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# Catalytic Hydrogenolysis of CFC-12 ($CCl_2F_2$) over Bimetallic Palladium Catalysts Supported on Activated Carbon

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**Abstract**−Experiments were conducted for the hydrogenolysis of CFC-12 ($CCl_2F_2$) to $CH_2F_2$ over bimetallic palladium catalysts (Pd-Bi, Pd-Ru) supported on activated carbon. The characteristics of the bimetallic palladium catalysts were examined with ICP, XRD, TPD, TEM, and $N_2$ physisorption/$H_2$ chemisorption and the Pd-F formation was identified by XPS analysis. The catalytic activity of the bimetallic palladium catalyst (Pd-Bi/C, or Pd-Ru/C) was superior to that of the monometallic palladium catalyst. The bimetallic palladium catalysts showed much higher conversion rates (more than 99% of it was converted) than did the monometallic palladium catalyst (<92%) and were deactivated to a lesser extent, even at high temperatures (>320 °C). The bimetallic components maintained the good dispersion of the Pd on the activated carbon support.

Key words: CFC-12, Hydrogenolysis, HFC-32, Bimetallic Palladium Catalyst

## INTRODUCTION

Since being synthesized by Thomas Midgley Jr. in 1930, chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents and cleaning solvents. However, due to the depletion of the ozone layer by CFCs first reported by Rowland and Molina in 1974, their use has been restricted by the Montreal Protocol [Molina et al., 1974]. Numerous CFC decomposition techniques have been proposed recently and some of them are based on catalytic decomposition.

Lee et al. [Lee et al., 2000], Wiersma et al. [Wiersma et al., 1998; van de Sandt et al., 1997] and Park et al. [Park et al., 2000] investigated the catalytic hydrogenolysis of CFC-12 and HCFC-142b over noble metal catalysts supported on activated carbon. They each reported that impurities in the activated carbon support were responsible for the formation of by-products, the dispersion of transforming metal during the reaction, the inhibition of strong adsorption of the products and carbonaceous deposition on the metal surface.

Coq et al. [Coq et al., 1993, 1995] investigated the effects of both the Pd particle size and the nature of the supporting material on the hydrogenolysis of CFC-12. They added K, Fe, Co and Ag to palladium catalysts supported on graphite to obtain the bimetallic effects. Malinowski et al. [Malinowski et al., 1997] reported that Pd-Re bimetallic catalysts were deactivated significantly in the early stage of the reaction and that the selectivity toward HFC-32 had been changed with the bimetal composition.

The present study aims to observe the effects of the second metals on the behavior of palladium during the hydrogenolysis of CFC-12. Palladium catalysts modified by Bi and Ru as the second metals supported on activated carbon were tested.

## EXPERIMENTAL

### 1. Chemicals

CFC-12 (99.99%) was obtained from Ulsan Chemical Co. Pure hydrogen (99.99%), nitrogen (99.999%) and helium (99.999%) were used for the catalytic reaction, gas chromatography (HP 5890 Series II Plus) analysis and chemisorption experiments. Palladium(II) chloride ($PdCl_2$, 59% Pd, Acros Organics), Bismuth(III) chloride ($BiCl_3$, Aldrich) and Ruthenium(III) chloride ($RuCl_3$, Aldrich) were used as the metal precursors.

### 2. Pretreatment of Activated Carbon

Activated carbon with a high surface area (Norit Co., RB-1) was used as the supporting material. The pretreatment of the activated carbon support was carried out in the laboratory by washing it with HF (1 M) solution at pH 3 and HCl (1 M) solution at pH 4, consecutively. The pretreated activated carbon was dried at 100 °C for 24 hours.

### 3. Preparation of Catalysts

The catalysts supported on activated carbon were prepared by an incipient wetness method using $PdCl_2$-0.087N HCl solution. After impregnation, the catalysts were dried at 100 °C overnight. The bimetallic catalysts with Bi and Ru were also prepared by impregnating them on the palladium monometallic catalyst. The monometallic and bimetallic catalysts were dried at 100 °C for 24 hours and calcined at 350 °C in an electric furnace for 24 hours. The description of the prepared bimetallic palladium catalysts (Pd-M/C)

**Table 1. Catalyst codes used in this experiment**

| Catalyst code | Description (pretreatment with HF and HCl solution) |
|---|---|
| Pd/C | 1 wt% Pd on activated carbon (Norit-RB-1) |
| Pd-Bi/C | 1 wt% Pd and 0.05-0.5 wt% Bi on activated carbon |
| Pd-Ru/C | 1 wt% Pd and 0.1-0.5 wt% Ru on activated carbon |

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is given in Table 1.

