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The Effect of Hydrogen on the Carbonaceous Layer Formed on Molybdenum Model Catalysts during High Temperature Propylene Metathesis

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The formation and hydrogen removal of the thick carbonaceous layer accumulated during metathesis of propylene at 880 K on molybdenum and molybdenum oxide model catalysts is examined. It is determined that a hydrocarbon layer several monolayers thick forms rapidly during reaction, and that a portion of this layer may be easily removed by heating the used catalyst in hydrogen. An activation energy of 6.4 ± 0.4 kcal/mol is observed for this process. A graphitic layer also forms slowly on the catalyst surface during reaction, and this layer is difficult to remove by reaction with hydrogen. It is demonstrated that addition of hydrogen to the metathesis reaction mixture reduces the thickness of the carbonaceous layer on the catalyst surface during reaction, thereby enhancing the observed metathesis rate. © 1998 Academic Press

INTRODUCTION

Molybdenum-based catalysts are used for wide range of hydrocarbon conversion reactions, for example, hydrogenation (1–3), hydrogenolysis (4, 5), desulfurization (6, 7), and olefin metathesis (8–12). Typically, the molybdenum is chemically modified so that, for instance, molybdenum oxide is used to catalyze olefin metathesis. The first active, heterogeneous olefin metathesis catalyst was discovered by Banks and Bailey (12), and active, homogeneous-phase catalysts were discovered shortly thereafter (13). It has been shown that the reaction is catalyzed by metallic molybdenum at sufficiently high temperatures (14, 15) and also by model oxide catalysts (16). In all cases, that is, for both metal and oxide, analysis of the sample using Auger spectroscopy following reaction using a catalytic reactor incorporated in an ultrahigh vacuum chamber reveals the presence of large amounts of carbon on the surface (14, 15, 16). Restart reactions, where the carbon-covered surface is reinserted into the catalytic reactor, indicate that the reaction proceeds at exactly the same rate on the "dirty" sample as on an initially clean sample (14, 15, 16). These results indicate that the reaction proceeds in the presence of this layer. Raman spectra of the catalytic surface of MoO_3 following reaction reveal that, in common with the carbonaceous layers formed on many catalyst surface (17–21), this layer consists of a graphitic and a hydrocarbon portion (16). It is known that strongly bound carbonaceous layers present during catalysis by transition metals, for example ethylidynes, can be removed only by reaction in high pressures (∼atmospheres) of hydrogen (22, 23). We find, in the following, that the hydrocarbon portion of the carbonaceous layer can similarly be removed by reaction in high pressures of hydrogen, but that the activation energy for this process is only ∼6.4 kcal/mol. The addition of hydrogen to the reaction mixture during olefin metathesis both decreases the amount of carbon present on the surface and correspondingly increases the rate of the metathesis reaction, even though this reaction does not require-hydrogen. This enhancement is ascribed to the removal of carbonaceous deposits by the hydrogen revealing vacant sites below leading to an increase in reaction rate.

EXPERIMENTAL

Experiments were carried out in an ultrahigh vacuum apparatus described in detail elsewhere (24, 25). In brief, the system consists of a bakeable, stainless-steel chamber containing an isolateable, high-pressure reactor. This arrangement allows catalytic experiments to be carried out at pressures up to 1000 Torr in the cell while maintaining ultrahigh vacuum ($P < 1 \times 10^{-9}$ Torr) conditions in the remainder of the system. Reactants are circulated so that the cell volume is turned over every 25 seconds to ensure that the gas remains well mixed. Small samples of the gas mixture in the cell may be diverted to a gas chromatograph equipped with a flame-ionization detector for analysis. During reaction temperature is controlled to ±1 K by an Electronic Control Systems temperature controller.

High-purity molybdenum foil (99.999%) is mounted to 2 mm tantalum rods so that it can be resistively heated to

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above 2000 K. Temperature is monitored using a W 5% Re/W 26% Re thermocouple spotwelded directly to the foil. The sample is cleaned by annealing to 1350 K in 2×10^{-7} Torr of oxygen until carbon could not be detected by Auger spectroscopy, and remaining oxygen is removed by annealing to 2000 K *in vacuo*. This process is repeated several times to remove carbon that diffuses from the metal bulk to the surface.

