Hydrodehalogenation with Mo_2C and W_2C

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Introduction

The environmental impact of chlorofluorocarbons (CFC's) and polychlorinated biphenyls (PCB's) has led to the strict regulation of halocarbons. Disposal of existing hydrocarbon contaminants and the prevention of future pollution is a serious problem that remains to be solved. Oxidative incineration of halocarbons can lead to more toxic secondary pollutants such as furans and dioxins. A promising solution is the hydrodehalogenation (HDH) of halogenated organic compounds to non-halogenated hydrocarbons.[1-3] Limited success has been achieved with various supported catalysts including Pd, Pt and Rh. However, these catalysts exhibit poor selectivity and are prone to attack by HCl produced during hydrodechlorination.[4-9] Recently, our group reported the sonochemical synthesis and catalytic dehydrogenation activity of molybdenum carbide(Mo_2C).[10,11] As part of ongoing studies in this laboratory concerned with heterogeneous catalysis over sonochemically prepared catalysts, the activity, selectivity and stability of sonochemically prepared Mo_2C and W_2C in HDH of several halogenated organics have been examined.

Experimental

The high purity (>99.5 %) halogenated hydrocarbons used in the present study were purchase from Aldrich and were used as received. Dichlorofluoromethane (CFC-12) was obtained from Mattex Service Company (Champaign, IL) and chlorodifluoromethane (CFC-22) was purchased from S.J. Smith. Organic solvents were purified, degassed and stored in an inert atmosphere (< 0.5 ppm O_2) glove box. Methane (99.99% purity), hydrogen (99.99% purity), and Helium (99.9% purity) were purchased from S.J. Smith and were further purified by passing through oxytraps prior to use.

Synthesis of Molybdenum and Tungsten Carbide. The sonochemical molybdenum carbide (Mo_2C) was prepared and characterized as previously described.[10] Typically, a slurry of molybdenum hexacarbonyl ($Mo(CO)_6$, 2.5 g, 9.5 mmol) in 35 mL of hexadecane was irradiated with high intensity ultrasound (20 kHz, 80 W/cm^2, 1 cm^2 titanium horn; Sonics & Materials VCX600) for 3 h at 80°C under argon. The resulting black powder was filtered and washed several times with purified degassed pentane inside an argon-filled glove box. The washed powder was then heated to 80°C for 3 h under vacuum to sublime off the unreacted $Mo(CO)_6$. Oxygen contaminants were removed by heating the amorphous product to 500°C for 12 h under a flowing (30 cm^3/min) CH_4/H_2 (1:1 ; v:v) atmosphere. The latter treatment also leads to crystallization of the initially amorphous carbide. Elemental analysis of the treated powder gives a Mo/C atomic ratio of 1.97, indicative of a stoichiometric Mo_2C. Tungsten carbide (W_2C) was prepared with tungsten hexacarbonyl using similar conditions. All parameters were the same except the sonication temperature of 90°C.

Catalysis. Fixed bed single-pass quartz and borosilicate microreactors operated at atmospheric pressure were used for all catalytic reactions. The vapors of the liquid substrates were carried from a thermally equilibrated saturator by a flow (flow rate = 27.5 cm^3 (STP)/min) of purified hydrogen and helium. The flow rates were monitored with digital mass-flow controllers (MKS). The reaction products were analyzed with an on-line gas chromatograph (Hewlett-Packard 6890) mass spectrometer (Hewlett-Packard 5973) and a (35%-Phenyl)-methylpolysiloxane capillary column (Agilent DB-35MS).

Results and Discussion

The HDH activities of aryl halides with Mo_2C and W_2C are show in Figure 1a. The HDH of aryl halides with Mo_2C leads exclusively to benzene, with activities following the unusual pattern of $C_6H_5I < C_6H_5Br < C_6H_5Cl < C_6H_5F$. With the exception of C_6H_5F, the activity of W_2C is greater than Mo_2C and follows a similar pattern. The catalysts are active at ambient pressure and low temperatures. Despite the high hydrogen to substrate ratio we observe *no* hydrogenation products. From figure 1b, the decrease in activity is less that 15% after 100 h and the calculated half-life of the sonochemically prepared Mo_2C catalyst is 350 h. Preliminary time-on-stream studies with chlorobenzene indicate W_2C has a longer half-life and greater stability than Mo_2C.

