Magnesium fluoride as a catalytic support in hydrodechlorination of CCl_2F_2 (CFC-12)

A. Malinowski,[a] W. Juszczyk,[a] J. Pielaszek,[a] M. Bonarowska,[a] M. Wojciechowska[b] and Z. Karpiński*[a]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01224 Warszawa, Poland. E-mail: zk@ichf.edu.pl*

[b] *Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, PL-60780 Poznań, Poland*

Received (in Liverpool, UK) 26th January 1999, Accepted 9th March 1999

Magnesium fluoride-supported palladium and ruthenium appear to be useful catalysts in the reaction of CCl_2F_2 (CFC-12) hydrodechlorination; after doping Pd/MgF_2 with gold the selectivity for CH_2F_2 increased from ~70 to almost 90%.

The need to replace environmentally detrimental chlorofluorocarbons (CFCs) by benign hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) has resulted in considerable interest in catalytic hydrodechlorination of CFCs.[1] It is obvious from the patent literature that there is much activity in the development of new catalysts capable of very selective chlorine removal from a CFC molecule, *i.e.* avoiding undesired hydrodefluorination. Although this can be achieved with the use of heterogeneous catalysts containing such transition metals as iridium, ruthenium and, especially, palladium,[2] nevertheless the formation of over-dehalogenated products still presents a major concern. The role of a support (active carbon[3] and AlF_3[4] are reported most often in the patent literature) appears important; however, for this class of reaction one must also consider modifying the catalyst by doping the active phase (preferably palladium) with other elements.[5,6]

This report presents preliminary results obtained for MgF_2-supported Pd and Ru catalysts. Several metal fluorides have exhibited interesting properties as carriers for palladium (AlF_3, ZrF_4, TiF_3[4,7,8]), but MgF_2 has not been tested yet. In addition, MgO, as a support in hydrodechlorination,[9] is not resistant to the highly corrosive conditions of this reaction which results from considerable evolution of HCl, which can transform the support into $MgCl_2$. Similarly, by analogy to the catalytic behaviour of alumina-supported catalysts,[7,8] due to inevitable (albeit undesired) formation of HF during CFCs hydrodehalogenation, MgO is (at least partly) transformed into magnesium fluoride, which when located at a metal/support interface might favorably modify the electronic state of the metal particles.[7,8] All these facts and speculations have encouraged us to investigate this area.

The MgF_2-supported Pd, Pd–Au, Ru and Ru–Au catalysts were prepared by impregnation of MgF_2 (obtained in the reaction of $MgCO_3$ with aqueous solution of HF[10]) with appropriate metal salts. X-Ray diffraction (XRD) examination of MgF_2 (BET surface area 43 $m^2\ g^{-1}$, Barrett–Joyner–Halenda average pore size 20 nm, micropore volume 0.22 $cm^3\ g^{-1}$) showed a rutile structure. The reaction of CF_2Cl_2 with dihydrogen was conducted in a glass flow system. The experimental procedure and reaction conditions have been reported elsewhere.[11] Turnover frequencies (TOFs) were calculated on the basis of metal loadings and dispersions (from chemisorption measurements) and are shown in Table 1.

Our results indicate that MgF_2-supported palladium-based catalysts exhibit interesting properties in CCl_2F_2 hydrodechlorination. The first positive point is that CHF_3 is not produced by these catalysts, as often happens on catalysts capable of Cl/F exchange. Secondly, the time-on-stream behaviour (Fig. 1) shows an initial increase in activity, which appears to be stable during the next 17 hours. Thirdly, the selectivity towards CH_2F_2 production is reasonably high (> 70%), resembling the catalytic behaviour of AlF_3-supported palladium catalysts.[7] It can be speculated as others[7,8] have done, that the Lewis acidity of MgF_2, as in the case of AlF_3, decreases electron density in neighbouring Pd sites. In effect, electron-deficient Pd species bind :CF_2 carbene radicals (commonly accepted intermediate species[2,7,8,12]) less strongly, so a hydrogenative desorption of these radicals distinctly prevails over

