JOURNAL OF CATALYSIS **119**, 230–237 (1989)

Molecular Approach to the Mechanisms of C–C Bond Formation and Cleavage on Metal Surfaces: Hydrogenolysis, Homologation, and Dimerization of Ethylene over Ru/SiO$_2$ Catalysts

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Received April 4, 1989

At temperatures above ca. 50°C, over Ru/SiO$_2$ catalysts and in the presence of hydrogen, ethylene undergoes hydrogenation, hydrogenolysis, homologation, and dimerization reactions. The influence of contact times and reaction temperatures on conversions and selectivities has been examined. At low temperatures (<ca. 150°C) and low contact times, the major hydrocarbons produced from ethylene are, in addition to ethane, 2-butenes (with a high selectivity for *cis*-2-butene), which is good evidence for a dimerization reaction. With increasing temperature, hydrogenolysis of ethylene to methane and homologation to propene increase. Hydrogenolysis and homologation seem to be mechanistically related in terms of elementary steps of C–C bond cleavage and formation; two mechanisms are proposed which involve either metallocarbene insertion–elimination reactions or formation and decomposition of dimetallacyclic intermediates. Several mechanisms are envisioned for dimerization of ethylene; experimental data seem to support a mechanism which involves formation and coupling of two ethylidene species.

1. INTRODUCTION

The hydrogenolysis of saturated hydrocarbons over metal catalysts converts an alkane, in the presence of hydrogen, to lower chain hydrocarbons plus methane (*1*, *2*). When applied to olefinic hydrocarbons, the same reaction, in the presence of hydrogen, leads to lower olefins and paraffins plus methane (*3*, *4*). We (*4–7*) and others (*8–12*) have shown that the hydrogenolysis of olefins is always accompanied by the formation of the next higher olefins (homologation reaction). It has been suggested by Pettit and co-workers (*3*) that hydrogenolysis of hydrocarbons is mechanistically related to the Fischer–Tropsch synthesis in terms of C–C bond formation and C–C bond cleavage. Evidence was also given for a mechanistic similarity between olefin homologation and the Fischer–Tropsch synthesis (same regioselectivity in the homologation of propene as in the syn-gas conversion to butenes) (*7*). Recently (*13*), we have also demonstrated a striking similarity of mechanism between the hydrogenolysis and homologation of various pentene isomers. These results show that for certain types of hydrocarbons at least there is a common mechanism to explain both the formation and rupture of C–C bonds. Two possibilities were proposed: one (mechanism A) based on a carbene insertion–deinsertion in (from) a metal–alkyl bond and the other (mechanism B) based on a carbene–olefin $\rightleftharpoons$ dimetallacyclopentane equilibrium. The weakness of mechanism B arises from the fact that it cannot apply to the hydrogenolysis of a simple olefin as ethylene for which a dimetallacyclopentane cannot be formed (*14–18*). In contrast, mechanism A applies quite well to ethylene which can easily give a methyl fragment via carbene deinsertion from a metal–ethyl bond (*3*, *19*, *20*). It was therefore of interest to

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0021-9517/89 $3.00

investigate ethylene homologation and hydrogenolysis under the same conditions as those of our previous studies (*4, 7, 13*). In addition, the choice of ethylene was also governed by its crucial role as a primary product in the Fischer–Tropsch synthesis (*5, 6, 9, 10, 21–32*).

2. EXPERIMENTAL

The Ru/SiO$_2$ catalyst was prepared by adsorbing Ru$_3$(CO)$_{12}$ (Johnson Matthey) from a hexane solution onto silica (Aerosil 200 Degussa) that had been pretreated at 500°C under 10^{-4} Torr for 16 h (it has been established that during this chemisorption process, Ru$_3$(CO)$_{12}$ reacts with surface silanol groups to give a grafted species (μ–H)(μ–OSi$\equiv$)Ru$_3$(CO)$_{10}$ (*33*)). The grafted cluster was then decomposed into metal particles under flowing H$_2$ at 300°C. The final metal content was 1.0%, and the average particle size determined by electron microscopy was ca. 15 Å.

