

Alkane Activation by Metal Atoms

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Vaporized metal has been used for over fifty years in industrial concerns for depositing thin metal films on materials ranging from plastics to metal supports [1]. Many studies of metal film deposition date from as early as 1937 [2], but it was not until 1965 that a technology was developed using vaporized atoms as reagents. Skell and Wescott devised a method of synthesis using carbon vapor cocondensed with organic compounds at 77 K [3]. P. L. Timms applied this technique to metals [4]. His use of inorganic and organic substrates helped establish metal vapor chemistry as a viable synthetic technique [5].

In metal vapor synthesis, highly reactive atoms or molecules are generated at a high temperature in vacuum and are brought together (cocondensed) with vaporized coreactants onto a cold surface [6]. Generally the coreactant to metal ratio is 10:1 to 100:1. Pressure requirements are 10^{-3} to 10^{-4} torr and the cold surface temperature can range from 10-273 K although 77-195 K is a more typical range.

Many transition metals have been used in metal vapor synthesis. To date nearly all transition metals have been tried [7]. Although each metal has a different reactivity, they all tend to aggregate if the cold surface temperature becomes too high.

Two main areas of research have developed since the first metal atom/alkane matrix experiment was reported. One area concerns single and di-atom insertion into carbon-hydrogen and carbon-carbon bonds in alkanes. The other involves metal aggregation and its effect on alkane matrices.

In 1977, Ozin, *et al.*, monitored the optical spectra of vanadium and divanadium in alkane matrices [8]. Although no direct interaction between the vanadium and the alkane matrix was seen, the nature of the alkane matrix did affect the optical spectrum. The following year, two metal insertions were reported. Barrett, *et al.*, found evidence of what was thought to be diiron insertion into the carbon-hydrogen bond of methane [9]. Skell, *et al.*, cocondensed zirconium atoms with various alkanes and found direct evidence of carbon-carbon and carbon-hydrogen bond insertion [10].

Photolysis has been used in conjunction with metal vapor synthesis by Billups, *et al.*, to effect insertion of iron atoms into a carbon-hydrogen bond in methane [11] and by Ozin and coworkers to insert copper atoms into methane and ethane carbon-hydrogen bonds [12,13]. Photolysis has also been used to remove iron atoms from a carbon-iron-hydrogen bond in HFeCH_3 [14].

M. L. H. Green and coworkers used metal vapor synthesis to insert molybdenum atoms into carbon-carbon bonds of spiro-[2,4]hepta-4,6-diene [15]. Using this reaction as a model, Green oxidatively added molybdenum atoms to carbon-carbon bonds in hexamethylcyclo-

pentadiene [16] and reacted tungsten atoms with spiro-[2,4]hepta-4,6-diene [17]. The tungsten moiety proved to have a rich chemistry and many derivatives of this compound were synthesized. Recently, Green reported an unusual Ti/ β -carbon interaction that provided insights into carbon-carbon and carbon-hydrogen bond activation [17].

In 1976, Klabunde and coworkers studied nickel and magnesium atom aggregation in alkane matrices [18]. Cluster formation was monitored between 77 K and 143 K. Both aggregates were then warmed to room temperature, dried under vacuum, and investigated for catalytic activity. The nickel aggregate proved to be an efficient hydrogenation catalyst while the magnesium aggregate was useful as a Grignard reagent. At the time of this investigation, Klabunde had assumed that the alkane species were physis- and chemisorbed onto the nickel clusters. Upon reinvestigation, Davis and Klabunde found evidence for carbon-carbon bond cleavage of the alkane matrix below 143 K [19]. Klabunde and coworkers continued their investigation of nickel aggregation in various solvents [20]. The catalytic activity of the nickel powders produced from these reactions was studied. They found nickel-pentane and nickel-hexane powders to be very active hydrogenation catalysts for benzene, 1-butene, 1-heptene and butadiene. Nickel-toluene powders were also active catalysts for selective hydrogenation of 1,3-butadiene to 1- and 2-butene. Nickel-THF powders were found to be fairly inactive as hydrogenation or olefin isomerization catalysts. In 1981, Klabunde, *et al.*, reported a detailed analysis of several nickel-alkene powders [21]. The magnetic and chemical properties of the powders were reported. Various amounts of carbon were incorporated into these small crystallites (<35 Å) depending upon preparative conditions.

References

1. Klabunde, K. J. Acc. Chem. Res. 1975, 8, 393.
2. Appleyard, E. T. S. Proc. Phys. Soc. 1937, 49, 118.
3. Skell, P. S.; Wescott, L. D., Jr.; Golstein, J.-P.; Engel, R. R. J. Am. Chem. Soc. 1965, 87, 2829-35.
4. Timms, P. L. Chem. Commun. 1968, 1525.
5. Timms, P. L. Adv. Inorg. Radiochem. 1972, 14, 121.
6. Blackborow, J. D.; Young, D. "Reactivity and Structure Concepts in Organic Chemistry; Vol. 9, Metal Vapor Synthesis in Organometallic Chemistry"; Springer-Verlag: Berlin, 1979; pp 2-4.
7. Klabunde, K. J. Chemtech. 1975, 10, 624.
8. Klotzbucher, W. E.; Mitchell, S. A.; Ozin, G. A. Inorg. Chem. 1977, 16, 3063-70.
9. Barrett, P. H.; Pasternak, M.; Pearson, R. G. J. Am. Chem. Soc. 1979, 101, 222-3.

10. Remick, R. J.; Asunta, T. A.; Skell, P. S. J. Am. Chem. Soc. 1979, 101, 1320-2.
11. Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. J. Am. Chem. Soc. 1980, 102, 7393-4.
12. Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. J. Am. Chem. Soc. 1981, 103, 1574-5.
13. Ozin, G. A.; Mitchell, S. A.; Garcia-Prieto, J. Angew. Chem. 1982, 21, 211.
14. Ozin, G. A.; McCaffrey, J. G. J. Am. Chem. Soc. 1982, 104, 7351-2.
15. Baretta, A.; Cloke, F. G. N.; Fergenbaum, A.; Green, M. L. H. J. Chem. Soc., Chem. Commun. 1981, 156.
16. Green, J. C.; Green, M. L. H.; Morley, C. P. J. Organomet. Chem. 1982, 233, C4-6.
17. Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. J. Chem. Soc., Chem. Commun. 1982, 802-3.
18. Klabunde, K. J.; Efner, H. F.; Murdock, T. O.; Ropple, R. J. Am. Chem. Soc. 1976, 98, 1021.
19. Davis, S. C.; Klabunde, K. J. J. Am. Chem. Soc. 1978, 100, 5973-4.
20. Klabunde, K. J.; Davis, S. C.; Hattori, H.; Tanlaka, Y. J. Catal. 1978, 54, 254-68.
21. Davis, S. C.; Severson, S. J.; Klabunde, K. J. J. Am. Chem. Soc. 1981, 103, 3024-9.