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Evidence for olefin metathesis catalyzed by metallic molybdenum proceeding via an associative mechanism at high temperature

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The reaction of ethylene catalyzed by metallic molybdenum at 875 K yields higher hydrocarbons ($> C_2$) with a distribution that is well described by a Schulz–Flory plot suggesting that their formation arises from the polymerization of surface C_1 species. This observation is in accord with results from surface science experiments that show facile C=C cleavage in alkenes. A similar molybdenum-catalyzed reaction of propylene yields metathesis and hydrogenolysis products. In view of the product distribution found with ethylene, these products are proposed to arise from the recombination of surface species formed by propylene dissociation. This result is confirmed by modifying the Schulz–Flory function assuming equal surface coverages of carbenes and methyl carbenes which adequately predicts the measured product distribution.

Keywords: molybdenum; high temperature; ethylene; carbenes

1. Introduction

Olefin metathesis is catalyzed at relatively modest temperatures (< 600 K) both in homogeneous and heterogeneous phases [1–3]. It is generally accepted that, in this temperature range, reaction proceeds via the initial formation of a carbene which provides the "active site" for catalysis. This is proposed to further react with an alkene forming a metallocycle which decomposes via the reverse of this reaction yielding metathesis products [4–11]. The overall activation energy for this reaction generally lies in the range of 7–9 kcal/mol [12–15].

Examples of heterogeneous metathesis catalysts include alumina- or silica-supported oxides of molybdenum, tungsten or rhenium [16]. However, we have shown that *metallic* molybdenum is also capable of catalyzing olefin metathesis, but at significantly higher temperatures than found for the supported oxides. The apparent activation energy for propylene metathesis catalyzed by metallic molybdenum is

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~ 65 kcal/mol (substantially higher than found for supported oxides) and proceeds with a relatively low rate [17]. Paradoxically, however, the rate of double bond scission for alkenes adsorbed on metallic molybdenum (Mo(100)) surfaces in ultra-high vacuum is rather high [18–20] implying a concomitantly rapid rate of formation of C_1 "active sites". Assuming that these species are similarly active on metallic molybdenum implies, in contrast to what is found experimentally, that there should be a correspondingly large rate of olefin metathesis on this surface.

It has also been shown, however, that organometallic carbenes can thermally decompose to yield alkenes, suggesting a possible alternative reaction pathway in which the carbenes, once formed, can recombine to yield products [21–23]. In addition, many transition metals can catalyze hydrocarbon formation from the reaction of carbon monoxide and hydrogen, where surface CH_x monomers formed by CO dissociation and subsequent hydrogenation of the carbon can polymerize [24–27]. Metallic molybdenum can effectively catalyze the latter reaction [28]. Thus, if molybdenum-metal catalyzed olefin metathesis proceeds via the formation and recombination of carbenes rather than via the carbene-metallocycle pathway, these should also be capable of polymerizing to yield higher molecular weight hydrocarbons. In order to more easily distinguish polymerization products from those due to metathesis, we have examined the reaction of ethylene catalyzed by metallic molybdenum using a high-pressure reactor incorporated into an ultra-high vacuum chamber since, in this case, metathesis of ethylene merely yields ethylene and only adsorbed C_1 monomers will form.

2. Experimental

The experimental equipment has been described in detail elsewhere [17]. Briefly, however, it consists of a stainless-steel, ultra-high vacuum (UHV) chamber operating at a base pressure of 2×10^{-10} Torr following bakeout. The molybdenum sample is mounted to the end of a coaxial sample manipulator and can be resistively heated to 2000 K and also cooled to 80 K by contact with a liquid-nitrogen-filled reservoir. The sample can also be inserted into an isolatable high-pressure reactor which can be pressurized to ~ 1 atm while maintaining ultra-high vacuum in the remainder of the apparatus. This operates as a recirculating batch reactor and reaction rates are measured by analyzing aliquots of the reaction mixture as a function of time for low ($< 1\%$) conversions using gas chromatography. Reactions were carried out either using 175 Torr of ethylene or 75 Torr of propylene. In all cases, the total pressure was made up to 760 Torr using nitrogen.

The sample was cleaned using a standard procedure [17] and adjudged clean when no Auger signals were detected due to contaminants (primarily carbon and oxygen). Ethylene and propylene (CP grade, Aldrich Chemicals) were transferred to glass bottles and further purified by repeated bulb-to-bulb distillations.

