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Novel Catalytic Hydrodechlorination of CCl_2F_2 over Supported $PdCl_2$-$(n$-$C_4H_9)_4N^+Cl^-$ Molten salts

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Abstract: A novel supported liquid phase film catalyst: Supported $PdCl_2$-$(n$-$C_4H_9)_4N^+Cl^-$ molten salts was found to be an effective catalyst with good stability for selective hydrodechlorination of CCl_2F_2 (CFC-12) to its alternatives CH_2F_2 and $CHClF_2$. Addition of $CoCl_2$, $GaCl_3$ and $CuCl_2$ to $PdCl_2$-$(n$-$C_4H_9)_4N^+Cl^-$ modifies the catalytic performance of supported molten salts.

Keywords: Liquid film catalyst, palladium chloride, tetrabutylammonium chloride, molten salts, CFC-12 hydrodechlorination, HFC-32, HCFC-22.

Chlorofluorocarbons (CFCs) such as CCl_2F_2 have been widely used as refrigerants, blowing agent *etc.* due to their remarkable properties, however for the global environmental concerns, they have been prohibited in production and use because of their ozone depletion effect and greenhouse effect[1]. Nevertheless there are still several million tons of CFCs in use all over the world, close attentions have been paid to the operable handling techniques and environmentally benign alternatives. Among these alternatives, hydrofluorocrabons (HFCs) and hydrochlorofluorocarbons (HCFCs) (*e.g.* CH_2F_2 and $CHClF_2$) are the most attractive, not only because they have almost zero values of ozone depleting potential (ODP), but also they provide a novel route to handle these banked CFCs[2]. The catalytic hydrodechlorination of CCl_2F_2 is feasible in thermodynamics, but it is still a challenging task for chemists to apply this technology in practical use. The main obstacles related to hydrodechlorination of CCl_2F_2 are the relatively low selectivity to CH_2F_2 and/or $CHClF_2$ and deactivation of catalysts within a short time[3-5]. In this paper, a novel supported liquid phase film catalyst: supported $PdCl_2$-$(n$-$C_4H_9)_4N^+Cl^-$ molten salts was reported as an effective catalyst for hydrodechlorination of CCl_2F_2 to environmentally friendly products CH_2F_2 and $CHClF_2$, with high selectivity and good stability.

The catalysts were prepared by impregnation of cocanut active carbon overnight with methanol solution containing $PdCl_2$, hydrated tetra-*n*-butyl ammonium chloride (TBAC). Then film of eutectics[6] was formed on the surface of micropore with 2% $PdCl_2$ and 12.5% TBAC by weight. Modifier such as $GaCl_3$, $CuCl_2$ and $CoCl_2$ was added with certain amounts if necessary and the prepared catalysts were denoted as Pd-TBAC, Pd-Ga-TBAC, Pd-Cu-TBAC and Pd-Co-TBAC respectively. The impregnated catalysts were dried in air at *ca.* 393 K for 2 hr. CCl_2F_2

hydrodechlorination reactions were conducted in a fixed bed micro-reactor system at atmospheric pressure.   Prior to reaction the catalyst (400 mg) was purged by N_2 at 433 K for 2 hr.   The purified H_2 and CCl_2F_2 were used as the reactants.   The H_2 and CCl_2F_2 had molar ratio of 5:1 and their total flow rate was 109 mL/min.   The exhaust gas was analyzed by G.C.1002 equipped with ϕ3 mm×3 m stainless steel Porapark Q packed column and FID.   Turnover frequency (TOF) was calculated on basis of $PdCl_2$ loading.