The reagents were a mixture of ethylene/hydrogen/argon. Hydrogen (99.995%) and argon (99.995%) were purified by passage through a Deoxo catalyst (BASF R-3-11) and 5-Å molecular sieves. Ethylene (Air Liquide, 99.95%) was used without further purification. That the methane, ethane and higher hydrocarbons contents in hydrogen and ethylene were negligible was checked by gas chromatography.

The reactor was a dynamic glass microreactor working under atmospheric pressure. Typically the catalyst (ca. 100 mg) was introduced into the reactor and heated at 250°C under a flow of pure hydrogen for 2 h. Then the reactant mixture was allowed to flow over the catalyst (0.5×10^4 h^{-1} < GSV < 2.5×10^4 h^{-1}) at the reaction temperature for 10 min before the products of the reaction were analyzed by gas-phase chromatography. Between two experiments, the catalyst was treated at 250°C for 2 h under flowing hydrogen ($P_{H_2} = 1$ bar). Under these conditions, the activity and the selectivity of the catalyst could be reproduced several times without significant variations.

Analysis of the products was carried out with an online gas-phase chromatograph equipped with a flame ionization detector (Intersmat IGC 120 FB) and a 0.22 cm i.d. × 6 m stainless-steel column packed with squalane (7%) on alumina. The system was calibrated with standard hydrocarbon mixtures (ALLTECH).

3. RESULTS

3.1. General Features of the Reaction $C_2H_4 + H_2$

When a C$_2$H$_4$/H$_2$ mixture is allowed to flow over a Ru/SiO$_2$ catalyst (at 250°C and under atmospheric pressure), the main reaction is the hydrogenation of ethylene to ethane. To a smaller extent, ethylene is also converted to methane and C$_3$–C$_4$ hydrocarbons (Fig. 1). Conversion of ethylene to C$_1$, C$_3$, and C$_4$ products is approximately 20 times lower than to ethane. It increases

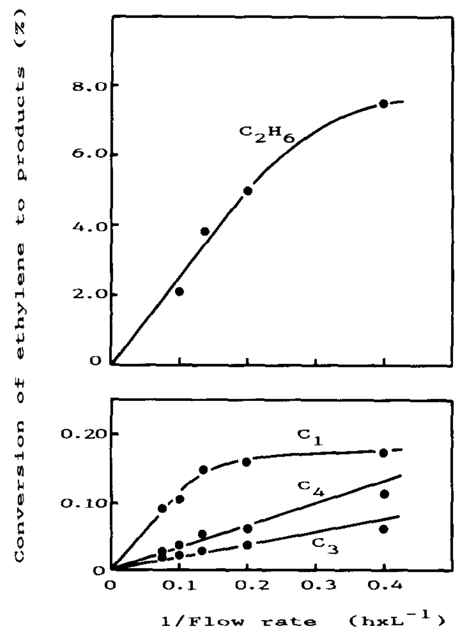


FIG. 1. Influence of contact time on the conversion of C$_2$H$_4$ to products in the reaction of C$_2$H$_4$ and H$_2$ over Ru/SiO$_2$ · m_{cata} = 100 mg; t = 250°C; C$_2$H$_4$/H$_2$/argon = 1/1/3 (mol).

with increasing contact time (roughly linearly for C_3 and C_4 hydrocarbons), C_4 hydrocarbon formation being higher than that of C_3 hydrocarbons.

