Novel catalysts for selective dehalogenation of CCl_2F_2 (CFC 12)

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Several supported and unsupported metal carbide catalysts were synthesized, characterized, and studied for their activity in the dehalogenation of CCl_2F_2 (CFC 12). Their catalytic properties were compared to those of a standard palladium catalyst. The turnover rates of the supported carbides were found to be higher than the unsupported carbides, but both deactivated quickly in the initial stages of reaction. X-ray photoelectron spectroscopic analysis of fresh and spent catalysts showed deposition of excessive amounts of carbon during the reaction which could be the cause of deactivation.

Keywords: dehalogenation; chlorofluorocarbon; hydrochlorofluorocarbon; hydrofluorocarbon; carbides

1. Introduction

Chlorofluorocarbons (CFCs) are very stable, low-toxicity materials which are widely used as refrigerants, blowing agents and industrial solvents. However, in the upper atmosphere they undergo photolysis, and it is generally accepted that this leads to the depletion of ozone [1,2]. It is therefore desirable to convert CFCs to environmentally safer hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). The halogen exchange reaction (F–Cl) is catalyzed by acidic oxides such as chromium oxide [3] and the hydrodechlorination reaction (H–Cl) is catalyzed by hydrogenation catalysts such as Pd/C [4]. This work was motivated by a report that a catalyst composed of WC granules mixed with $Al(OH)_3$ and spread on an Al_2O_3 honeycomb support was active for the dehalogenation of haloethane (CFC 114a) [5]. The conversion after 50 h at 623 K was 91%, compared to 5% for a Pd catalyst (both at a space velocity of 530 h^{-1}), but the method of preparation of the carbide was rudimentary and the external surface area was probably low ($< 5\ m^2\ g^{-1}$). The intrinsic acidity [6] and hydrogenation activity [7] of transition metal carbides and nitrides makes them suitable for the dehalogenation reaction.

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2. Experimental

2.1. SYNTHESIS

Supported carbide catalysts were prepared by a temperature programmed reaction method consisting of carburizing supported oxide precursors in a reactive stream while the temperature was progressively raised. The oxide precursors were prepared by impregnating Al_2O_3 (Degussa Aluminum Oxid C) with ammonium molybdate and ammonium metatungstate (20% loading of oxide). These were pelletized (16/20 mesh, 0.85–1.18 mm) and placed in a quartz tubular reactor. A 20% CH_4/H_2 gas at a flow rate of 1630 μmol s^{-1} (multiply by 1.5 to obtain cm^3 min^{-1}) was used for carburization, and the reaction products were monitored by an on-line mass spectrometer. The catalysts were synthesized in two stages. In the first stage, the sample was heated at a rate of 0.17 K s^{-1} to 646 K. In the second stage, the temperature was raised at 0.025 K s^{-1} to the final temperature (T_{max}) and held for (t_{hold}) until the reaction was complete. The sample was cooled in He and passivated with 0.5% O_2/He to form a protective layer of oxide on the surface. The synthesis parameters are summarized in table 1. The Pd-metal carbide catalysts were prepared by impregnating a solution of $PdCl_2$ on the carbide by the incipient wetness technique. The sample was dried at 423 K for 1 h and heated to 773 K for 3 h at 0.17 K s^{-1} with a H_2 flow of 680 μmol s^{-1}. The catalyst was cooled in He and passivated with 0.5% O_2/He.

2.2. CHARACTERIZATION

The catalysts were characterized by CO chemisorption at room temperature, BET surface area (S_g) measurements at 77 K, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The catalysts were reduced in a 10% H_2/He gas at 723 K for 3 h and cooled to room temperature in He before CO chemisorption and surface area measurements were carried out. XRD analysis of the fresh and spent catalysts was carried out using a powder diffractometer (Scintag, model ASC0007 with a Cu Kα monochromatized radiation source), operated at 45 kV and 40 mA. XPS (Perkin Elmer, model 5300 with Mg source, operated at 15 kV and 30 mA) analysis was done on the catalysts before and after reaction to study changes in surface characteristics. C 1s = 285 eV was taken as the reference.