Four activated carbon-supported $PdCl_2$-(n-C_4H_9)$_4N^+Cl^-$ molten salts were prepared in this study.   **Table 1** disclosed their composition, steady state TOFs and product selectivity in hydrodechlorination of CCl_2F_2.   With respect to the reaction behaviors on time, CCl_2F_2 hydrodechlorination catalyzed by Pd-TBAC, Pd-Co-TBAC or Pd-Ga-TBAC exhibited an initial activation period followed by a gradual approach to steady state (**Figure 1 a**).   Interestingly, a deactivation followed by a slight activation course was observed for Pd-Cu-TBAC before it reached the stationary state.   However, over conventional supported metal palladium catalysts[5], an obvious deactivation appeared with a factor of 1/3 ~ 1/5.   The steady-state activity of Pd-Co-TBAC was only *ca.* 40% of that of Pd-TBAC (~13 h^{-1} *vs* ~ 5.2 h^{-1}).   **Figure 1 b** showed that the reaction activity strongly depended on CCl_2F_2/H_2.   The CCl_2F_2/H_2 dependence behavior of other catalysts was similar to that of Pd-TBAC.

Table 1   Steady state turnover frequencies, product selectivity of hydrodechlorination of CCl_2F_2 in supported molten salt catalysts[a].

Catalyst[b]	Product selectivity			TOF/ h^{-1}
	CH_2F_2	$CHClF_2$	CH_4 and others	
Pd-TBAC	33.9	15.3	50.8	12.90
Pd-Ga-TBAC	39.8	18.4	41.8	13.35
Pd-Cu-TBAC	50.2	21.3	28.5	8.77
Pd-Co-TBAC	31.7	13.9	54.4	5.28

a) Reaction temperature 433 K, H_2:CCl_2F_2 = 5:1, total flow rate 109 mL/min.
b) b) containing 2.0% $PdCl_2$, 12.5%TBAC, 2.0%$GaCl_3$, 1.5%$CuCl_2$ and 1.5%$CoCl_2$ respectively by weight.

Time on stream behavior of the product selectivity revealed that there was no significant change in selectivity, different from typical supported metal catalysts[5], which suffered remarkable change in product selectivity with operating time.   On the other hand, the selectivity of desired CH_2F_2 and $CHClF_2$ had strong dependence on the modifier (**Table 1**).   In the testing conditions Pd-Cu-TBAC performed the highest selectivity to the desired products CH_2F_2+$CHClF_2$.   Different from the conventional supported metal palladium catalysts[3], $CHClF_2$ presented as a main product with comparable selectivity in supported molten salts.   According to the XRD result of Pd-Ga-TBAC after reaction, the diffraction peaks of Pd^0 almost could not be detected. It could be assumed that Pd(II) rather than metal palladium played the role of active center in stable liquid film formed by molten salts on the surface of micropore of support. CCl_2F_2 underwent a consecutive chlorine atom removal process, leading to the formation of CH_2F_2 and $CHClF_2$.

Figure 1 Catalytic activity of molten salt catalyst expressed as turnover frequency in CCl$_2$F$_2$ hydrodechlorination
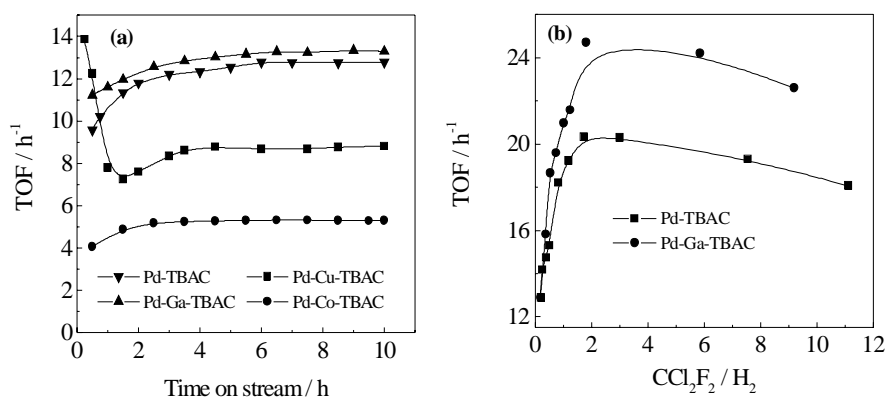
(a) the dependence of catalytic activity on time;
(b) the dependence of catalytic activity on CCl$_2$F$_2$/H$_2$, operating condition was the same in
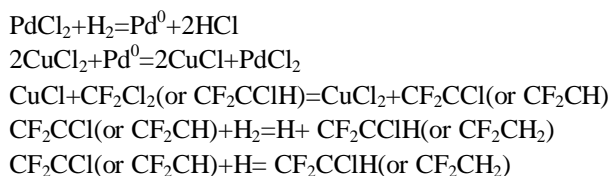   **Table 1**.