3.2. Formation of C_1, C_3, and C_4 Hydrocarbons from C_2H_4/H_2 Mixtures

3.2.1. Conversion of ethylene to C_1, C_3, and C_4 hydrocarbons. The effect of reaction temperature on conversion of ethylene to C_1, C_3, and C_4 hydrocarbons and on product distribution is shown in Figs. 2 and 3. At temperatures as low as 35°C, formation of C_4 hydrocarbons in measurable amounts is observed. The conversion of ethylene to C_4 hydrocarbons (which are mainly olefins) increases rapidly with increasing temperatures, reaches a maximum at ca. 150°C, and then decreases at higher temperatures. At low temperatures, the amounts of methane and C_3 hydrocarbons are small: they become significant only at temperatures higher than 100°C. Conversion of ethylene to C_3 hydrocarbons increases slowly with increasing temperature and formation of methane follows an exponential-type curve. These results suggest that two different reactions are responsible for the formation of C_3 and C_4 hydrocarbons. One can already reasonably assume that C_4 hydrocarbons are obtained mainly via a dimerization reaction which would occur at temperatures lower than that of the actual homologation reaction by C_1 fragments. On the other hand, it appears that high temperatures favor hydrogenolysis reaction at the expense of the formation of higher hydrocarbons.

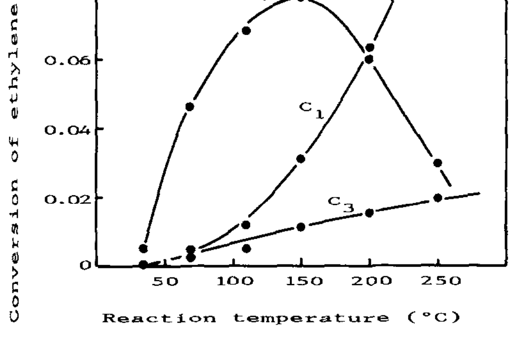


FIG. 2. Influence of reaction temperature on the conversion of C_2H_4 to C_1, C_3, and C_4 hydrocarbons in the reaction of C_2H_4 and H_2 over $Ru/SiO_2 \cdot m_{cata} = 100$ mg; $C_2H_4/H_2/\text{argon} = 1/1/3$ (mol); overall flow rate = 12 liters h^{-1}.

3.2.2. Distribution of butene isomers. The distributions of the butene isomers produced from ethylene at various contact times are shown in Fig. 4. At low contact times, the major products are 2-butenes (*cis* and *trans*, 70%) with *cis*-2-butene > *trans*-2-butene. The fraction of 1-butene is two times lower than the fraction of 2-butene and there is only 2% of isobutene. Surprisingly, with increasing contact times, there is only a small variation in the distribution of butene isomers, and the thermodynamic equilibrium is not reached (at equilibrium one would expect *trans*-2-butene > *cis*-2-butene). This result suggests that, in the presence of ethylene, secondary *cis–trans* isomerization and double-bond migration in the butenes produced are very slow reactions. A likely explanation involves the existence of a competitive coordination of ethylene on ruthenium which inhibits recoordination of the primarily formed butenes. The formation of isobutene in small but measurable amounts can be explained by a very limited secondary reaction of propene homologation (propene would be obtained by the homologation of ethylene (*5*)). At low contact times, the isobutene fraction is almost negligible. This result supports the hypothesis that a large amount of the butenes is not produced by propene homologation since in previous work it has been shown that propene homologation over Ru/SiO_2 gives a ratio of isobutene/*n*-butenes equal to 0.08 ± 0.01 (*4*), a value which is far from our results.