Table 1
Summary of catalyst synthesis

Catalyst	T_{max} (K)	t_{hold} (h)
Mo_2C/Al_2O_3	1000	0.5
W_2C/Al_2O_3	1160	1

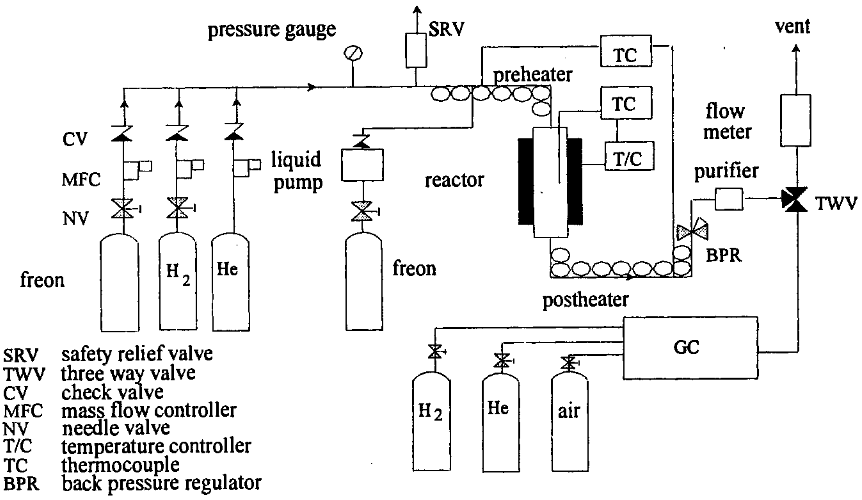

Fig. 1. Schematic of the medium-pressure testing unit.

2.3. ACTIVITY

The catalysts were tested for the conversion of CCl_2F_2 (CFC 12) in a medium-pressure reactor system (fig. 1). It consisted of two 316 SS flow reactors in parallel, heated in a clam shell furnace (series 3210, Applied Test Systems, Inc.) and controlled by a temperature controller (model CN9000, Omega). The reactor dimensions were 19.1 mm o.d., 15.9 mm i.d. and 380 mm length. The catalysts were loaded on quartz wool placed on a 316 SS filter screen with a thermocouple located at the center of the reactor. The reactant gases were dried and purified before flowing through the system and the flow was controlled by mass flow controllers (model 5850 E, Brooks). The pressure of the system was maintained by a back pressure regulator (BP-60, GO Inc.). The reaction products were analyzed on-line by a gas chro-

Table 2
Summary of catalyst characterization

Catalyst	CO uptake (μmol/g)	S_g (m^2/g)	Site density (10^{17} sites/m^2)
0.1% $Pd-Mo_2C/Al_2O_3$	63	73	5.2
1% $Pd-Mo_2C/Al_2O_3$	56	64	5.3
1% $Pd-W_2C/Al_2O_3$	15	61	1.5
Mo_2C/Al_2O_3	69	74	5.6
W_2C/Al_2O_3	34	63	3.3
Mo_2C	99	42	14
WC	30	32	5.6
1% Pd/activated carbon	20	500	0.24

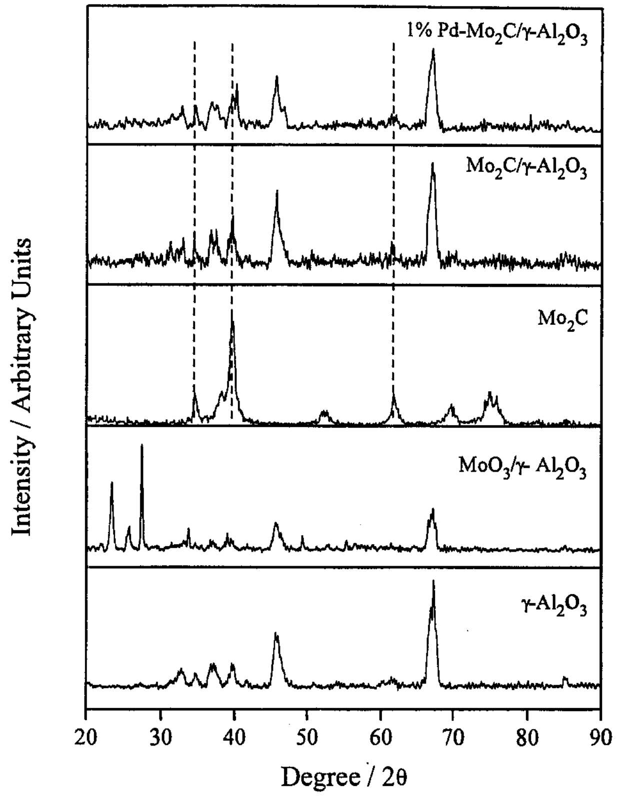

Fig. 2. XRD pattern of supported Mo_2C. The dashed lines indicate the presence of Mo_2C in the supported samples.

matograph (model 3700, Varian) after passing through a filter (a mixture of NaOH pellets and Drierite) to remove HCl and HF formed during the reaction. A FID detector and PoraPLOT Q (25 m × 0.53 mm) column (Chrompack, Inc.) were used and the gas was injected to the column through a ten-way valve.