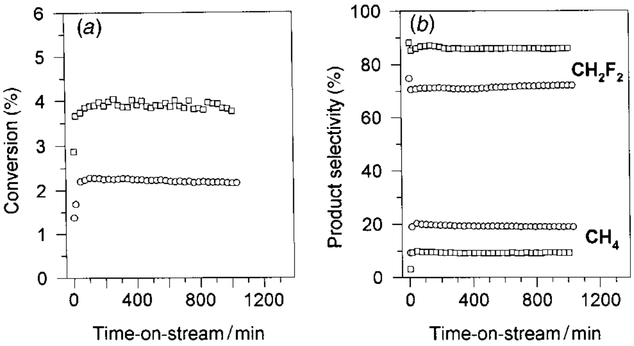

Fig. 1 Time-on-stream behaviour of 2 wt% Pd/MgF_2 (0.121 g, circles) and Pd–Au/MgF_2 (0.201 g, squares) catalysts in CCl_2F_2 hydrodechlorination. (*a*) Overall conversion, (*b*) selectivities to CH_4 and CH_2F_2.

Table 1 Hydrodechlorination of CCl_2F_2 on Pd/MgF_2, Pd–Au/MgF_2, Ru/MgF_2 and Ru–Au/MgF_2 catalysts: steady-state turnover frequencies (TOFs), product selectivities and apparent activation energies (E_as). Reaction temperature 453 K, H_2–CCl_2F_2 ratio 10 : 1.

	Selectivity[a] (%)							
Catalyst	CH_4	CH_2F_2	$CClF_3$	$CHClF_2$	C_2H_6	$C_2H_4F_2$	TOF/s^{-1}	E_a/kJ mol^{-1}
Pd/MgF_2[b]	19.0	72.0	—	8.5	0.2	—	0.0765	61.0 ± 0.4
Pd–Au/MgF_2[b]	9.3	86.0	0.4	3.8	0.1	—	0.0820	61.8 ± 1.0
Ru/MgF_2[b]	67.5	7.0	—	19.2	3.8	2.5	0.0053	60.3 ± 0.3
Ru–Au/MgF_2[b]	56.4	12.9	3.4	21.7	3.2	1.9	0.0160	54.1 ± 2.5

[a] Minor products (*e.g.* CH_3Cl, $\Sigma\% < 0.5\%$). [b] 2 wt% Pd/MgF_2 (metal dispersion, H/Pd = 0.02_3); 3.5 wt% $Pd_{0.7}Au_{0.3}/MgF_2$ (H/Pd = 0.02); 2.4 wt% Ru/MgF_2 (CO/Ru = 0.20); 2 wt% $Ru_{0.75}Au_{0.25}/MgF_2$ (CO/Ru = 0.03_2). Subscripts in chemical formulae denote atomic fractions.

hydrodefluorination. Interestingly enough, the selectivity for CH_2F_2 increases with Au doping: from ~ 72% for the Pd/MgF_2 to 86% for the Pd–Au/MgF_2 (Fig. 1 and Table 1).

As expected, preliminary XRD data manifest a substantial degree of Pd–Au mixing in the MgF_2-supported catalyst after reduction. Two Pd–Au solid solutions are present: $Pd_{0.81}Au_{0.19}$ and $Pd_{0.4}Au_{0.6}$ (indexes denote atomic fractions). This significant alloying concerns both reduced as well as spent Pd–Au/MgF_2 catalyst. XRD profiles obtained with used Pd–Au catalyst are somewhat complicated because large amounts of carbon (originating from CCl_2F_2) are incorporated into the Pd-based phase.[11,12] Since a Pd–C solution has a lattice parameter ($a_{PdC_{0.13}}$ = 0.399 nm[13,14]) larger than Pd (a_{Pd} = 0.3890 nm), it is difficult to assess whether an increase in the lattice parameter of Pd is due to Au (a_{Au} = 0.4078 nm) or C incorporation. In order to estimate to what extent Pd diffraction lines are affected by carbon dissolution and alloying with Au further studies are underway in our laboratory. This issue seems important, because, as is expected, a close contact between Pd and Au is essential for obtaining higher selectivity towards CH_2F_2. The Pd–Ag/graphite catalyst tested in CFC-12 hydrodechlorination by Coq *et al.*[15] showed selectivity for CH_2F_2 to be similar to that of the Pd/graphite catalyst. Such a result can be interpreted by an apparent absence of Pd–Ag interaction in the catalyst and, indeed, their XRD study of Pd–Ag/graphite showed no formation of Pd–Ag solid solution.