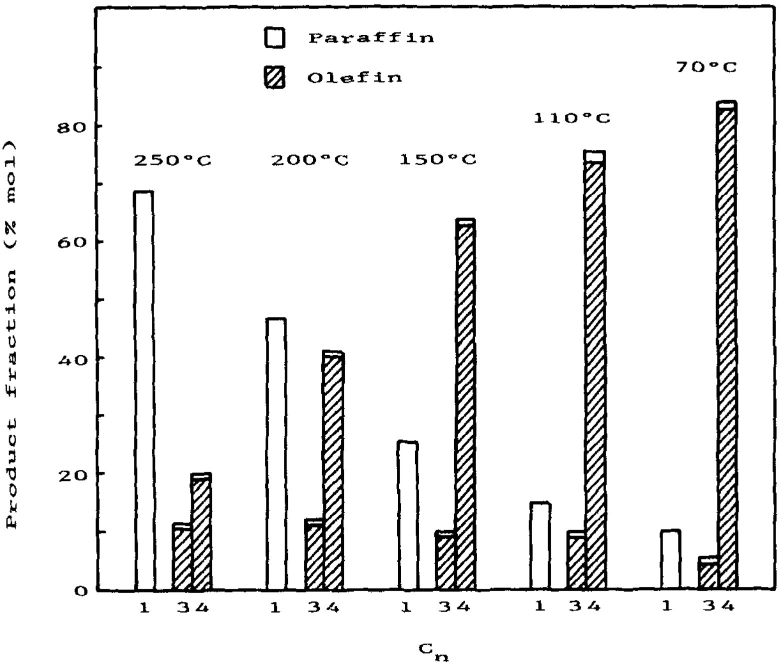


FIG. 3. Influence of reaction temperature on the distribution of C_1, C_3, and C_4 hydrocarbons produced in the reaction of C_2H_4 and H_2 over Ru/SiO_2 · m_{cata} = 100 mg; C_2H_4/H_2/argon = 1/1/3 (mol); overall flow rate = 12 liters h^{-1}.

2-Butenes, and especially *cis*-2-butene, are the main C_4 primary products formed in the reaction of ethylene with H_2. This result also supports the hypothesis that butenes come mainly from ethylene dimerization rather than from propene homologation; in

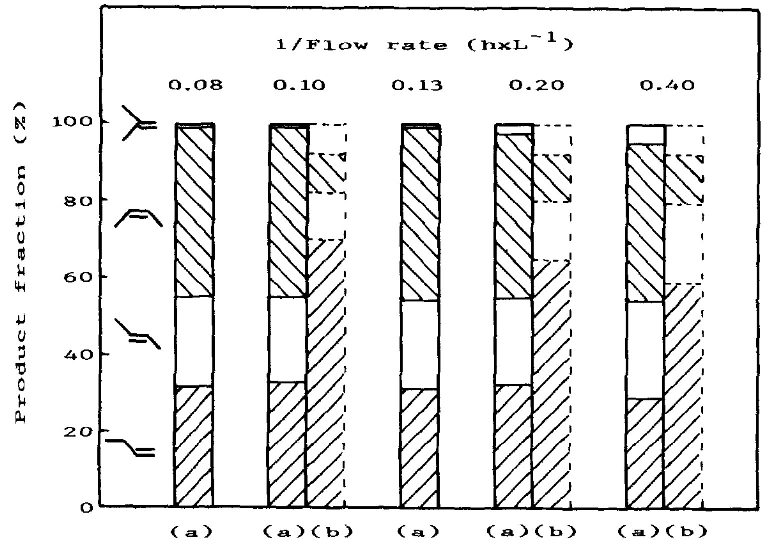


FIG. 4. (a) Influence of contact time on the distribution of the butene isomers produced in the reaction of C_2H_4 and H_2 over Ru/SiO_2. m_{cata} = 100 mg; t = 250°C; C_2H_4/H_2/argon = 1/1/3 (mol). (b) Distribution obtained in propene homologation (see Ref. (*4*)).

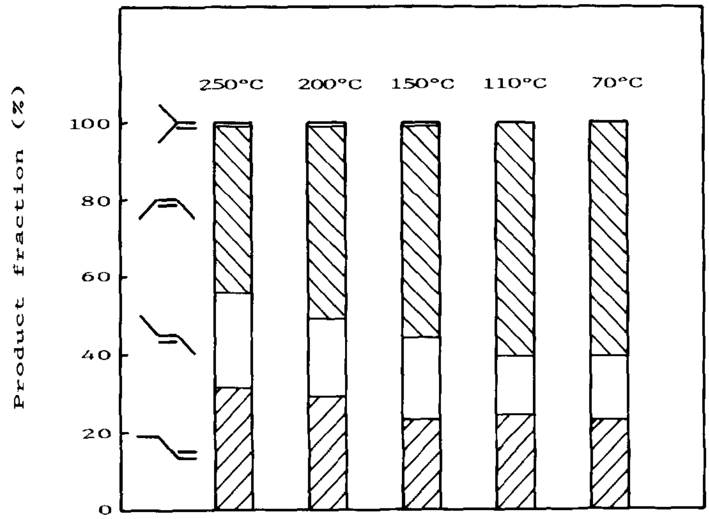


FIG. 5. Influence of reaction temperature on the distribution of the butene isomers produced in the reaction of C_2H_4 and H_2 over Ru/SiO_2. m_{cata} = 100 mg; C_2H_4/H_2/argon = 1/1/3 (mol); overall flow rate = 12 liters h^{-1}.