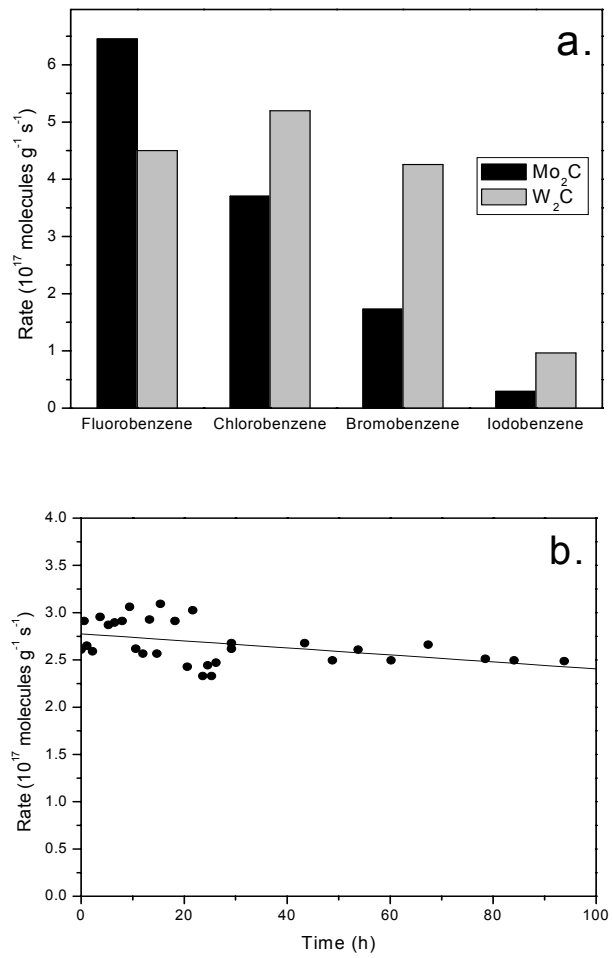

Figure 1: Catalytic activity of Mo_2C and W_2C for the HDH of halobenzenes with partial pressure = 7 mbar, $P_{substrate}/P_{H2}$ = 1:200, temperature at 300°C, and flow rate = 27 cm^3 (STP)/min.; **a.** Activity for halobenzenes ($P_{fluorobenzene}/P_{H2}$ = 1:100); **b.** Activity for chlorobenzene with Mo_2C as a function of time-on-stream at 300°C.

The HDH of hexafluorobenzene with sonochemically prepared Mo_2C and W_2C is shown in Figure 2. After 12 hours, the activities for Mo_2C and W_2C at 300°C are $4.5x10^{17}$ and $2.2x10^{17}$ molecules g^{-1} s^{-1}, respectively. The rates increase with temperature and the selectivities are temperature dependent. Above 400°C, benzene is the only product from the HDH of hexafluorobenzene with Mo_2C. The lower activity of W_2C with respect to Mo_2C is consistent with the trend observed for fluorobenzene.

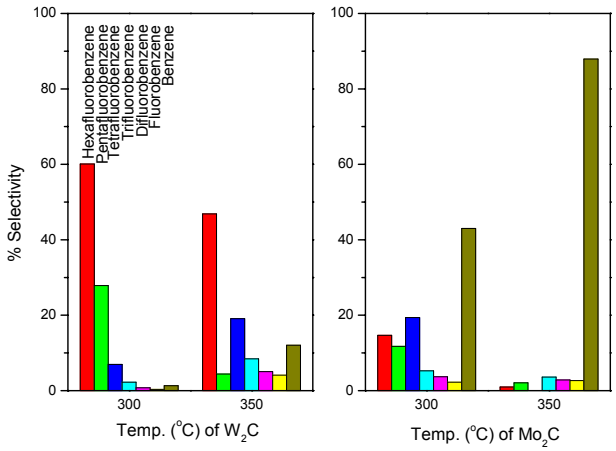

Figure 2. Catalytic selectivity of sonochemically prepared Mo_2C and W_2C for the HDH of hexafluorobenzene; Conditions: Substrate partial pressure = 29 mbar, $P_{substrate}/P_{H2}$ = 1:196, and flow rate = 27.5 cm^3(STP)/min.

Several HDH studies were carried out with chlorocyclohexane, 1-chlorobutane, and 1-chloropropane under similar experimental conditions used for the halobenzenes. The hydrodechlorination (HDC) rate for chlorocyclohexane, $3.6x10^{18}$ molecules g^{-1} s^{-1} at 300°C, is at least an order of magnitude faster than the rate observed with chlorobenzene. Methylcyclopentane was the only product observed. The HDC of 1-chlorobutane and 1-chlorobutane resulted in rates approximately five times greater than those observed with chlorobenzene. The majority of the products were dehydrogenated analogues of butane and propane. The higher rates of these substrates are consistent with the lower bond dissociation energy for the $C_{aliphatic}$-Cl versus the C_{areve}-Cl bond.[12-14]

The HDH of CFC's with sonochemically prepared Mo_2C results in methane as the major observed product. The activity at 300°C is $1.5x10^{19}$ molecules g^{-1} s^{-1}. The rate increases with temperature and the selectivity is temperature independent. Figure 3 illustrates the distribution of products from the HDH of dichlorodifluoromethane (CFC-12). A similar activity and selectivity (> 75% methane) was observed with chlorodifluoromethane (CFC-22). The selectivity towards methane differs from the selectivity observed with a conventional W_2C catalyst.[15] The HDH of CFC-22 with conventional W_2C gives CH_2F_2 (CFC-32) as the major product. No halogen-exchange products were detected during the HDH of either CFC.