Reactants used are propylene (Matheson, CP grade), nitrogen (Matheson, High Purity grade), and hydrogen (Matheson, Ultra High Purity grade). The propylene is further purified by bottle-to-bottle distillation and its purity is verified by gas chromatography and mass spectroscopy. Nitrogen and hydrogen are used as supplied directly from the bottle.

RESULTS

The average thickness of the carbonaceous layer formed on the surface of molybdenum metal during reaction with propylene is estimated from the ratio of the carbon KLL Auger peak intensity at ~270 eV (C(270)) to the molybdenum MNN Auger peak at ~220 eV (Mo(220)). The relationship between carbon coverage and this Auger ratio has been determined to be (14):

$$\text{Thickness (ML)} = 3.3\left(\ln\left(\frac{\text{C}(270)}{\text{Mo}(220)} + 1\right)\right)$$

By inserting a clean molybdenum sample into the high-pressure cell and heating the sample at 880 K in 200 Torr of propylene for various times, it is possible to monitor the accumulation of carbonaceous deposits as a function of reaction time using Auger electron spectroscopy where the signal intensity is converted to film thickness using the above equation.

The result of this experiment is shown in Fig. 1, which reveals an initial very rapid build-up of a carbonaceous layer ~6 monolayers thick followed by a slow increase in thickness. The total number of catalytic turnovers under these conditions is greater than 10,000. The inset in Fig. 1 shows the carbon 270 eV Auger peak lineshape, which is typical of an adsorbed hydrocarbon (26) suggesting that, at least, the surface of this layer consists of a hydrocarbon. It has been shown using Raman spectroscopy (16) that the film consists of both a hydrocarbon and a graphitic portion and the Auger peak shape of the carbon KLL peak (Fig. 1) indicates that the hydrocarbon portion is preferentially detected under these conditions. This may mean that there is substantially less graphite than hydrocarbon or else that the graphite is closer to the metal surface and the hydrocarbon is more exposed.

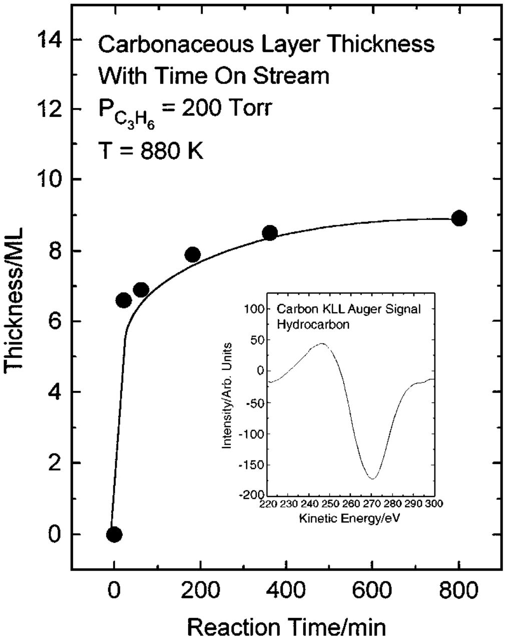

FIG. 1. Thickness of carbonaceous deposits formed on a molybdenum model catalyst by reaction of 200 Torr of propylene at 880 K plotted as a function of catalyst time on stream. The carbon KLL Auger signal lineshape is shown as an inset.

After the carbonaceous layer is formed and its thickness determined, the effect of hydrogen on the carbonaceous layer is examined by reinserting the sample in the reaction cell and heating the carbon-covered catalyst in hydrogen. Figure 2 shows the effect on the layer thickness of heating the sample in 5 Torr of hydrogen with time at various temperatures. Here, the carbonaceous layer was deposited by inserting a clean molybdenum foil into the reaction cell and heating it in 450 Torr of propylene for four hours, resulting in an initial deposit thickness of about 10 monolayers. It is clear from these data that hydrogen is effective at removing carbon from the molybdenum surface over a wide range of temperatures. Shown as an inset in Fig. 2 is the carbon 270 Auger peak lineshape for a spectrum taken after 10 min of reaction in hydrogen at 650 K. The lineshape of this peak is typical of graphitic carbon deposits (26).

