Molybdenum metal catalyzed reaction of ethylene

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The reaction of ethylene catalyzed by clean molybdenum foil is examined between 800 and 880 K. Products up to C_7 are detected in measurable quantities and hydrocarbons up to C_8 are observed. The product distribution is well described by a Schulz–Flory function where a plot of $\ln(W_n/n)$ versus n, where W_n is the yield of each C_n hydrocarbon, is a good straight line. Analysis of the slope and intercept of the distribution shows that the slope has a zero-order ethylene pressure dependence and varies with temperature with an activation energy of 4.6 ± 0.6 kcal/mol, while the intercept has a pressure dependence of 1.3 ± 0.3 and an activation energy of 46 ± 4 kcal/mol. A kinetic model is proposed that successfully accounts for these pressure dependences. These data suggest that the activation energy for degenerate ethylene metathesis should be 55 ± 5 kcal/mol and that the reaction should be first order in ethylene. These kinetic parameters are in good agreement with those found experimentally for the non-degenerate metathesis of propylene.

Keywords: molybdenum, ethylene, model catalyst, product distribution, kinetic measurements

1. Introduction

Molybdenum-based materials are capable of catalyzing a wide range of chemical reactions including hydrogenation [1–6], hydrogenolysis [7,8], metathesis and desulfurization [11,12]. The most active catalysts for olefin metathesis generally consist of supported molybdenum oxides where the activity has been found to be a relatively strong function of catalyst loading [13–15]. It has also been shown that, at sufficiently high temperatures, metallic molybdenum is capable of catalyzing olefin metathesis albeit with a relatively low selectivity and activity compared to the most effective supported catalysts [16].

It is now well accepted, predominantly based on mechanistic studies using homogeneous catalysts, that the metathesis reaction is initiated by the formation of a carbene "active site" and that this further reacts with an alkene forming a surface metallacycle which thermally decomposes by the reverse of the formation pathway resulting in an overall metathesis of the alkene [17–33].

The chemistry of alkenes adsorbed on a clean Mo(100) surface has been studied in ultrahigh vacuum and the results reveal that an adsorbed overlayer of alkene thermally decomposes on heating to room temperature via carbon–carbon bond cleavage; carbene formation appears to be facile on these surfaces [34,35]. In the context of the carbene-metallacycle model described above, this should presumably result in a high rate of olefin metathesis whereas it is found experimentally that the reaction rate is rather low [16].

More recently we have investigated the catalytic activity of a range of model oxide catalysts formed in situ in an ultrahigh vacuum chamber and indeed find that oxidized molybdenum is more active than the metal, in line with previous experience with these catalysts [36]. Measurements of the temperature dependence of the reaction rate catalyzed by MoO_2 shows two distinct regions in the Arrhenius plot, one below about 650 K where the reaction activation energy is ~6 kcal/mol and another region above this temperature where the activation energy is ~60 kcal/mol [37]. This latter value compares well with that found for metathesis catalyzed by metallic molybdenum (~65 kcal/mol). Moreover, the absolute rate and activation energy measured in the low-temperature regime for an oxidized molybdenum catalyst agree well with those found for supported oxides. These results suggest that the oxide mimics the supported MoO_2 catalyst rather well below 650 K and that the commonly accepted carbene-metallacycle mechanism operates in this case. However, the high activation energy found for metallic molybdenum and for MoO_2 above 650 K implies that another mechanism may operate under these conditions.

It has been suggested that carbenes, once formed, may recombine on the surface and this pathway has been invoked as one route by which a carbene can be removed from the surface [38]. This is exactly analogous to the polymerization step in Fischer–Tropsch catalysis where monomeric species formed on the surface by hydrogenation of carbon formed from carbon monoxide dissociation yield higher hydrocarbons [39–42]. A similar reaction pathway could lead to metathesis products when using a metallic molybdenum catalyst. That is, car-

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benes formed on the surface of the catalyst could recombine to form products rather than reacting with an alkene. This proposed pathway reconciles the apparently large rate of carbene formation with an overall low rate of metathesis since the carbenes are no longer active sites, but reactants.