3. Results and discussion

It has been shown previously that propylene metathesis is catalyzed by metallic molybdenum at sufficiently high temperatures (>600 K) [17]. The corresponding metathesis of ethylene is degenerate (merely yielding ethylene). The results of experiments performed in this work, however, show hydrocarbons up to C_6 are detected in the reaction mixture. The resulting higher hydrocarbon formation rates for reaction at 875 K are shown plotted as a Schulz–Flory distribution (by plotting $\ln(W_n/n)$ versus n, where n is the carbon number of the hydrocarbon with yield W_n) in fig. 1. Reaction rates measured for each product were 0.106 reactions per site per second for C_3 products, 0.033 for C_4's, 0.0063 for C_5's and 0.0012 for C_6 hydrocarbons using 175 Torr of ethylene at 875 K. A site was taken to be a unit cell on the (100) face of molybdenum with a concentration of $10^{15}/\text{cm}^2$. This yields a good straight line so that the experimentally found hydrocarbon yield is well described by a Schulz–Flory plot indicating that products are formed by the polymerization of a common monomer consisting of surface C_1 species. This result sug-

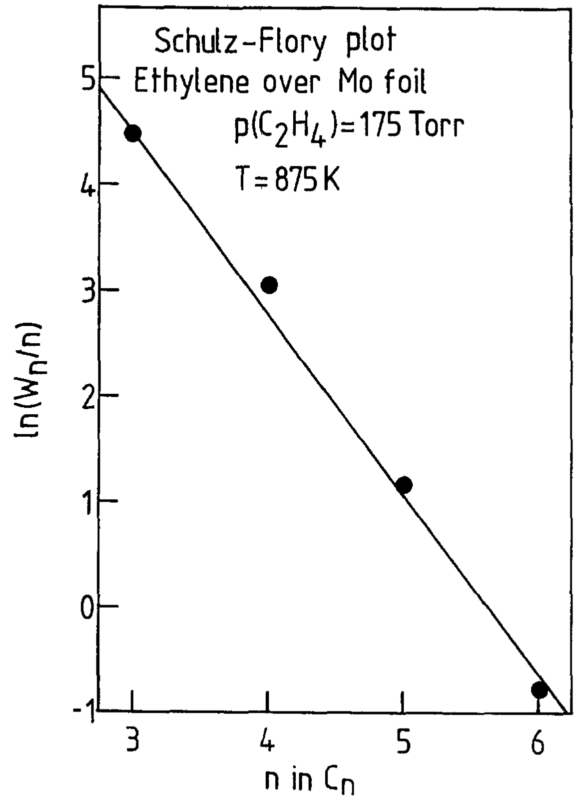

Fig. 1. Hydrocarbon distribution arising from the reaction of ethylene catalyzed by metallic molybdenum at 875 K plotted as a Schulz–Flory distribution.

gests that, on metallic molybdenum at high temperatures, reaction proceeds by the initial formation of surface C_1 species:

$$C_2H_4(g) \rightarrow 2CH_{2(ads)} \tag{1}$$

This reaction is consistent with the chemistry of ethylene on Mo(100) found in ultra-high vacuum. The formation of higher hydrocarbons is also compatible with the catalytic activity of metallic molybdenum which is capable of producing hydrocarbons up to C_3 from a reaction of CO and hydrogen [28]. The hydrogen required for the termination step in the latter reaction is supplied as a reactant. Surface science experiments have shown that alkenes dehydrogenate on metallic molybdenum [18–20] and this may provide a source of hydrogen in this case. Similarly, since chain propagation to form polymers in Fischer–Tropsch synthesis proceeds via carbene / alkyl coupling, alkyls, in the case of ethylene reactions, may be formed by carbene hydrogenation. An analogous carbene–carbene coupling (the reverse of the reaction depicted in eq. (1)) leads to the formation of metathesis products. Such carbene recombination has been proposed previously [32] and has been observed in homogeneous phase [21–23]. It is therefore proposed that olefin metathesis proceeds on metallic molybdenum at high temperatures via a dissociative / associative mechanism where carbenes dissociate and recombine to yield products.

The surface chemistry of propylene has been shown to be very similar to that of ethylene where adsorbed propylene both dehydrogenates and undergoes C=C bond scission. It also reacts at high pressures forming both hydrogenolysis and metathesis products [17,20]. The resulting metathesis selectivity for the molybdenum-catalyzed reaction is shown in fig. 2 where the selectivity is defined as $r(\text{metathesis})/[r(\text{metathesis})+r(\text{hydrogenolysis})]$, where r represents the reaction rate. A typical product distribution is shown for reaction at 880 K using 175 Torr of propylene in fig. 3 plotted as shaded histograms. Note that small amounts of polymerization products up to C_8 are also formed in this reaction. Modification of the Schulz–Flory distribution, assuming equal surface coverages of carbenes and methyl carbenes arising from propylene dissociation, predicts a hydrocarbon distribution for W_n for each C_n hydrocarbon of the form

$$W_n/n = (kp^{n-1}/\alpha)[(1+\alpha)^{n+1} - (1-\alpha)^{n+1}], \tag{2}$$

where $\alpha = \sqrt{[1 + (8/p)]}$, where p and k are constants. p represents the propagation probability and k is a normalization constant. This distribution is plotted for reaction at 880 K as open histograms in fig. 3 and agrees well with the experimental results, and similar good agreement is obtained for distributions at all reaction temperatures. Note that two independent parameters (p and k) are used for the fit of three data points. The observed distribution is, however, consistent with the proposed dissociative / associative reaction scheme.