The initial rate of carbon removal may be estimated for various temperatures from the data in Fig. 2, and these rates are plotted in Arrhenius form in Fig. 3. It is clear from these data that carbon removal by hydrogen exhibits Arrhenius behavior, and an activation energy for the removal process may be determined from the slope of the Arrhenius plot as 6.4 ± 0.4 kcal/mol. This is the first measurement of an activation energy for removal of this “strongly bound” carbonaceous layer.

The data in Figs. 2 and 4 clearly show the presence of two different types of carbon on the surface of the sample, a layer comprising an easily removed hydrocarbon along with a graphitic species. It seems likely from the shape of the carbon accumulation curve in Fig. 1, that the hydrocarbon layer forms quickly and maintains an equilibrium thickness,

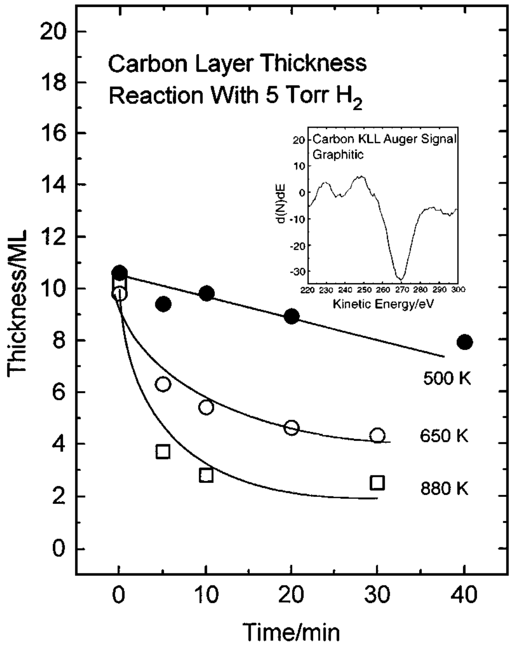

FIG. 2. Carbon layer thickness versus heating time in 5 Torr of hydrogen at various temperatures. Shown as an inset is the carbon KLL Auger signal after reaction confirming the presence of graphitic species on the catalyst surface.

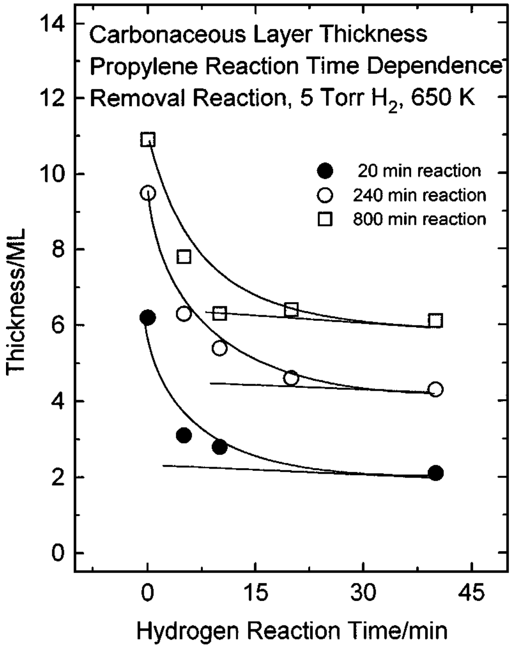

FIG. 4. Hydrogenation kinetics in 5 Torr of hydrogen at 650 K of films formed by reaction of propylene (450 Torr, 880 K) for various lengths of time.

while the graphitic species beneath form slowly as the reaction proceeds, probably from slow thermal decomposition of the hydrocarbon layer. This observation may be verified by conducting hydrogen removal experiments on catalysts that have been on stream for different amounts of time. Figure 4 shows the kinetics of carbonaceous layer removal by hydrogen for catalysts reacted in 450 Torr of propylene at 880 K for various lengths of time. These curves show the effect of heating the used catalyst in 5 Torr of hydrogen at 650 K as a function of time. It is clear from these data that the removal curve in each case has essentially the same shape, but the amount of residual carbon that cannot be removed by hydrogen increases with reaction time. This suggests that the thickness of the readily removed carbonaceous layer is relatively constant during reaction in propylene, while the amount of the coadsorbed graphitic layer increases with time.