In order to test this proposal, we have studied the reaction of ethylene catalyzed by metallic molybdenum using a high-pressure reactor incorporated into an ultrahigh vacuum chamber. This strategy allows an atomically clean sample to be obtained and its catalytic behavior to be tested without intervening exposure to air. In this case, olefin metathesis is degenerate in the sense that metathesis of ethylene merely results in the formation of ethylene. It, however, has the advantage that, if any higher homologs are formed via surface polymerization, these will include all carbon numbers n where the yield of hydrocarbon, W_n, should be described by a Schulz–Flory distribution where a plot of $\ln(W_n/n)$ versus n should be linear. It has also been found from ultrahigh vacuum studies that ethylene adsorbs dissociatively on Mo(100) and oxygen-covered Mo(100) and that methane is formed on oxygen-covered Mo(100) by the reaction of surface carbenes with hydrogen [45]. This indicates that carbenes can be formed by reaction of ethylene with model molybdenum catalysts.

2. Experimental

The apparatus used for these experiments has been described in detail in previous publications [43]. Briefly, it consists of a bakeable, stainless-steel chamber that operates at $\sim 1 \times 10^{-10}$ Torr following bakeout. It incorporates facilities for sample cleaning, Auger and LEED analysis, and a quadrupole mass spectrometer for residual gas analysis and temperature-programmed desorption experiments. The ultrahigh vacuum equipment also incorporates an isolatable, high-pressure reactor which allows catalytic reactions to be carried out at pressures up to ~1 atm while maintaining ultrahigh vacuum in the rest of the equipment. The reactor operates as a recirculating batch reactor and the reaction mixture is analyzed by diverting aliquots to a gas chromatograph equipped with a flame ionization detector. The output of the detector is interfaced to a PC via a Keithly picoammeter which is used to amplify the ion current. This allows gas-chromatograph peak positions and areas to be determined directly from the trace of current versus retention time. The relative yield of each hydrocarbon component was measured by assuming that the flame-ionization detector sensitivity is proportional to the number of carbon atoms in the hydrocarbon.

The molybdenum foil sample was cleaned using a standard procedure and its cleanliness established using Auger spectroscopy. It has been shown previously that propylene metathesis is catalyzed with exactly identical rates using both a Mo(100) single crystal and polycrystalline foil. That implies that the reaction is not strongly structure sensitive [43].

The ethylene (Linde, CP grade) was transferred from the cylinder to a glass bottle and further purified by repeated bottle-to-bottle distillation and stored in glass until use. The purity of the ethylene was tested using mass spectroscopy and gas chromatography and no significant impurities are detected after purification.

3. Results

A range of hydrocarbon products are formed by the molybdenum-catalyzed reaction of ethylene in the studied temperature range between 800 and 880 K with ethylene pressures up to 450 Torr. Reaction rates are measured from the initial slope of the product accumulation curves for low conversions ($< 1\%$). It has been shown previously that metallic molybdenum catalyzes propylene metathesis in this temperature range [43]. Ethylene metathesis, however, merely yields ethylene and these products cannot therefore be distinguished from the reactants. Nevertheless, measurable amounts of hydrocarbon are detected up to C_7 under these conditions and hydrocarbons up to C_8 have been observed where each carbon number C_n is represented. The formation of these products was followed for several thousand turnovers of the model catalyst. In order to test whether these are formed from reaction of a C_1 monomer, the product distribution is plotted in a Schulz–Flory form so that $\ln(W_n/n)$ is plotted versus n, where n is the carbon number and W_n is the yield of the hydrocarbon C_n. A typical plot of this type is displayed in fig. 1 and clearly yields a good straight line. Similarly good results are obtained for reaction under all studied conditions. This indicates that reaction products are formed from the polymerization of a surface C_1 monomer and means that ethylene undergoes rapid dissociation into surface C_1 species which react to form polymeric products rather than an adsorbed C_2 species reacting, since polymerization of a surface C_2 species would only yield even-numbered hydrocarbons.