previous work on propene homologation on Ru/SiO_2 at 250°C it was found that the main primary product was 1-butene (ca. 70% at low contact times) (*4*).

The distribution of the butene isomers was determined at various reaction temperatures (Fig. 5). At low temperatures, isobutene is not produced and *cis*-2-butene fraction is higher than that found at 250°C. These results are in agreement with the previous observation that low temperatures would favor ethylene dimerization to homologation reaction via reaction of C_1 fragments.

4. DISCUSSION

In the presence of hydrogen, over a Ru/SiO_2 catalyst, ethylene undergoes hydrogenation, hydrogenolysis to methane, and conversion to higher hydrocarbons. Hydrogenation of ethylene to ethane is evidently the main reaction (ethane formation is easily explained by the hydrogenation of a metal–alkyl species which could be formed by insertion of π-coordinated ethylene in a metal–hydrogen bond).

At temperatures higher than 50°C, ethylene undergoes carbon–carbon bond cleavage (leading to methane) and carbon–carbon bond formation (leading to olefinic and paraffinic C_3 and C_4 hydrocarbons). Interestingly, whereas ethylene is converted significantly to ethane, the C_3 and C_4 hydrocarbons are mostly olefinic which means that olefins and not paraffins are primary products. Although the conversions of ethylene to propene and butenes are small, they are reproducible, roughly proportional to contact time, and consequently they are meaningful for a mechanistic understanding of the mode of C–C bond formation.

One of the most significant results is the strong effect of temperature on product distribution (Figs. 2 and 3). At low temperatures mainly dimerization of ethylene to C_4 occurs, whereas at higher temperatures this reaction is progressively competing with the well-known process of hydrogenolysis–homologation of ethylene to methane and propene.

Regarding hydrogenolysis and homologation reactions (i.e., formation of methane and C_3 hydrocarbons), two mechanisms (A and B) can be envisioned. These mechanisms, based on elementary reactions demonstrated in organometallic chemistry, have been already considered in previous reports related to the hydrogenolysis–homologation of other olefins such as propene or pentene (*4, 13*). According to mechanism (A) (*3, 19, 20*), the formation of C_1 and C_3 hydrocarbons can be explained by deinsertion or insertion of a CH_2 fragment from (into) the M–C_2H_5 species obtained after insertion of ethylene into an M–H bond. According to mechanism (B), C_3 hydrocarbons could be obtained via reaction of a surface CH_2 fragment to the coordinated ethylene to give a dimetallacyclopentane intermediate (*4–6, 16–18*), which leads to propene after decomposition. Concerning the origin of the carbene fragment, one possibility would be a kind of homolytic cleavage of ethylene via a "dimetallacyclobutane" (*34–36*) which is the reverse of a reaction of carbene coupling (*37*).

Regarding the dimerization reaction, various experimental data support, in the particular case of ethylene, the existence of a mechanism of C–C bond formation which is superimposed on that occurring stepwise by addition of a C_1 fragment to any olefin (*19*):

(i) the iso/*n* ratio in butenes is zero (within experimental error) at 50°C, the temperature for which dimerization is the only reaction; this ratio is usually higher (0.08 ± 0.01) in the case of propene homologation on Ru/SiO$_2$ (*4, 7*);

(ii) the distribution of linear butene isomers is also different from that observed in propene homologation (*cis*-2-butene is the major isomer whereas 1-butene is the major isomer in propene homologation on Ru/SiO$_2$ (*4, 7*, Fig. 4);

(iii) the rather low temperature at which dimerization occurs.