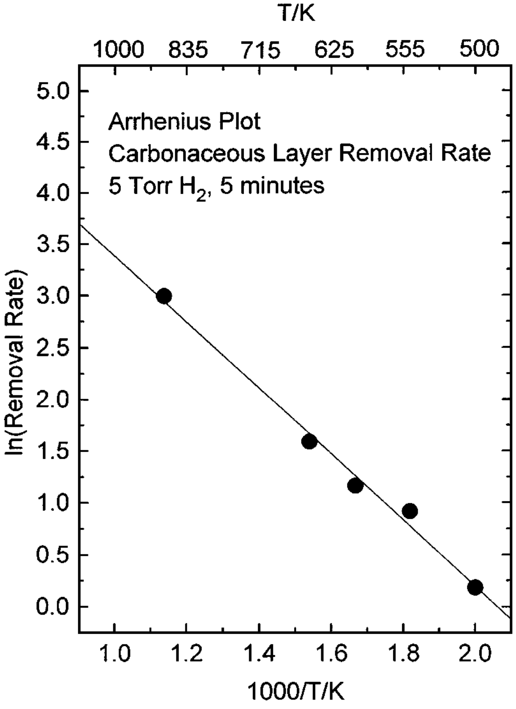

FIG. 3. Initial carbonaceous layer removal rate during heating in 5 Torr of hydrogen plotted in Arrhenius form.

If heating a carbon-covered molybdenum sample in hydrogen decreases the amount of the carbon, then it seems reasonable that addition of hydrogen to the propylene used for reaction might reduce the extent of carbon build-up on the sample during reaction. Figure 5 shows the carbonaceous layer thickness found on a molybdenum model catalyst after heating in 200 Torr of propylene with various amounts of added hydrogen for 20 min at 880 K. These data show that the addition of just 5 Torr of hydrogen substantially reduces the amount of carbon found on the catalyst surface by almost 30%. 200 Torr of added hydrogen lowers the thickness of the carbonaceous layer by two-thirds.

Figure 6 shows the corresponding rate of metathesis observed for reaction of 200 Torr of propylene over a molybdenum foil at 880 K in the presence of between 0 and 200 Torr of hydrogen. This figure shows that addition of a small amount of hydrogen, 5 Torr, provides about a 3-fold

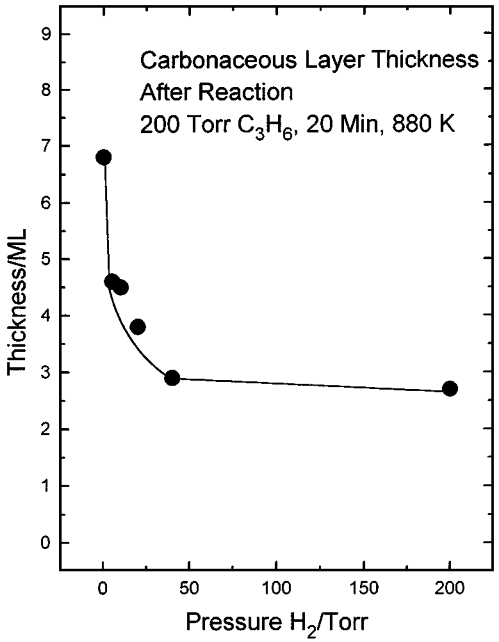

FIG. 5. Carbonaceous layer thickness after reaction in 200 Torr of propylene for 20 min at 880 K as a function of pressure of added hydrogen.

increase in the rate of metathesis product appearance, although addition of larger amounts of hydrogen, up to 200 Torr, does not provide a significant additional increase in rate under these conditions. These data essentially mirror the results shown in Fig. 5.