The temperature and pressure dependencies of both the slope and intercept of the Schulz–Flory plot can be measured. The pressure dependence of the slope of the Schulz–Flory distribution for reaction at 870 K is shown in fig. 2 as slope versus $\ln(P)$, where P is the ethylene pressure. This plot shows a straight line with a slope of 0 ± 0.1. Similarly, the pressure dependence of the intercept of the Schulz–Flory distribution, again for reaction at 870 K, is plotted as intercept versus $\ln(P)$ in fig. 3 and yields a slope of 1.3 ± 0.2. The reason for plotting slope and intercept directly rather than their logarithms will be discussed below.

The temperature dependence of both the slope and intercept of the Schulz–Flory distribution are plotted in

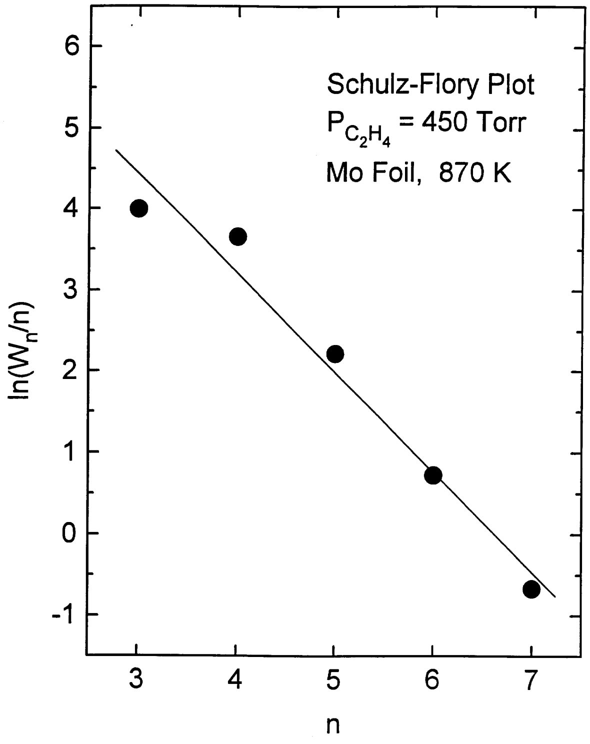

Fig. 1. A typical Schulz–Flory plot for the formation of hydrocarbons from the reaction of ethylene catalyzed by molybdenum at 870 K using 450 Torr of ethylene.

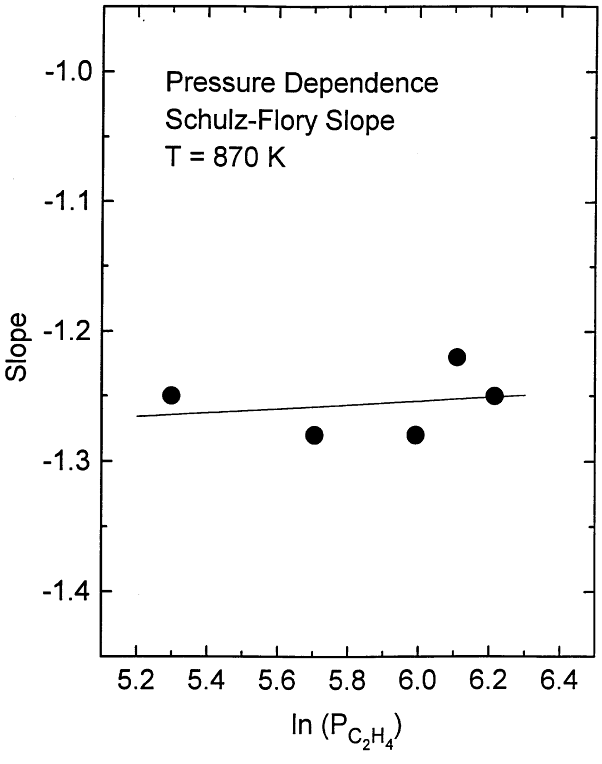

Fig. 2. Plot of the pressure dependence of the slope of the Schulz–Flory distribution plotted as slope versus $\ln(P)$, where P represents the ethylene pressure for reaction at 870 K.