At least three mechanisms can be envisioned to account for ethylene dimerization to butenes; some of these are derived from elementary steps demonstrated in organometallic chemistry:

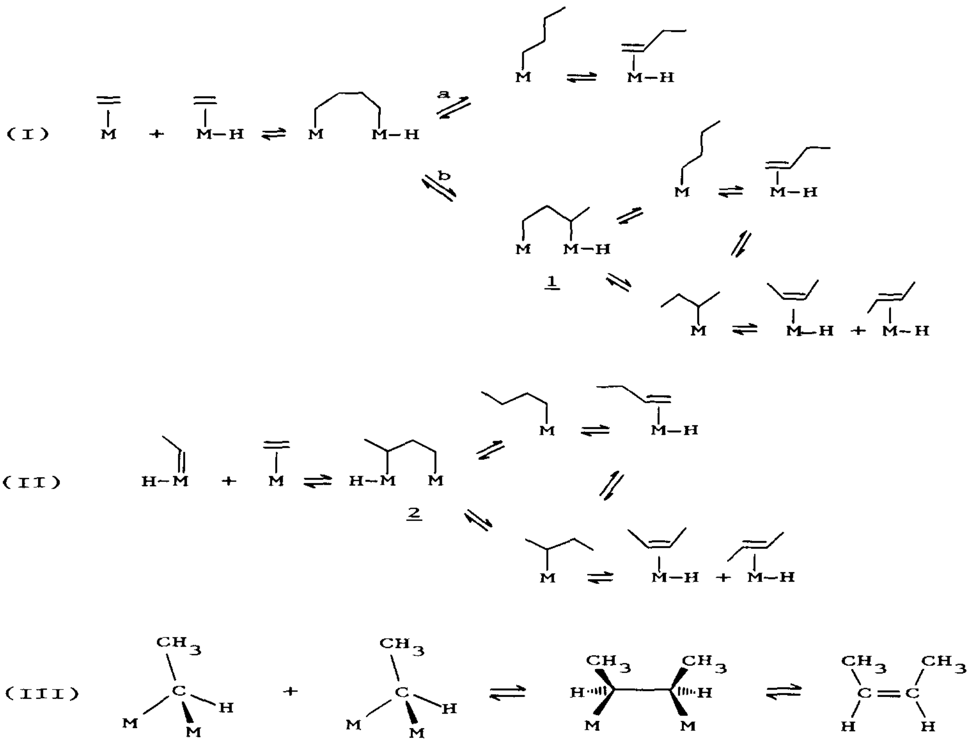
1. Coupling of two ethylene molecules to give a dimetallacyclohexane which could undergo either hydrogen cleavage to a metal-*n*-butyl (path (a)) or ring contraction (path (b)) (Scheme 1-I) (*38–41*). Path (a) should lead selectively to 1-butene which is contradictory to our results. Path (b) goes through intermediate **1** which gives preferentially 1-butene in the case of propene homologation on Ru/SiO$_2$ (*4, 7*). Consequently we do not favor either path (a) or path (b).

2. Coupling of an ethylidene group with a coordinated olefin (the ethylidene would be formed by α-H elimination from a metal–ethyl group) (Scheme 1-II). Again the reaction path goes through intermediate **2** which should lead more selectively to 1-butene (vide supra).

3. Coupling of two ethylidene species, as already suggested by Kokes and Bartek (*42*), which could explain the preferential formation of 2-butene (Scheme 1-III). Dimerization of the ethylidene groups would be achieved via the formation of dimetallacyclobutane intermediates (*36*), the decomposition of which would give mainly *cis*-2-butene.

These hypotheses are supported by the results of Knox *et al.* (*43*) who have shown that the decomposition of ruthenium-based bimetallic complexes with two bridging alkylidene groups leads to the internal olefin corresponding to the coupling of the two alkylidenes. Also, Bock *et al.* (*44*) have reported the formation of 40% of tetramethylethylene by decomposition of diazopropane on Raney–Ni. This result is good evidence for the occurrence of a dimerization reaction of a dimethyl–carbene species.