Catalytic activity was compared by loading weights of catalysts in the reactor giving equal amounts of CO uptake (20 μmol). Typically 0.2–1 g of sample were pretreated at 723 K in H_2 gas flow at 68 μmol s^{-1} for 3 h. The reaction was performed at 523–623 K, with Mo_2C and WC tested at 0.1 MPa and the rest of the catalysts at 0.2 MPa at a total gas flow of 85 μmol s^{-1} (He : H_2 : CFC 12 = 5 : 4 : 1) corresponding to a volumetric space velocity of 1800 h^{-1}.

3. Results and discussion

A summary of the catalyst properties is given in table 2. The Pd-metal containing catalysts have lower CO uptakes than the original supported carbides. This is partly due to the sintering of Pd [8] at the treatment conditions (773 K), but also probably

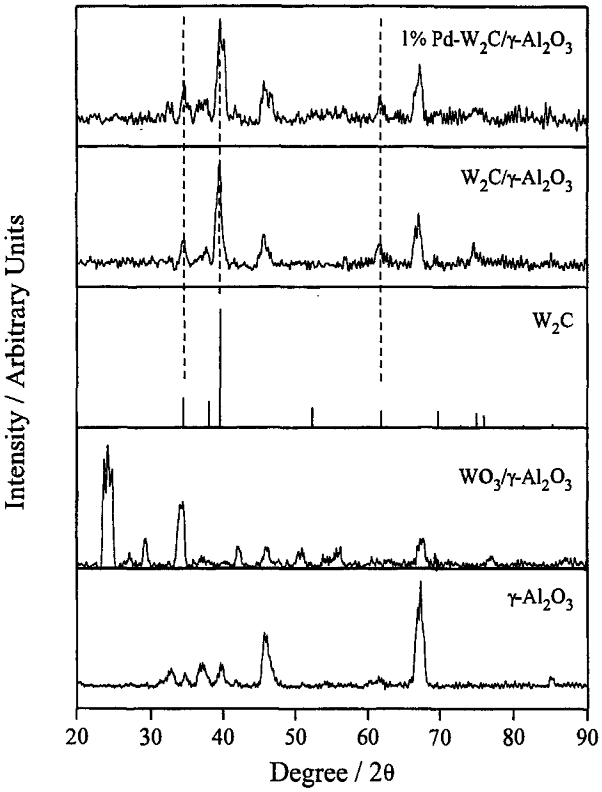

Fig. 3. XRD pattern of supported W_2C. The dashed lines indicate the presence of W_2C in the supported samples.

due to poisoning of the carbide surfaces by chloride in the course of the Pd salt impregnation. On the Pd catalysts, both H_2 and CO chemisorption gave consistent values, assuming adsorption stoichiometries of 2 and 1, respectively, and hence, the turnover rates presented in table 2 were calculated based on CO chemisorption values. XRD patterns of the catalysts synthesized are shown in figs. 2 and 3. Although the Al_2O_3 supported catalysts show predominant features from the support, the presence of dispersed Mo_2C and W_2C can be discerned from the patterns

Table 3
Steady-state rate and selectivity of 1% Pd/C

	% selectivity		Temp. (K)	CCl_2F_2/H_2	Space velocity (h^{-1})	Turnover rate (s^{-1})
	CH_4	CH_2F_2				
present	52	38	523	0.25	1800	0.15
2.5% Pd/graphite [4]	47	52	473	0.35	2000	0.02 (0.10[a])

[a] Calculated at 523 K using a reported E_a of 67 kJ mol^{-1} [4].

Table 4
Initial activities of the catalysts. The total gas flow rate was 85 μmol s^{-1} (He : H_2 : CFC 12 = 5 : 4 : 1) at a volumetric space velocity of 1800 h^{-1}. The turnover rate is based on sites titrated by the chemisorption of CO

Catalyst	Temp. (K)	% conv. of CFC 12	% selectivity to HFC 32	Turnover rate (s^{-1})
0.1% Pd–Mo_2C/Al_2O_3	573	13	100	0.055
1% Pd–Mo_2C/Al_2O_3	623	43	100	0.183
Mo_2C/Al_2O_3	623	46	100	0.196
W_2C/Al_2O_3	623	73	100	0.310
Mo_2C	623	4	100	0.017
WC	623	6	100	0.026
1% Pd/activated C	523	47	45	0.200

(dashed lines). Importantly, no lines due to the precursor oxides are visible.