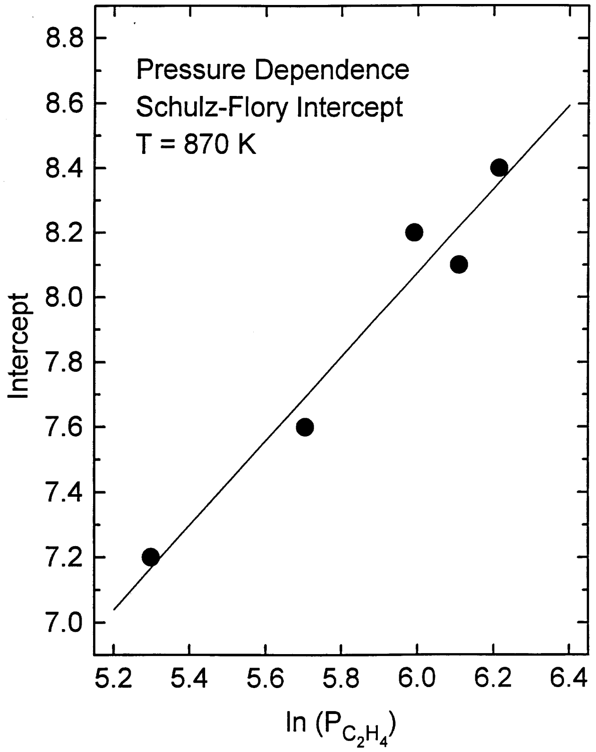

Fig. 3. Pressure dependence of the intercept of the Schulz–Flory distribution plotted as intercept versus $\ln(P)$, where P is the ethylene pressure for reaction at 870 K.

figs. 4 and 5 respectively. Since these quantities are functions of elementary step rate constants, they would be expected to exhibit Arrhenius behavior. Fig. 4 shows the slope of the distribution when using 450 Torr of ethylene, plotted versus $1/T$, which yields a good straight line. Measurement of the slope of this curve yields an activation energy of 4.6 ± 0.4 kcal/mol. Similarly, the temperature dependence of the intercept of the Schulz–Flory distribution when using 450 Torr of ethylene (fig. 5) plotted as intercept versus $1/T$ yields a good straight line. The activation energy measured from the slope is 46 ± 4 kcal/mol. Again, the reason for plotting slope and intercept directly will be discussed below.

4. Discussion

The formation of higher hydrocarbon products that include all carbon numbers with a distribution that is well described by a Schulz–Flory distribution (fig. 1) indicates that these hydrocarbons are produced from the polymerization of surface C_1 species. It has been shown from experiments on the chemistry of ethylene on clean and oxygen-covered Mo(100) that carbon–carbon bond scission in these species on molybdenum is facile [34,35,44]. The monomeric species are therefore proposed to form by this process. These are then suggested to polymerize on the surface to form higher hydrocar-

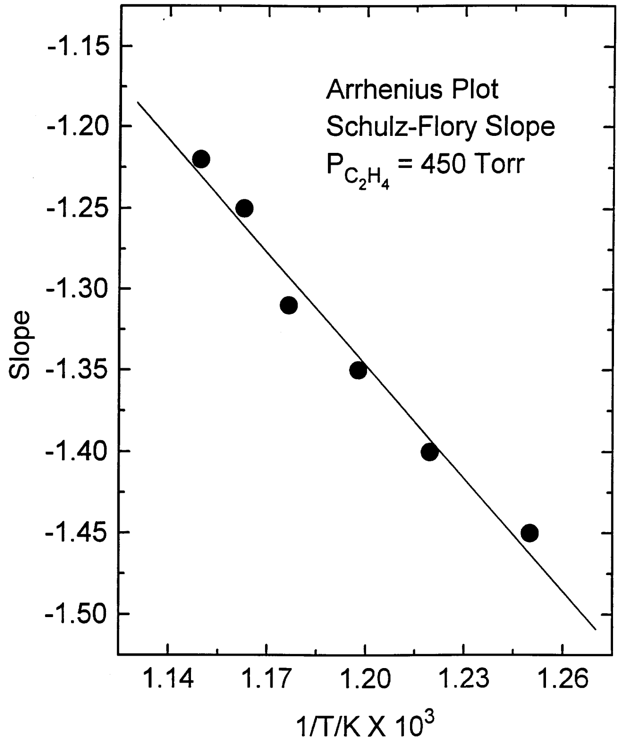

Fig. 4. Temperature dependence of the slope of the Schulz–Flory distribution plotted as slope versus $1/T$ for reaction using 450 Torr of ethylene.