The Ru/MgF_2 catalyst showed rather low selectivity to CH_2F_2 (Table 1), but the selectivity to $CHClF_2$ was higher than in the case of Pd/MgF_2, in a qualitative agreement with Wiersma *et al.*[2] Again, doping with gold increased the selectivity towards partial hydrodechlorination (CH_2F_2 + $CHClF_2$) at the cost of CH_4 formation.

In conclusion, we have shown fair to respectable selectivities towards partial hydrodehalogenation of CCl_2F_2 over Pd, Pd–Au, Ru and Ru–Au catalysts supported on MgF_2. Our results indicate that the presence of gold in the catalyst is beneficial for selectivity variations. Studies are in progress to prepare new Pd–Au and Ru–Au catalysts (with different gold contents), supported on MgF_2 and active carbon.

Footnotes and references

1 Z. Ainbinder, L. E. Manzer and M. J. Nappa, in *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, VCH, Weinheim, 1997, vol. 4, p. 1677.
2 A. Wiersma, E. J. A. X. van de Sandt, M. A. Hollander, H. van Bekkum, M. Makkee and J. A. Moulijn, *J. Catal.*, 1998, **177**, 29.
3 For example, J. I. Darragh, UK Patent 1980, 1578933; V. N. M. Rao, US Patent 1992, 5136113.
4 For example, S. C. Kellner and V. N. M. Rao, US Patent 1989, 4873381.
5 R. Onishi, I. Suzuki and M. Ichikawa, *Chem. Lett.*, 1991, 841; R. Onishi, W.-L. Wang and M. Ichikawa, *Appl. Catal. A: Gen.*, 1994, **113**, 29.
6 V. N. M. Rao, US Patent 1995, 5447896; S. Morikawa, S. Samejima, M. Yositake and S. Tatematsu, Eur. Patent 1989, 0 347830 A2.
7 B. Coq, J.-M. Cognion, F. Figuéras and D. Tournigant, *J. Catal.*, 1993, **141**, 21.
8 B. Coq, F. Figuéras, S. Hub and D. Tournigant, *J. Phys. Chem.*, 1995, **99**, 11 159.
9 H. C. Choi, S. H. Choi, O. B. Yang, J. S. Lee, K. H. Lee and Y. G. Kim, *J. Catal.*, 1996, **161**, 790.
10 J. Haber and M. Wojciechowska, *J. Catal.*, 1988, **110**, 23.
11 W. Juszczyk, A. Malinowski and Z. Karpiński, *Appl. Catal. A: Gen.*, 1998, **166**, 311.
12 E. J. A. X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum and J. A. Moulijn, *Catal. Today*, 1997, **35**, 163.
13 J. Stachurski and A. Frąckiewicz, *J. Less-Common Metals*, 1985, **108**, 249.
14 S. B. Ziemecki, G. A. Jones, D. G. Swartzfager, R. L. Harlow and J. Faber, Jr., *J. Am. Chem. Soc.*, 1985, **107**, 4547.
15 B. Coq, S. Hub, F. Figuéras and D. Tournigant, *Appl. Catal. A: Gen.*, 1993, **101**, 41.

Communication 9/00731H