To sum up, the observed distribution of butene isomers obtained at low temperatures (at which the butene fraction coming from homologation of propene is less pronounced) for the ethylene dimerization on Ru/SiO$_2$ catalysts supports a mechanism which involves the coupling of ethylidene species. Nevertheless, we cannot totally exclude other possibilities such as coupling of ethylene molecules or reaction of an eth-



SCHEME 1. Possible mechanisms for dimerization of ethylene. (I) Via coupling of ethylene molecules; (II) via reaction of an ethylidene fragment with ethylene; (III) via coupling of ethylidene fragments.

ylidene group with ethylene (since 1-butene is produced in quite a notable amount).

5. CONCLUSION

Apparently, like olefins, ethylene undergoes hydrogenation, hydrogenolysis, and homologation to give methane, propene and butenes over a Ru/SiO_2 catalyst in the presence of hydrogen. However, after a careful analysis of the effect of experimental parameters on the distribution of products, it appears that ethylene presents a very peculiar behavior. In fact, several reactions are observed: (i) at low temperatures, a direct dimerization reaction via coupling of C_2 entities, (ii) at high temperatures, a hydrogenolysis reaction which leads to the formation of C_1 surface fragments which can be hydrogenated to methane, and (iii) a homologation reaction in which C_1 fragments react with ethylene or C_2 surface species to give propene. Several hypotheses can be proposed concerning the mechanism of the dimerization reaction. One of these, which is supported by our results and by data in the literature, involves coupling rections of alkylidene species and appears to be a reasonable reaction pathway at low temperatures and with low-molecular-weight olefins.

ACKNOWLEDGMENT

Eloy Rodriguez thanks the foundation Gran Mariscal de Ayacucho (Venezuela) for financial support.

REFERENCES

1. Anderson, J. R., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and Paul B. Weisz, Eds.), Vol. 23, p. 1. Academic Press, New York, 1973; Sinfelt, J. H., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and Paul B. Weisz, Eds.), Vol. 23, p. 91. Academic Press, New York, 1973.