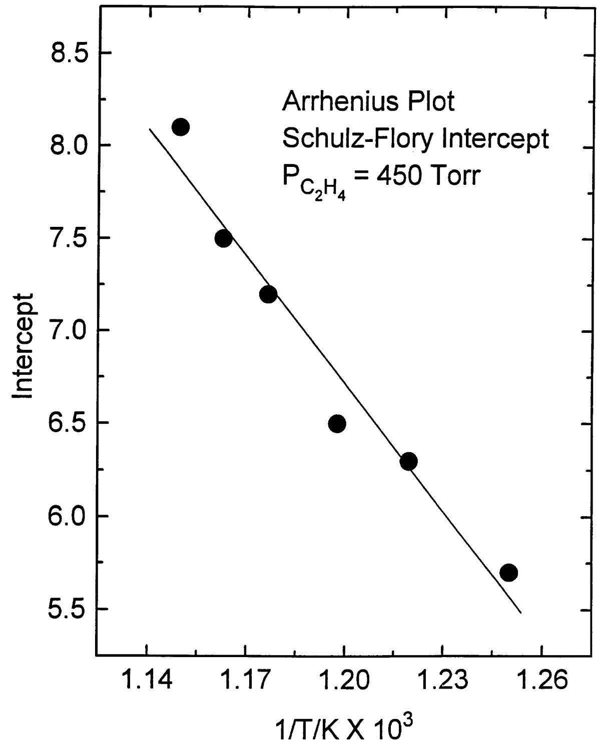

Fig. 5. Temperature dependence of the intercept of the Schulz–Flory distribution plotted as intercept versus $1/T$ for reaction using 450 Torr of ethylene.

bons. Note again that the reaction of CO and hydrogen over Mo(100) leads to formation of hydrocarbons up to C_3, so there is a precedent for this reaction scheme [45].

If the equilibrium coverage of a hydrocarbon of chain length n adsorbed on the surface is θ_n, it is assumed that this can react with an adsorbed C_1 species of coverage θ_1 to form a hydrocarbon with an additional carbon with a rate constant k_p. It is also assumed that the chain terminates by reaction between a C_n and a C_1 hydrocarbon with rate constant k_t. The rate of change of coverage of each C_n hydrocarbon is then given by:

$$\frac{d\theta_n}{dt} = k_p\theta_1\theta_{n-1} - k_t\theta_1\theta_n - k_p\theta_n\theta_1 \,. \tag{1}$$

Assuming steady-state conditions so that $d\theta_n/dt = 0$, yields for the relative coverage of each C_n hydrocarbon:

$$\theta_n = \left(\frac{k_p}{k_t + k_p}\right)^{n-1} \theta_1 \,. \tag{2}$$

If θ_1 is written as α, then the rate of evolution of each C_n hydrocarbon into the gas phase, r_n, is given by:

$$r_n = k_t\alpha\theta_{n-1} \,. \tag{3}$$

Substituting from eq. (2) into eq. (3) yields a Schulz–Flory distribution of reaction products as follows:

$$\ln\left(\frac{r_n}{n}\right) = n\ln\left(\frac{k_p}{k_t + k_p}\right) + \ln\left(\frac{k_t\alpha^2}{[k_p/(k_t + k_p)]^2}\right) . \tag{4}$$

This reproduces the experimentally found product distribution (fig. 1). Note therefore that the slope of this distribution S is given by:

$$S = \ln\left(\frac{k_p}{k_t + k_p}\right) \tag{5}$$

and the intercept I is given by:

$$I = \ln\left(\frac{k_t\alpha^2}{[k_p/(k_t + k_p)]^2}\right) . \tag{6}$$

Thus, these values are already written in terms of logarithms so that the pressure and temperature dependences are obtained by plotting the slope and intercept versus $\ln(P)$ and $1/T$ respectively.