## 4. Characterization of Catalysts

The BET surface area and the pore volume distribution of the catalysts were measured by a sorption analyzer (Gemini, Micromeritics ASAP 2010). The hydrogen chemisorption was determined by the double isotherm method proposed by Benson et al. [Benson et al., 1973]. The crystalline structures of the catalyst were analyzed by an X-ray diffractometer (Rigaku Model RINP-2000) using Cu $K_{\alpha 1}$ radiation (30 kV, 40 mA) with a Ni-filter. The crystalline phase was identified by comparing XRD patterns before and after the hydrogenolysis reaction with JCPDS (Joint Committee on Powder Diffraction Standards) powder diffraction file data and other reports [Ziemecki et al., 1985; Stachurski et al., 1985]. The chemical composition of the catalysts was also determined before and after the reaction by elemental analysis by using ICP (Perkin-ELN5000) & AA. The particle size of the palladium was determined by using a transmission electron microscope (TEM; CMS30, Phillips, US).

## 5. Catalytic Reaction

The reaction of dichlorodifluoromethane (CFC-12) with hydrogen was carried out at 760 mmHg atmospheric pressure in a fixed bed reactor made of Inconel-600 tube (0.25 m×0.095 m (OD)). The schematic diagram of the hydrogenolysis apparatus is shown in Fig. 1. One gram of the catalyst was placed in the reactor and reduced in-situ under flowing $H_2$ of 99.9% purity. The flow rates of the reac-

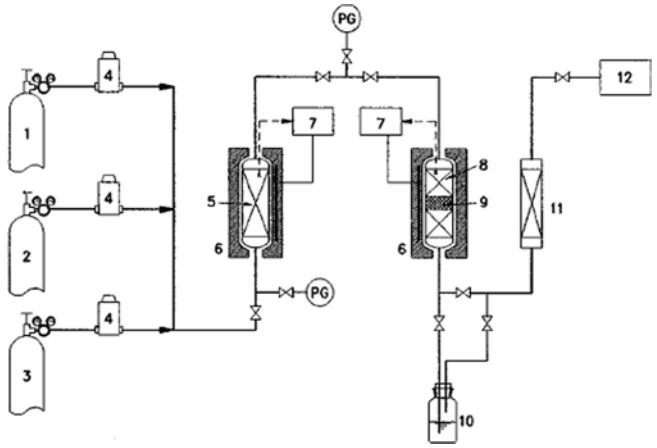


**Fig. 1. Schematic diagram of CFC-12 hydrogenolysis reaction system.**

1. CFC-12 cylinder
2. $H_2$ cylinder
3. $N_2$ cylinder
4. Mass flow controller
5. Preheater
6. Electric furnace
7. Temp. controller
8. Reactor
9. Catalyst
10. Trap
11. Silicagel trap (Blue)
12. On-line GC

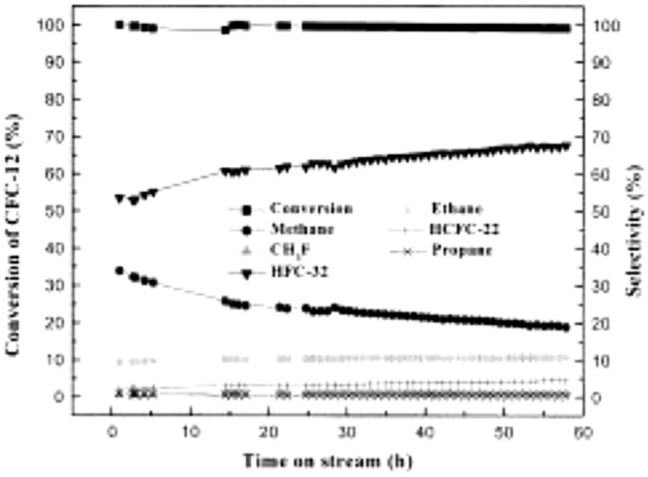


**Fig. 2. Activity and selectivities changes over 1 wt%Pd-0.1 wt% Bi/C for the hydrogenolysis of CFC-12($CF_2Cl_2$) (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=280 °C, reduction temp.=280 °C (for 1 h), $H_2$/CFC-12 feed ratio=6).**