The 1% Pd/activated carbon (Aldrich Chemical Co.) was used as a reference catalyst to compare the activity of the catalysts synthesized. The catalyst performance was monitored with time. The steady state percent conversion of CFC 12 and the selectivity of the products (CH_4, CH_2F_2, $CHClF_2$) are given in table 3. The initial activities of the different catalysts are given in table 4. It must be stressed that this is a fair comparison based on quantities of catalyst loaded giving *equal uptakes of CO*. The unsupported carbides had lower initial conversions than supported carbides and $W_2C/\gamma\text{-}Al_2O_3$ had a higher conversion than $Mo_2C/\gamma\text{-}Al_2O_3$. The addition of palladium to the carbide did not improve the activity. The only product observed in all cases was CH_2F_2. However, the carbide catalysts deactivated slowly with time (2 h), while the Pd catalyst showed little activity loss over 12 h.

The high selectivities to CH_2F_2 observed are partly due to the favorable C–Cl

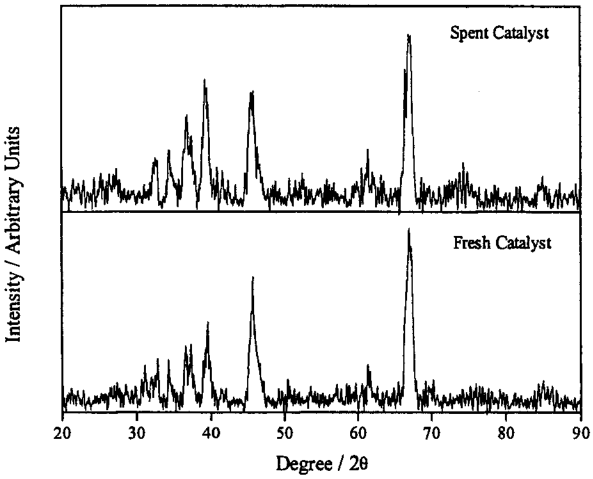

Fig. 4. XRD pattern of fresh and spent $Mo_2C/\gamma\text{-}Al_2O_3$.

Table 5
Atomic concentrations of Mo_2C/γ-Al_2O_3

Catalyst	C	O	Mo	Al	Cl	F
fresh	16.6	50.4	3.2	29.8	0	0
spent	49.1	18.6	1.1	15.2	1.3	14.7

and C–F bond strengths [9] (318 and 460 kJ mol^{-1}, respectively) in the CCl_2F_2 reactant molecule. The best catalysts appear to be those that have moderate dehalogenation properties. Moderate dehalogenation is defined here as the replacement of 1–3 halogen atoms in a CFC molecule. Once such a replacement has taken place the remaining C–F bonds remain strong (510 kJ mol^{-1} in F–CH_2F, 452 kJ mol^{-1} in F–CH_3) and resist further reaction. Morikawa et al. [5] studied the dehalogenation of CFC 114 ($C_2Cl_2F_4$) by WC. The products obtained at a reaction temperature of 623 K and a space velocity of 530 h^{-1} were C_2HF_4, $C_2H_2F_4$ and $C_2H_3F_4$. These are moderate dehalogenated products since only two chlorine atoms have been replaced by hydrogen, qualitatively our results compare with those of Morikawa et al.

A comparison of the XRD patterns (fig. 4) of the spent and fresh Mo_2C/γ-Al_2O_3 shows that the bulk structure did not change during the reaction. However, XPS analysis (table 5) of Mo_2C/γ-Al_2O_3 indicates that excessive amounts of fluorine and carbon were deposited during the reaction. The acidity generated by the surface fluoride may have resulted in cracking and carbon deposition leading to the deactivation of the catalyst. The better performance of the supported catalysts over the unsupported materials may have been due to the ability of the support to hold the excess carbon.

4. Summary

In summary, the unsupported carbides have lower initial conversions than the supported carbides and the only product formed was CH_2F_2. All carbide catalysts have lower activity than the supported palladium catalyst, possibly due to coking.

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