

Decomposition of Dichlorodifluoromethane with Simultaneous Halogen Fixation by Transition Metal Oxides Supported on Magnesium Oxide

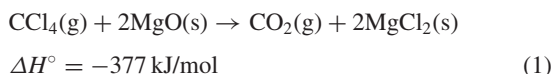
Tsukasa Tamai, Koji Inazu, and Ken-ichi Aika*

Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502

(Received February 6, 2003; CL-030111)

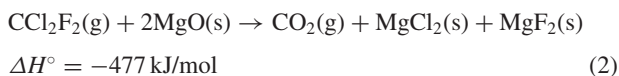
CFC12 (CCl_2F_2) decomposition with simultaneous halogen fixation by MgO was significantly promoted by supporting transition metal oxides. Vanadium oxides were the most effective and over 80% of halogen was fixed as magnesium halides in 3.3 h (stoichiometric CFC12 feeding to MgO) at 723 K.

Various methods for CFCs decomposition such as catalytic hydrolysis have been reported,¹⁻³ while in many cases formation of corrosive HCl and HF requires gases neutralizer and corrosion proof system. Destructive adsorption of halocarbons onto metal oxides has been recently reported as a novel method to mineralize halocarbons directly to CO_2 and solid halides.⁴⁻⁸ Klabunde and co-workers have intensively investigated CCl_4 decomposition by nanosized particles of MgO or CaO shown in Eq 1 for MgO.⁵⁻⁸



They reported that deposition of another metal oxides on MgO or CaO was effective to the decomposition and almost stoichiometric chlorine conversion to the corresponding chlorides was achieved by the reaction at 698 K. Although they suggested possible application of this method to decomposition of fluorine containing halocarbons such as CFCs,^{7,8} no work has been done regarding CFC decomposition using MgO or CaO based materials.

In this paper we report the first application of this type of destructive adsorption method to CFC decomposition using MgO-based materials to show the feasibility of its application to practical use and to reveal effects of transition metal oxides addition onto MgO. CFC12, the simplest CFC containing both chlorine and fluorine, was chosen to clarify the effects of fluorine of CFCs to have very strong carbon-fluorine bondings. Employing MgO as a basic metal oxide, destructive adsorption of CFC12 is expected to proceed to follow Eq 2.



MgO used in this study was prepared from $\text{Mg}(\text{OH})_2$ which was formed by suspending commercial MgO in highly purified water. For all the transition metals (V, Mn, Fe, Co, Ni, and Cu), MgO was impregnated with the corresponding metal acetylacetonato complexes dissolved in THF to have metal loading of 5 wt%. After the impregnation, the ligands of precursors were removed at 873 K for 3 h under gentle stream of air. The prepared samples were denoted as VO_x/MgO for vanadium oxides added MgO. The reaction gas was 1% CFC12 balanced with He

at total flow rate of 30 mL/min. For each run 0.2 g of pelletized metal oxide added MgO was employed. Before the reaction, the samples were pretreated at 873 K for 3 h under helium flow and all the experiments were carried out under dry condition to eliminate influences of water in the system. CFC12 and other gas products were analyzed by GC-TCD.

CFC12 decomposition by MgO did not proceed without any additive at 723 K. By supporting common transition metals (V, Mn, Fe, Co, and Cu) as oxide onto MgO significant enhancement of decomposition was observed as shown in Table 1. Major gas-phase product was CO_2 that shows mineralization of CFC12. CCl_4 was the only by-product observed. The percentage of mass balance for carbon based on conversion of CFC12 and yields of CO_2 and CCl_4 was substantially 100% and no carbon deposition was observed. Since at reaction time of 3 h, CFC12 loading became 0.45 mol/mol to MgO near stoichiometric ratio of Eq 2, total MgO conversion was calculated based on oxygen balance using the CO_2 yield. The order in the activity for CFC12 decomposition with simultaneous halogen absorption was as follows: $\text{V} \gg \text{Cu} = \text{Fe} > \text{Mn} > \text{Co} \gg \text{Ni}$. Except for VO_x/MgO and NiO_x/MgO the same inclination was observed, i.e. capability for halogen absorption of the metal oxides was considerably low compared to VO_x/MgO as indicated by low CO_2 selectivity of about 50% and high yield of CCl_4 . This observation clearly indicates that decomposition of CFC12 by these metal oxides takes place via following reaction as Eq 3.