The rate of metathesis can also be calculated from eq. (3) and is given by:

$$r_m = k_t\alpha^2 \,. \tag{7}$$

Since the slope of the Schulz–Flory plot depends only on the rate constants k_t and k_p (eq. (4)), it does not depend on pressure in accord with the results displayed in fig. 2 where the slope is essentially zero. In contrast, the intercept depends on α, the coverage of C_1 species. According to the data of fig. 3, the pressure dependence of the intercept is 1.3 ± 0.3 and so has an approximately first-order pressure dependence. The rate constants k_p and k_t in the equation for the value of the intercept (eq.

(6)) do not depend on pressure so that the pressure dependence is contained in the C_1 coverage α. This means $\alpha^2 \propto p^1$ so that $\alpha \propto p^{1/2}$. Since α is the concentration of adsorbed C_1 species that are proposed to derive from the dissociative adsorption of ethylene, this rationalizes the half-order pressure dependence in this case. The temperature dependence of the rate constants in the slope of the Schulz–Flory distribution is given in the Arrhenius plot of fig. 4 as 4.6 ± 0.4 kcal/mol and therefore reflects the temperature dependence of $[k_p/(k_t + k_p)]$. A stronger temperature dependence of the intercept is found from the data plotted in fig. 5 where the activation energy in this case is 46 ± 4 kcal/mol. The formula for the intercept is given in eq. (6) and allows the contributions to the activation energy of the intercept to be written as:

$$E_{act}(I) = E_{act}(k_t\alpha^2) - 2E_{act}[k_p/(k_t + k_p)] . \qquad (8)$$

Note that $E_{act}[k_p/(k_t + k_p)]$ is found to be 4.6 ± 0.4 kcal/mol and yields a value of $E_{act}(k_t\alpha^2)$ of 55 ± 7 kcal/mol. Note that from eq. (7) this is the calculated rate of olefin metathesis and predicts that this reaction should proceed with an activation energy of 55 ± 7 kcal/mol. This is close to the experimentally measured value for propylene metathesis of 64 ± 5 kcal/mol [43] for metallic molybdenum. In addition, eq. (7) predicts that the reaction rate is proportional to α^2 and should therefore be first order in reactant pressure as previously found for propylene metathesis catalyzed by metallic molybdenum [43].

5. Conclusions

The reaction of ethylene catalyzed by molybdenum metal between 800 and 880 K produces hydrocarbons with chain lengths up to C_8. The product distribution is well described by a Schulz–Flory function suggesting that products are formed via a carbene recombination pathway where surface carbenes combine with C_n surface species. The kinetic parameters for the degenerate meta-thesis of ethylene calculated based on this mechanism give its activation energy as 55 ± 7 kcal/mol and its ethylene pressure dependence as 1.3 ± 0.2. These parameters are consistent with the activation energy and pressure dependence observed for propylene metathesis catalyzed by molybdenum metal and MoO_2 under similar temperature and pressure conditions indicating that this reaction also proceeds by a recombination mechanism.