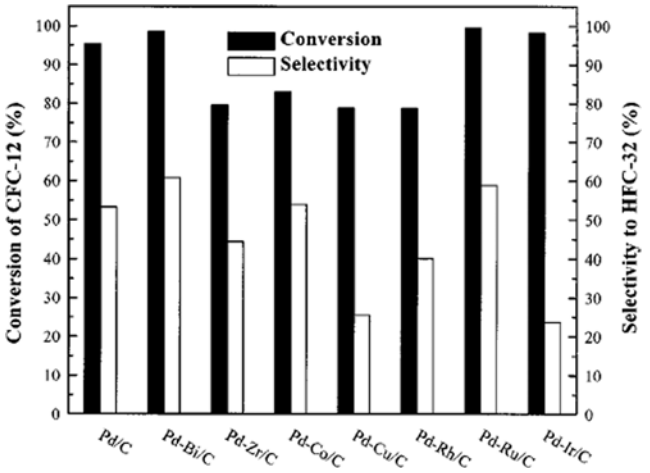


**Fig. 3. The final conversion and selectivities for CFC-12 hydrogenolysis to HFC-32 over the selected 1wt%Pd/C and 1 wt%Pd-0.1 wt%M/C catalysts (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=280 °C (time on stream≈50 h), reduction temp.=280 °C (for 1 h), $H_2$/CFC-12 feed ratio=6).**

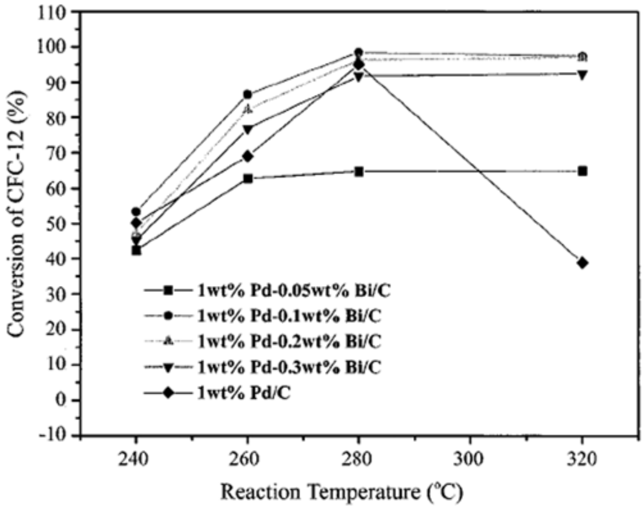


**Fig. 4. The catalytic activities of the monometallic and the bimetallic palladium catalysts with different metal loading (Condition: amount of catalyst used=1 g, P=101.3 kPa, time on stream≈25 h, reduction temp.=450 °C (for 5 h), $H_2$/CFC-12 feed ratio=6).**

tants (CFC-12 and $H_2$) were controlled by mass flow controllers (Matheson model 8272). The effluent from the reactor was bubbled through a water trap to remove any HCl and HF formed, and subsequently passed through a silica gel trap to remove moisture. The reaction product was analyzed with a gas chromatograph equipped with a Poraplot Q column (Plot Fused Silica 25 m×0.32 mm Coating Poraplot Q), a flame ionization detector (FID), Supelco-5 (2 m× 3.2 mm (OD)) connected in a series and a thermal conductivity detector (TCD). The product components were identified by GC mass chromatography (HP 5890 GC, 5971A MSD) with a Poraplot Q capillary column (Plot Fused Silica 25 m×0.32 mm, Coating Poraplot Q). The experimental conditions used for the catalytic tests were: (1) reduction at 280 °C for 1 hour and the reaction at 280 °C for 50 hours with an $H_2$/CFC-12 feed ratio of 6; (2) the reduction temperature at 450 °C for 5 hours and the reaction at 240 °C, 260 °C, 280 °C and 320 °C with an $H_2$/CFC-12 feed ratio of 6.