Carbene recombination to yield ethylene (the reverse of eq. (1)) has been investigated theoretically using extended-Hückel theory [29] and the results of these calculations suggest that the surface activation energy for carbene recombination is

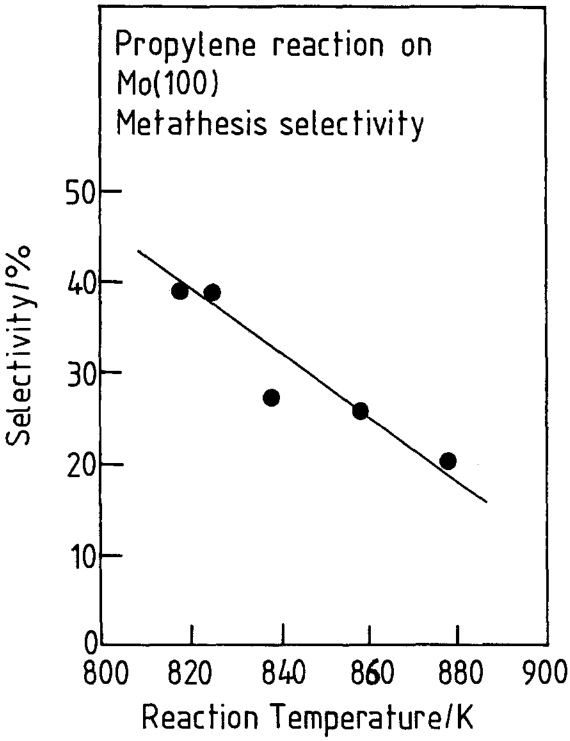

Fig. 2. Olefin metathesis selectivity measured as a function of temperature for reaction catalyzed by metallic Mo(100). The selectivity is defined as $r(\text{metathesis})/[r(\text{metathesis}) + r(\text{hydrogenolysis})]$, where r refers to the reaction rate.

small. The low-temperature (< 300 K) dissociation of alkenes found in ultra-high vacuum is in accord with this view [18–20]. The strength of the metal–carbene bond can be estimated from the activation energy for olefin metathesis catalyzed by molybdenum metal (~ 65 kcal/mol), assuming that coupling is the rate-limiting step in the reaction, from

$$E_{\text{act}} = 2\Delta H_{(\text{ads})}(\text{carbene}) - E(\text{C=C}) , \tag{3}$$

where E_{act} is the activation energy for olefin metathesis (65 kcal/mol), $E(\text{C=C})$ is the carbon–carbon double bond strength for ethylene (173 kcal/mol [30]) and $\Delta H_{(\text{ads})}$(carbene) the heat of adsorption of the carbene. This yields a value of ~ 120 kcal/mol. This value is somewhat larger than that estimated for the heat of adsorption of carbenes on supported MoO_x catalysts of 104 ± 6 kcal/mol [31] suggesting that carbene adsorb more strongly onto the metal than on an oxide.

4. Conclusions

The molybdenum-catalyzed reaction of ethylene yields higher hydrocarbons up

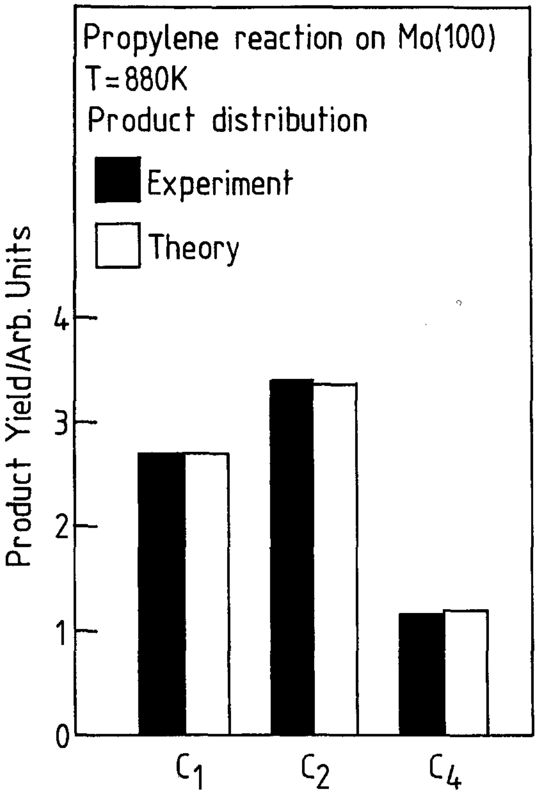

Fig. 3. Histogram showing the product distribution of hydrocarbons up to C_4 formed by the reaction of propylene catalyzed by Mo(100) (shaded histogram) compared with theory (open histogram; see text).