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References

[1] J.H. Sinfelt and D.S.L. Yates, Nature Phys. Sci. 229 (1971) 27.
[2] M. Boudart, S.T. Otama and L. Leclerq, in: *Proc. 7th Int. Congr. on Catalysis*, Tokyo 1980, eds. T. Seiyama and K. Tanabe (Elsevier, Amsterdam, 1981) p. 578.
[3] K.J. Leary, J.N. Micheals and A.M. Stacy, J. Catal. 101 (1986) 301.
[4] R.G. Bowman and R.L. Burwell Jr., J. Catal. 63 (1980) 463.
[5] R.G. Bowman and R.L. Burwell Jr., J. Catal. 88 (1984) 388.
[6] A. Kouskova, J. Adamek and V. Ponec, Collection Czech. Chem. Commun. 35 (1970) 2538.
[7] R. Nakamura, D. Pioch, R.G. Bowman and R.L. Burwell Jr., J. Catal. 93 (1985) 388.
[8] R. Nakamura, R.G. Bowman and R.L. Burwell, J. Am. Chem. Soc. 103 (1891) 673.
[9] J.C. Mol and J.A. Moulijn, Adv. Catal. 24 (1975) 131.
[10] J.J. Rooney and A. Stewart, Catalysis 1 (1977) 277.
[11] A.J. Gellman, M.H. Farias and G.A. Somorjai, J. Catal. 88 (1984) 564.
[12] A.J. Gellman, M.H. Farias and G.A. Somorjai, Surf. Sci. 136 (1984) 217.
[13] R. Thomas and J.A. Moulijn, J. Mol. Catal. 15 (1982) 157.
[14] V.B. Kazansky, B.N. Sheliman and K.A. Vikulov, in: *New Frontiers in Catalysis*, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 515.
[15] W. Grünert, A. Stakheev, R. Feidhaus, K. Andres, E. Shapiro and K. Mihachev, J. Catal. 135 (1992) 287.
[16] L.P. Wang, C. Soto and W.T. Tysoe, J. Catal. 143 (1993) 92.
[17] J.L. Hérisson and Y. Chauvin, Makromol. Chem. 141(1970) 161.
[18] J.P. Soufflet, D. Commercue and Y. Chauvin, C.R. Hebd. Séances Acad. Sci. C 276 (1973) 169.
[19] R.J. Haines and G.J. Leigh, Chem. Soc. Rev. 4 (1975) 155.
[20] C.P. Casey and J. Burkhardt, J. Am. Chem. Soc. 96 (1974) 7808.
[21] E.O. Fischer and K.H. Dotz, Chem. Ber. 105 (1972) 3966.
[22] R.R. Schrock, J. Am. Chem. Soc. 96 (1974) 6976.
[23] R.R. Schrock, J. Am. Chem. Soc. 98 (1976) 5399.
[24] B.A. Dolgoplosk, Dokl. Chem. 216 (1974) 380.
[25] R.H. Grubbs, P.C. Burk and D.D. Carr, J. Am. Chem. Soc. 97 (1975) 3265.
[26] R.H. Grubbs, D.D. Carr, C. Hoppin and P.C. Burk, J. Am. Chem. Soc. 98 (1976) 3478.
[27] T.J. Katz and J. Rothschild, J. Am. Chem. Soc. 98 (1976) 2519.
[28] T.J. Katz and W.H. Hersch, Tetrahedron Lett. (1977) 585.
[29] C.P. Casey, H.E. Hunstra and M.C. Searnan, J. Am. Chem. Soc. 98 (1976) 608.
[30] F.N. Tebbe, G.W. Parshall and D.W. Overnall, J. Am. Chem. Soc. 101 (1979) 5074.
[31] J. Wengorius, R.R. Schrock, M.R. Churchill, J.R. Mussert and W.J. Young, J. Am. Chem. Soc. 102 (1980) 4515.
[32] T.R. Howard, J.B. Lee and R.H. Grubbs, J. Am. Chem. Soc. 102 (1980) 6878.
[33] R.H. Grubbs and T.K. Brunck, J. Am. Chem. Soc. 94 (1972) 25
[34] L.P. Wang and W.T. Tysoe, Surf. Sci. 230 (1990) 74.
[35] L.P. Wang and W.T. Tysoe, Surf. Sci. 245 (1991) 41.
[36] B.F. Bartlett, C. Soto, H. Molero and W.T. Tysoe, in preparation.
[37] B.F. Bartlett, H. Molero and W.T. Tysoe, J. Catal., in press.
[38] B.F. Bartlett, V. Schneerson and W.T. Tysoe, Catal. Lett. 32 (1995) 1.

[39] D.W. Goodman, R.D. Kelley, T.E. Madey and J.T. Yates Jr., J. Catal. 63 (1980) 226.
[40] C.B. Young and G.N. Whiteside, J. Am. Chem. Soc. 100 (1978) 5808.
[41] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[42] R.C. Brady and R.J. Pettit, J. Am. Chem. Soc. 103 (1981) 1287.
[43] L.P. Wang and W.T. Tysoe, J. Catal. 28 (1991) 320.
[44] G. Wu, B.F. Bartlett and W.T. Tysoe, in preparation.
[45] M. Logan, A.J. Gellman and G.A. Somorjai, J. Catal. 94 (1985) 60.