## RESULTS AND DISCUSSION

### 1. Hydrogenolysis of CFC-12

In the hydrogenolysis of CFC-12, the catalytic activity and the selectivity of the various bimetallic palladium catalysts (Pd-M/C) were investigated. The catalytic conversion and selectivities of the Pd-Bi bimetallic catalyst (Pd-Bi/C) are shown in Fig. 2. HFC-32 was 67% of the product, and CFC-22, $CH_4$ and $C_2H_6$ were also produced in quantities less than 4%, 19% and 10%, respectively, after 50 hours elapsed. The conversion over the Pd-Bi/C catalyst was over 99% and the selectivity to HFC-32 increased while that to methane decreased.

The catalytic conversion and selectivity to HFC-32 over the other bimetallic palladium catalysts are presented in Fig. 3. As shown in the figure, a stable catalyst operation was obtained after 50 hours elapsed. The catalytic activity of the bimetallic palladium catalyst (Pd-Bi/C or Pd-Ru/C) appeared to be better than that of the monometallic palladium catalyst. The bimetallic palladium catalysts showed much higher conversion rates (more than 99% of it was converted)

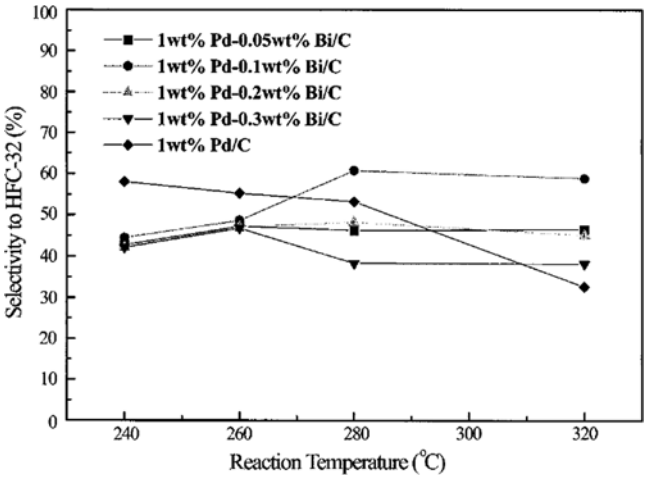


**Fig. 5. The selectivity for the CFC-12 hydrogenolysis to HFC-32 over the monometallic and the bimetallic palladium catalysts with different metal loading (Condition: amount of catalyst used=1 g, P=101.3 kPa, time on stream≈25 h, reduction temp.=450 °C (for 5 h), $H_2$/CFC-12 feed ratio=6).**

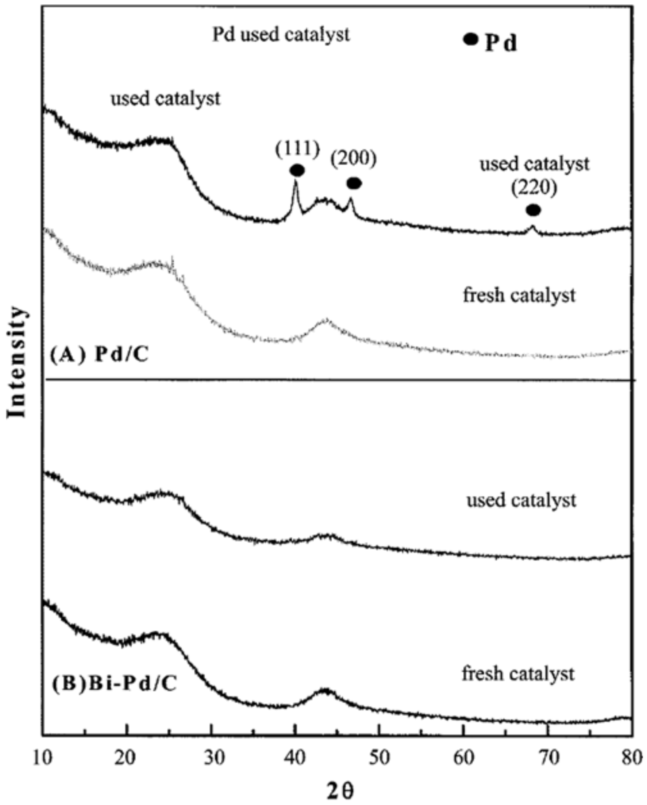


**Fig. 6. X-ray diffraction patterns of 1 wt%Pd/C, and 1 wt%Pd-0.5 wt%Bi/C catalysts before and after the reaction (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=320 °C (time on stream≈25 h), reduction temp.=450 °C (for 5 h), $H_2$/CFC-12 feed ratio=6).**