to C_6 where the relative amounts of each hydrocarbon is well described by a Schulz–Flory distribution consistent with the rapid formation and polymerization of surface C_1 species. These results suggest that olefin metathesis catalyzed by metallic molybdenum *at high temperature* proceeds via carbene recombination rather than the usual carbene-metallocycle mechanism. This proposed dissociative/associative pathway is consistent with the surface chemistry of alkenes found on Mo(100) in ultra-high vacuum [18–20] and analogous carbene coupling reactions have been observed in homogeneous phase [21–23]. Finally, carbene recombination has also been suggested previously as a carbene removal pathway in olefin metathesis catalysis [32].

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References

[1] R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Dev. 94 (1965) 60.
[2] L.F. Heckelsberg, R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Dev. 7 (1969) 29.
[3] L.F. Heckelsberg, R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Dev. 8 (1969) 259.
[4] C.P. Casey and J. Burkhardt, J. Am. Chem. Soc. 96 (1974) 7808.
[5] E.O. Fischer and K.H. Dotz, Chem. Ber. 105 (1972) 3966.
[6] R.R. Schrock, J. Am. Soc. 98 (1976) 5399.
[7] R.H. Grubbs, D.D. Carr, C. Hoppin and P.C. Burk, J. Am. Chem. Soc. 98 (1976) 3478.
[8] T.R. Howard, J.B. Lee and R.H. Grubbs, J. Am. Chem. Soc. 102 (1980) 6878.
[9] R.H. Grubbs and T.K. Brunck, J. Am. Chem. Soc. 94 (1972) 25.
[10] P.P. O'Neill and J.J. Rooney, J. Am. Chem. Soc. 94 (1972) 4383.
[11] M. Anpo and Y. Kubokawa, J. Catal. 75 (1982) 204.
[12] E.S. Davie, D.A. Whan and C.J. Kemball, J. Catal. 24 (1972) 272.
[13] R.F. Howe, D.E. Davidson and D.A. Whan, J. Chem. Soc. Faraday Trans. I 68 (1972) 2266.
[14] A.J. Moffat and A.J. Clark, J. Catal. 17 (1970) 264.
[15] R.C. Luckner, G.E. McConocie and G.B. Wells, J. Catal. 28 (1973) 63.
[16] J.C. Mol and J.A. Moulijn, Adv. Catal. 24 (1975) 131.
[17] L.P. Wang, C. Soto and W.T. Tysoe, J. Catal. 92 (1993) 143.
[18] L.P. Wang and W.T. Tysoe, Surf. Sci. 230 (1990) 74.
[19] L.P. Wang and W.T. Tysoe, Surf. Sci. 236 (1990) 325.
[20] L.P. Wang and W.T. Tysoe, Surf. Sci. 245 (1991) 41.
[21] C.P. Casey, T.J. Burkhardt and C.A. Bunnell, J. Am. Chem. Soc. 99 (1977) 2127.
[22] C.P. Casey and T.J. Burkhardt, J. Am. Chem. Soc. 69 (1974) 7808.
[23] B.K. Ravi Shankar and H. Schechter, Tetrahedron Lett. 23 (1982) 2277.
[24] D.W. Goodman, R.P. Kelley, T.E. Madey and J.M. White, J. Catal. 64 (1980) 479.
[25] C.B. Young and G.N. Whiteside, J. Am. Chem. Soc. 100 (1978) 5808.
[26] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[27] R.C. Bradey and R.J. Pettit, J. Am. Chem. Soc. 103 (1981) 1287.
[28] M. Logan, A.J. Gellman and G.A. Somorjai, J. Catal. 63 (1980) 226.
[29] C. Zheng, A. Yithak and R.J. Hoffman, J. Am. Chem. Soc. 110 (1988) 749.
[30] R.C. Weast and S.M. Selby, eds., *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, 1976).
[31] K.A. Vikulov, B.N. Shelimov and V.B. Kazansky, J. Mol. Catal. 72 (1992) 1.
[32] A.K. Rappé and W.A. Goddard III, J. Am. Chem. Soc. 102 (1980) 5115.