and the reaction is first order in propylene pressure. Both the reaction kinetics and product distribution suggest that the reaction proceeds on Mo(100) via the carbene mechanism. The reaction rate is significantly lowered (by a factor of ~ 17) by a monolayer of chemisorbed oxygen adsorbed at a fourfold hollow site. This suggests that this is the active site for reaction.

Acknowledgments

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