**Table 2. Surface area and dispersion of the Pd/C and Pd-M/C catalysts (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=320 °C (time on stream≈25 h), reduction temp.=450 °C (for 5 h), $H_2$/CFC-12 feed ratio=6)**

| Catalyst | Surface area ($m^2$/g)/Pore volume (cc/g) | | Particle size* (nm) | Dispersion** $(H/Pd)_{irr}$ | Surface area /Pore volume decrease (%) |
|---|---|---|---|---|---|
| | Before the reaction | After the reaction | Before/After the reaction | Before/After the reaction | |
| Pd(1 wt%)/C | 886/0.65 | 643/0.32 | 1.5/14.2 | 0.78/0.08 | 27/51 |
| Pd(1 wt%)-Bi(0.5 wt%)/C | 873/0.65 | 836/0.64 | 1.5/1.5 | 0.77/0.76 | 4/2 |
| Pd(1 wt%)-Ru(0.5 wt%)/C | 855/0.63 | 830/0.63 | 1.5/1.6 | 0.77/0.72 | 3/0 |

*Particle size was calculated by using the equation developed by Benson et al. [10].

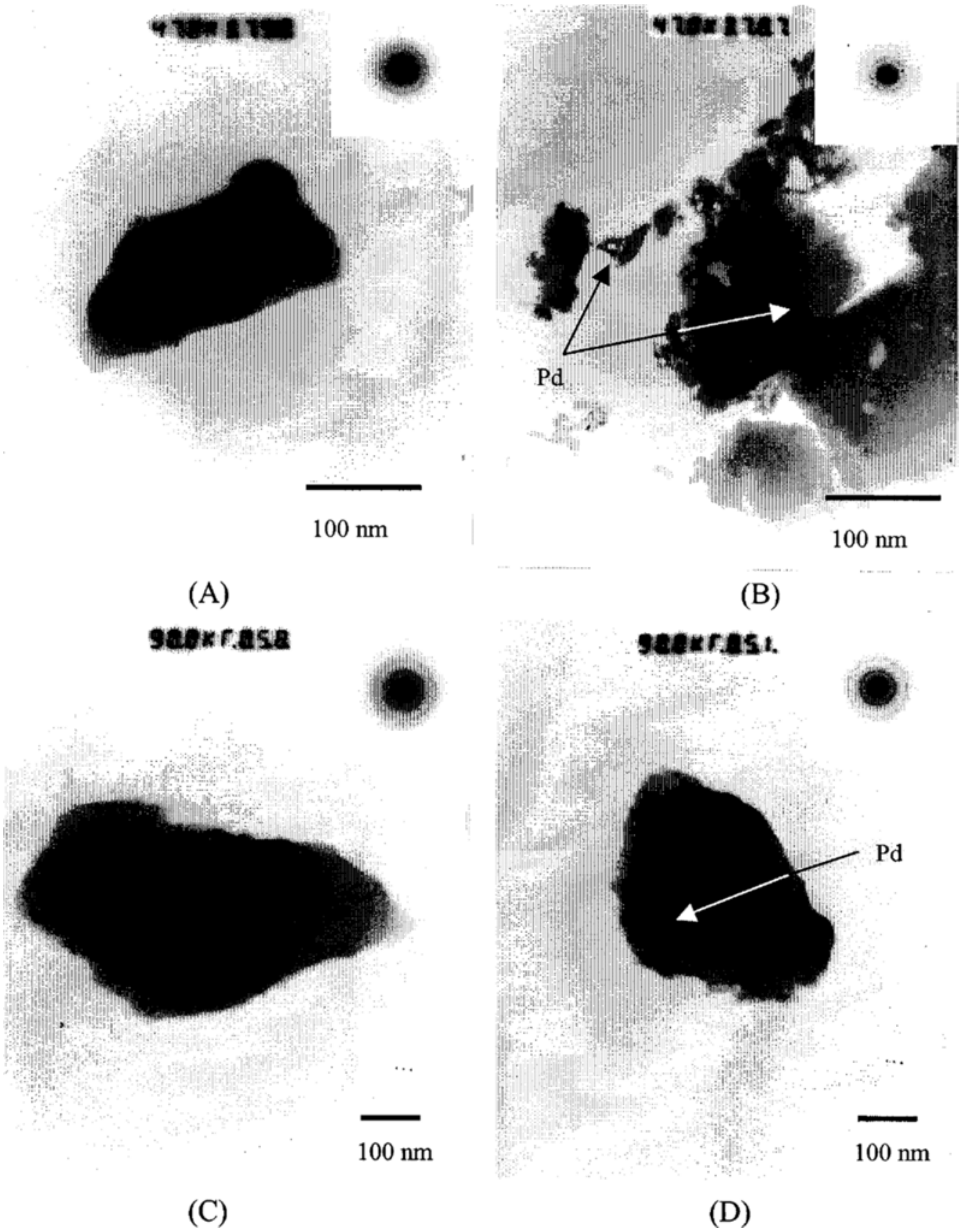
**Dispersion was measured by $H_2$ pulse chemisorption.