2. Engstrom, J. R., Goodman, D. W., and Weinberg, W. H., *J. Amer. Chem. Soc.* **110,** 8305 (1988).
3. Osterloh, W. T., Cornell, M. E., and Pettit, R., *J. Amer. Chem. Soc.* **104,** 3759 (1982).
4. Leconte, M., Théolier, A., and Basset, J. M., *J. Mol. Catal.* **28,** 217 (1985).
5. Hugues, F., Besson, B., and Basset, J. M., *J. Chem. Soc. Chem. Commun.,* 719 (1980).
6. Hugues, F., Besson, B., Bussière, P., Dalmon, J. A., Basset, J. M., and Olivier, D., *Nouv. J. Chim.* **5,** 207 (1981).
7. Leconte, M., Théolier, A., Rojas, D., and Basset, J. M., *J. Amer. Chem. Soc.* **106,** 1141 (1984).
8. Strehlow, R. A., and Douglas, E. C., *J. Chem. Soc. Chem. Commun.,* 259 (1983).
9. Kibby, C. L., Pannell, R. B., and Kobylinski, T. P., *Prep. Amer. Chem. Soc. Div. Pet. Chem.* **29,** 1113 (1984).
10. Jordan, D. S., and Bell, A. T., *J. Phys. Chem.* **90,** 4797 (1986).
11. Jordan, D. S., and Bell, A. T., *J. Catal.* **107,** 338 (1987).
12. Jordan, D. S., and Bell, A. T., *J. Catal.* **108,** 63 (1987).
13. Rodriguez, E., Leconte, M., Basset, J. M., Tanaka, K., and Tanaka, K. I., *J. Amer. Chem. Soc.* **110,** 275 (1988).
14. Foley, P., and Whitesides, G. M., *J. Amer. Chem. Soc.* **101,** 2732 (1979).
15. Foley, P., Di Cosimo, R., and Whitesides, G. M., *J. Amer. Chem. Soc.* **102,** 6713 (1980).
16. Sumner Jr., C. E., Riley, P. E., Davis, R. E., and Pettit, R., *J. Amer. Chem. Soc.* **102,** 1752 (1980).
17. Motyl, K. M., Norton, J. R., Schauer, C. K., and Anderson, O. P., *J. Amer. Chem. Soc.* **104,** 7325 (1982).
18. Theopold, K. H., and Bergman, R. G., *J. Amer. Chem. Soc.* **105,** 464 (1983).
19. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
20. Brady, R. C., III, and Pettit, R., *J. Amer. Chem. Soc.* **102,** 6181 (1980).
21. Smith, D. F., Hawk, C. O., and Golden, P. L., *J. Amer. Chem. Soc.* **52,** 3221 (1930).
22. Eidus, Ya. T., *Russ. Chem. Rev. (Engl. Transl.)* **36,** 338 (1967); and references therein.
23. Hall, W. K., Kokes, R. J., and Emmett, P. H., *J. Amer. Chem. Soc.* **82,** 1027 (1960).
24. Dwyer, D. J., and Somorjai, G. A., *J. Catal.* **56,** 249 (1979).
25. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **62,** 19 (1980).
26. Reymond, J. P., Meriaudeau, P., Pommier, B., and Bennett, C. O., *J. Catal.* **64,** 163 (1980).
27. Molina, W., Perrichon, V., Sneeden, R. P. A., and Turlier, P., *React. Kinet. Catal. Lett.* **13,** 69 (1980).
28. Kellner, C. S., and Bell, A. T., *J. Catal.* **70,** 418 (1981).
29. Barrault, J., Forquy, C., and Perrichon, V., *J. Mol. Catal.* **17,** 195 (1982).
30. Kobori, Y., Yamasaki, H., Naito, S., Onishi, T., and Tamaru, K., *J. Chem. Soc. Faraday Trans. 1* **78,** 1473 (1982).
31. Satterfield, C. N., Huff, G. A., and Summerhayes, R. J., *J. Catal.* **80,** 486 (1983).
32. Morris, S. R., Hayes, R. B., Wells, P. B., and Whyman, R., *J. Catal.* **96,** 23 (1985).
33. Théolier, A., Choplin, A., D'Ornelas, L., Basset, J. M., Zanderighi, G. M., Ugo, R., Psaro, R., and Sourisseau, C., *Polyhedron* **2,** 119 (1983).
34. Hills, M. M., Parmeter, J. E., Mullins, C. B., and Weinberg, W. H., *J. Amer. Chem. Soc.* **108,** 3554 (1986).
35. Hembre, R. T., Scott, C. P., and Norton, J. R., *J. Amer. Chem. Soc.* **109,** 3468 (1987).
36. Avery, N. R., and Sheppard, N., *Proc. R. Soc. London A* **405,** 27 (1986).
37. Zheng, C., Apeloig, Y., and Hoffmann, R., *J. Amer. Chem. Soc.* **110,** 749 (1988).
38. Grubbs, R. H., and Miyashita, A., *J. Amer. Chem. Soc.* **100,** 7416 (1978).
39. Fellmann, J. D., Rupprecht, G. A., and Schrock, R. R., *J. Amer. Chem. Soc.* **101,** 5099 (1979).
40. McLain, S. J., Sancho, J., and Schrock, R. R., *J. Amer. Chem. Soc.* **102,** 5610 (1980).
41. Bré, A., Chauvin, Y., and Commereuc, D., *Nouv. J. Chim.* **10,** 535 (1986).
42. Kokes, R. J., and Bartek, J. P., *J. Catal.* **12,** 72 (1968).
43. Colborn, R. E., Dyke, A. F., Knox, S. A. R., MacPherson, K. A., Mead, K. A., Orpen, A. G., Roue, J., and Woodward, P., *Philos. Trans. R. Soc. London A* **308,** 67 (1982).
44. Bock, H., Tschmutowa, G., and Wolf, H., *J. Chem. Soc. Chem. Commun.,* 1068 (1986).