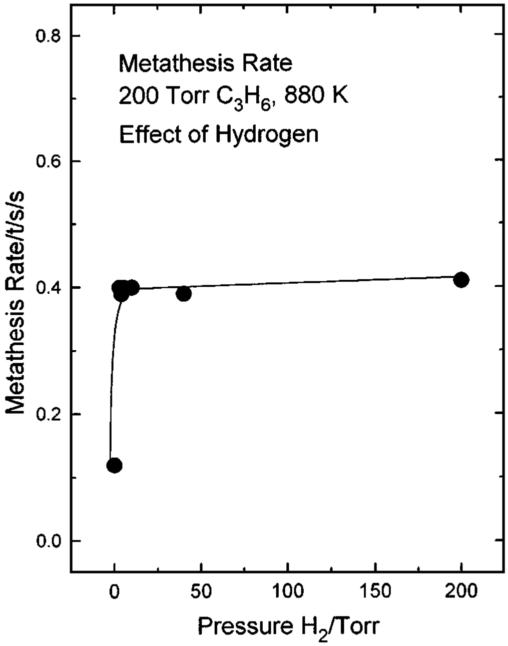

FIG. 6. Effect of varying pressures of added hydrogen on the observed rate of metathesis of 200 Torr of propylene at 880 K.

DISCUSSION

The formation of carbonaceous deposits on the surface of a metal or metal oxide during reaction is a common feature in heterogeneous catalysis (17–21). Figure 1 shows the accumulation of carbonaceous species on the catalyst surface during reaction where an initial layer ~6 ML thick forms quickly after the reaction is started, and then the amount of carbon increases slowly with time on stream. Auger electron spectroscopy shows that the lineshape of the 270 eV carbon Auger peak is consistent with that of an adsorbed hydrocarbon, indicating that the surface of this layer is composed primarily of hydrocarbon species, in agreement with Raman spectroscopic data (16). The hydrocarbon species is readily removed by hydrogen at temperatures as low as 500 K (Fig. 2) to reveal a more durable carbon species underneath. The carbon 270 eV kinetic energy peak lineshape of this species (Fig. 2) indicates that the unreactive carbon is graphitic in nature. Figure 4 displays the effect of hydrogen removal of the carbonaceous layer on catalysts heated for various lengths of time in propylene. The equivalent of about five monolayers of carbon is removed with identical kinetics and, in each case, Auger spectroscopy indicates that the remaining carbon is graphitic in nature. The thickness of this remaining layer increases from the equivalent of about two monolayers to about six monolayers in going from 20 to 800 min reaction time in 450 Torr of propylene at 880 K. Together, these results suggest that an initial carbonaceous layer consisting primarily of hydrocarbons initially forms rapidly but which slowly converts to graphite as the reaction proceeds.

Finally, Fig. 5 shows the effect of adding hydrogen to the metathesis reaction mixture which reduces the thickness of the carbonaceous layer by titrating hydrocarbon species from the surface (Figs. 2 and 4). Addition of hydrogen to the propylene results in a significant rate enhancement for the appearance of metathesis products (Fig. 6) corresponding to a decrease in the amount of surface carbon. This correlation suggest that the hydrogen added to the reaction mixture can react with the surface carbon to remove it to reveal active metals below and thereby increase the catalytic reaction rate.

CONCLUSIONS

The thick hydrocarbon layer found on the surface of metallic molybdenum after and during metathesis catalysis is shown, using Auger electron spectroscopy, to consist of surface-bound hydrocarbon fragments and tightly bound graphitic carbon species. Hydrogen removal of the hydrocarbon layer is facile above ~600 K and the activation energy is ~6.5 kcal/mol, while the graphitic layer is difficult to remove with hydrogen even at 880 K. The presence of hydrogen during metathesis is found to reduce the thickness of the carbonaceous layer found during reaction, resulting in an increase in the observed rate of metathesis.

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