A heterogenized homogeneous catalysis was more likely to be present here. In this process, the reactants diffused through the liquid film of PdCl$_2$–(n-C$_4$H$_9$)$_4$N$^+$Cl$^-$ molten salts and undergo homogeneous catalytic reaction. The volatile products then diffused back out of the porous support. This novel system retained the advantages of homogeneous catalysts such as high selectivity and milder operating conditions. At the same time it also possessed the merits of heterogeneous catalysts, such as convenient handling, large interfacial areas and consequently small liquid diffusion paths, ease of separation of catalyst from products[7].

At the initial stage of hydrodechlorination in supported PdCl$_2$ containing molten salts, the exchange between Cl$^-$ in TBAC and F$^-$ inevitably originating from CCl$_2$F$_2$ increased the polarity of molten medium. A polar solvent would be beneficial to the dissociation of reactive species, and led to increase in reaction rate. In addition, the presence of relatively stable tetrabutyl ammonium fluoride stabilized the catalyst even at a higher reaction temperature.

According to literature[6] a two chlorine bridged stable structure could be formed between CoCl$_2$ and PdCl$_2$. In effect, it increased the electron density around Pd(II), these active sites would bond active intermediate such as: CF$_2$ strongly, so hydrodefluorination of these species was possible to prevails over a hydrogenolysis reaction, and consequently resulted in relatively high CH$_4$ selectivity. At the same time, the relatively slow collision between reactive species and Pd(II) active center led to decrease in reaction rate. While due to the strong Lewis acidity of GaCl$_3$, contrast effect on electron environment of Pd(II) sites might account for the relatively low CH$_4$ selectivity and high reaction rate.

With respect to CuCl$_2$ modified supported molten salts, as suggested in literature[6], the following reaction mechanism might take place. Pd(0)/Pd(II) and Cu(II)/Cu(I) might

couple, and formed the main reaction pathway as in conventional Wacker catalyst[8]:

$$PdCl_2+H_2=Pd^0+2HCl$$
$$2CuCl_2+Pd^0=2CuCl+PdCl_2$$
$$CuCl+CF_2Cl_2(or\ CF_2CClH)=CuCl_2+CF_2CCl(or\ CF_2CH)$$
$$CF_2CCl(or\ CF_2CH)+H_2=H+\ CF_2CClH(or\ CF_2CH_2)$$
$$CF_2CCl(or\ CF_2CH)+H=\ CF_2CClH(or\ CF_2CH_2)$$

In fact, CuCl could easily react with polyhalogenated compounds to produce poly-halogen radicals[9,10], and rather than on Pd-Ga-TBAC, Pd^0 was detected by XRD on the surface of Pd-Cu-TBAC after reaction. Obviously, Pd^0 was necessary to carry out the catalytic cycle like Wacker catalyst. An equilibrium-reach-process between redox cycles rather than the change of polarity of molten medium mainly accounted for the deactivation at the initial stage, while the consequent activation following deactivation was led by a relatively slow change of polarity of molten medium. The high selectivity to $CH_2F_2+CHClF_2$ might be mainly determined by the high selectivity of reaction of CuCl with chlorine containing species. Further study was in progress.

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