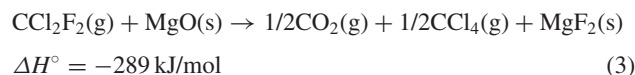


Table 1. CFC12 decomposition by various transition metal oxides supported on MgO

Sample	BET	Integrated conv.		
	surface area m^2g^{-1}	CFC12 %	MgO ^a %	CO_2 select. %
MgO	204	0	0	—
VO_x/MgO	139	87	75	96
MnO_x/MgO	53	90	42	52
FeO_x/MgO	75	98	46	52
CoO_x/MgO	80	52	24	51
NiO_x/MgO	102	0	0	—
CuO_x/MgO	97	97	48	54

Reaction temperature: 723 K, Reaction gas: 1% CFC12, 30 mL/min.

Reaction time: 3 h, Metal loading: 5 wt%.

^aCalculated based on oxygen balance using amount of CO_2 formed.

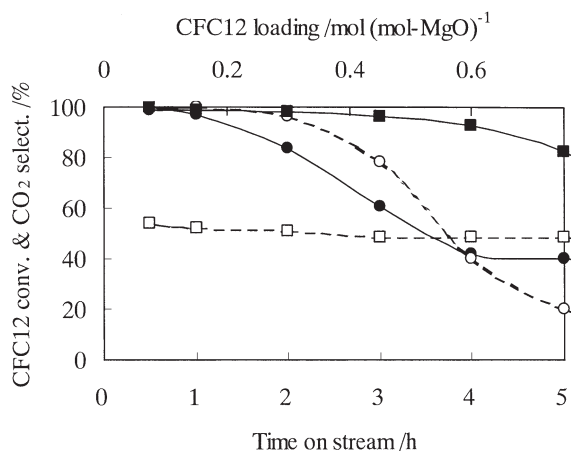


Figure 1. CFC12 decomposition by VO_x/MgO (●, ○) and FeO_x/MgO (■, □). CFC12 conv. (solid), CO_2 select. (open). Reaction temperature: 723 K.

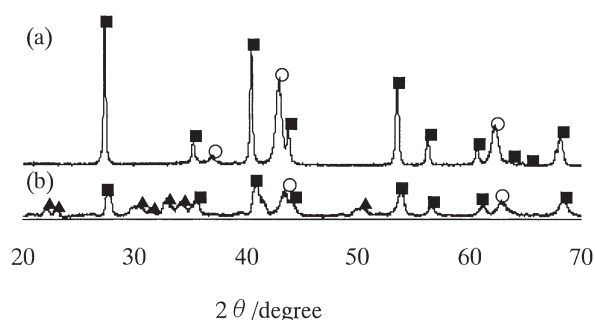


Figure 2. XRD patterns of FeO_x/MgO (a) and VO_x/MgO (b) after reaction with CFC12 for 3 h. MgO (○), MgF_2 (■), and $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ (▲).

In short, selective fluorine absorption happened to proceed throughout the CFC12 decomposition. However, VO_x/MgO showed high CO_2 selectivity of 96% and negligible formation of CCl_4 , hence remarkable activity to CFC12 decomposition and simultaneous halogen fixation.

Since FeO_x/MgO exhibited high activity to CFC12 decomposition with selective fluorine absorption, VO_x/MgO and FeO_x/MgO were studied further to understand details of the decomposition of CFC12 with halogen absorption. As time course of CFC12 decomposition shown in Figure 1, VO_x/MgO exhibited high activity by the reaction time of 1 h to decomposition of CFC12 to form CO_2 as the only gas-phase product. However, as MgO was consumed to be halides, the efficiency of the decomposition gradually decreased. FeO_x/MgO showed high CFC12 conversion, but CO_2 selectivity was just around 50% throughout the reaction and CCl_4 was always formed as a dominant by-product.