Based on previous success with supported sonochemically prepared catalysts, we studied the HDH activity of sonochemically prepared Mo_2C supported on HZSM-5, activated carbon and Al_2O_3.[16,17] The activities (per g of metal) of Mo_2C/ZSM-5 and $Mo_2C/C_{activated}$ for the HDH of chlorobenzene were similar to the unsupported catalyst. No activity was observed with the Al_2O_3 supported catalyst.

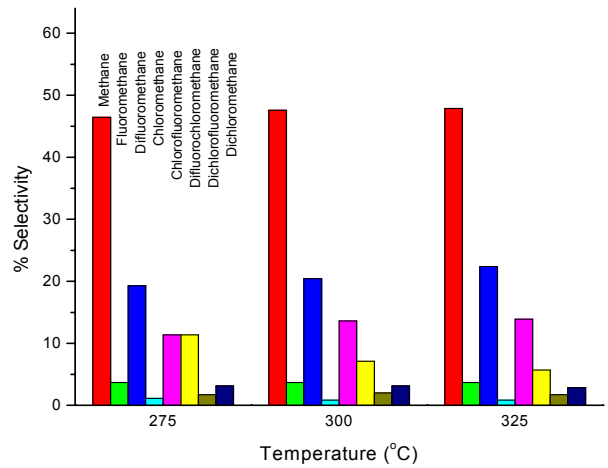

Figure 3: Catalytic selectivity of sonochemically prepared Mo_2C for HDH of CFC-12; Conditions: Substrate partial pressure = 100 mbar, $P_{substrate}/P_{H2}$ = 1:9, and flow rate = 27.5 cm^3(STP)/min.

Conclusion

We have demonstrated that sonochemically prepared Mo_2C and W_2C are active, stable, and selective catalysts for the HDH of halocarbons. The activity of Mo_2C is greater towards fluorocarbons while the activity of W_2C is greater for chloro-, bromo-, and iodocarbons. Other halocarbons to be studied include chlorophenols, PCB's and polybromo diphenyl ethers (PBDE's).

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References

1. Olie, K.; Vermeulen, P. L.; Hutzinger, O. *Chemosphere* **1977**, *6*, 455.
2. Ahling, B.; Lindskog, A.; Jansson, B.; Sundstrom, G. *Chemosphere* **1977**, *6*, 461.
3. Buser, H. R.; Bosshardt, H. P. *Chemosphere* **1978**, *7*, 165.
4. Coq, B.; Farrat, G.; Fiqueras, F. *J. Catal.* **1986**, *101*, 434.
5. Harper, R. J.; Kemball, C. *Trans. Faraday Soc.* **1969**, *65*, 2224.
6. Coq, B.; Farrat, G.; Fiqueras, F. *React. Kinet. Catal. Lett.* **1985**, *27*, 157.
7. Srinivaas, S. T.; Lakshmi, L. J.; Lingaiah, N.; Prasad, P. S. S.; Rao, P. K. *Appl. Catal. A* **1996**, *135*, L201.
8. Creyghton, E. J.; Burgers, M. H. W.; Jansen, J. C.; Van Bekkum, H. *Appl. Catal. A* **1995**, *128*, 275.
9. Choi, H. C.; Choi, S. H.; Lee, J. S.; Lee, K. H.; Kim, Y. G. *J. Catal.* **1997**, *166*, 284.
10. Hyeon, T.; Fang, M.; Suslick, K. S. *J. Amer. Chem. Soc.* **1996**, *118*, 5492.
11. Suslick, K. S.; Hyeon, T.; Fang, M. *Chem. Mat.* **1996**, *8*, 2172.
12. Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; Wiley and Sons: New York, 1976.
13. Benson, S. W. *J. Chem. Phys.* **1958**, *29*, 546.
14. Lide, D. R., Ed. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1993.
15. Sherif, F. G. U.S. Patent 5426252, 1995
16. Dhas, N. A.; Ekhtiarzadeh, A.; Suslick, K. S. *J. Amer. Chem. Soc.* **2001**, *123*, 8310.
17. Danstin, G.; Suslick, K. S. *J. Amer. Chem. Soc.* **2000**, *122*, 5214.