XRD patterns of VO_x/MgO and FeO_x/MgO after the reaction indicated formation of magnesium halides (Figure 2). Probably because of high dispersion and low content of vanadium oxides and iron oxides, all observed diffraction patterns were originated from magnesium compounds. For FeO_x/MgO after the reaction, only MgF_2 and remained MgO were found and MgCl_2 was not clearly observed while diffraction pattern originated from $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$, which was formed by the hydration of hygroscopic MgCl_2 by exposure to ambient air during sample-

handling for XRD analysis, was observed for VO_x/MgO as well as those from MgF_2 and MgO . These observations agree with the gas-phase product analysis shown in Figure 1.

The reason why only deposition of vanadium oxides promoted chlorine absorption should be related to capability for decomposition of CCl_4 . Klabunde et al. reported that vanadium oxides supported on MgO showed the highest ability for CCl_4 decomposition among several metal oxides and the order in the activity was as follows: $\text{V} > \text{Mn} > \text{Co} > \text{Fe} > \text{Cu} > \text{Ni}$.⁶ Facile formation of unstable vanadium halides (or oxyhalides) would be related to the activity for chlorine absorption, i.e. CCl_4 decomposition. After the CFC12 decomposition by VO_x/MgO , a small amount of yellowish deposition of VF_3O was observed in the reactor and at downstream of reaction gas flow, a dark green hygroscopic material, which was assigned to VClO by XRD analysis, was formed. VClO was probably originated from VCl_3O . These two oxyvanadium compounds are easily melted or evaporated under the reaction condition employed in this system (boiling point for VF_3O and VCl_3O are 753 K and 400 K, respectively). Such unstable intermediate compounds can migrate to MgO -rich sites to react with MgO to alter back to vanadium oxides with formation of magnesium halides until almost all of MgO are consumed. However, as available amount of MgO decreased, they evaporated to loss from the MgO . In this way, addition of vanadium oxides can enhance CFC12 decomposition and the absorption of both chlorine and fluorine as magnesium halides.

From these results, supporting transition metal oxides on MgO was effective for destructive adsorption of CFC12 with halogen fixation as magnesium halides, but fixation of chloride was found to be difficult except for VO_x/MgO . Even for VO_x/MgO , which exhibited the highest activity, the complete decomposition of CFC12 to CO_2 and halides takes place until MgO consumption becomes below 30%, and then efficiency of decomposition decreased as more MgO is consumed. But even when stoichiometric amount of CFC12 was loaded to the system, MgO conversion reached over 80% and formations of by-products were still quite small at CFC12 loading of stoichiometric amount to MgO . Destructive halogen fixation by transition metal supported MgO is a promising method to decompose CFCs without releasing corrosive acid gases. Further studies to reveal detail mechanism of this destructive halogen fixation and to improve the system are under way.

References

- 1 Y. Takita, G.-R. Li, R. Matsuzaki, H. Wakamatsu, H. Nishiguchi, Y. Moro-oka, and T. Ishihara, *Chem. Lett.*, **1997**, 13.
- 2 Y. Takita, H. Wakamatsu, M. Tokumaru, H. Nishiguchi, M. Ito, and T. Ishihara, *Appl. Catal., A*, **194**, 55 (2000).
- 3 S. Karmakar and H. L. Greene, *J. Catal.*, **151**, 394 (1995).
- 4 B. M. Weckhuysen, G. Mestl, M. P. Rosynek, T. R. Klawietz, J. F. Haw, and J. H. Lunsford, *J. Phys. B: At. Mol. Opt. Phys.*, **102**, 3773 (1998).
- 5 K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic, and D. Zhang, *J. Phys. Chem.*, **100**, 12142 (1996).
- 6 Y. Jiang, S. Decker, C. Mohs, and K. J. Klabunde, *J. Catal.*, **180**, 24 (1998).
- 7 K. J. Klabunde, A. Khaleel, and D. Park, *High Temp. Mater. Sci.*, **33**, 99 (1995).
- 8 S. P. Decker, J. S. Klabunde, A. Khaleel, K. J. Klabunde, *Environ. Sci. Technol.*, **36**, 762 (2002).