than did the monometallic palladium catalyst (<92%).

The effects of the reaction temperature on the conversion and selectivities of the Pd-Bi/C catalysts are shown in Fig. 4 and Fig. 5, respectively. Regardless of the amount of Bi loading, the conversion of all the Pd(1 wt%)-Bi/C catalysts increased until the reaction temperature reached 280 °C, and remained almost invariant to 320 °C. However, the conversion and selectivities of the Pd/C catalyst decreased markedly at 320 °C. The catalytic activity of Pd(1 wt%)-Bi(0.1 wt%)/C catalyst was the highest among those of the employed Pd-Bi/C catalysts. Therefore, 0.1 wt% of bismuth loading was applied in the following experiments.

## 2. Surface Area and Hydrogen Chemisorption

The surface area, degree of dispersion of Pd, and particle size of the catalysts before and after the reactions are given in Table 2. The surface area and pore volume of the bimetallic palladium catalysts were not significantly changed after the reaction. However, the monometallic palladium catalyst showed a 27% decrease in surface area and 50% decrease in pore volume after the reaction. This phenomenon was elucidated by the decrease in the pore volume of the support due to the accumulation of dissolved carbon or the migration of Pd during the reaction. A hydrogen chemisorption experiment showed that after the reaction the bimetallic palladium catalysts ex-



(A) (B)

(C) (D)

**Fig. 7. TEM image of the fresh and used Pd/C and Pd-Ru/C catalyst. A: Pd(1 wt%)/C fresh catalyst; B: Pd(1 wt%)/C used catalyst; C: Pd(1 wt%)-Ru(0.5 wt%)/C fresh catalyst; D: Pd(1 wt%)-Ru(0.5 wt%)/C used catalyst (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=320 °C (time on stream≈25 h), reduction temp.=450 °C (for 5 h), $H_2$/CFC-12 feed ratio=6).**

hibited a high dispersion (>72-76%) of palladium metal particles, but the monometallic palladium catalyst showed poor dispersion (<8%). Pd catalysts characterized by higher metal dispersion showed better activity as well as selectivity towards CH$_2$F$_2$ desired [Malinowski et al., 1997; Shin et al., 2000]. The Pd particle sizes of the catalysts (Pd-Bi/C, Pd-Ru/C, Pd/C) after the reaction were calculated by using the empirical equation developed by Benson et al. [Benson et al., 1973]. As shown in the table, the Pd particle sizes of Pd-Bi/C (1.5 nm) and Pd-Ru/C (1.6 nm) catalysts were much smaller than that of the monometallic palladium catalyst (14.2 nm). Therefore, dispersion of the metallic components in the bimetallic catalyst is expected to be greater than that of the metallic components in the monometallic catalyst. This result is similar to that reported by Tang et al. [Tang et al., 1999].

## 3. XRD & TEM Analysis

X-ray diffraction patterns of the Pd/C and bimetallic palladium catalysts before and after the reactions are shown in Fig. 6. The monometallic palladium catalyst after the reaction showed an increase in the intensity of the palladium peak, which indicated that crystalline growth or sintering occurred during the reaction. However, such an increase was not observed for the bimetallic catalysts. TEM analysis was also carried out in order to observe the particle size and dispersion of the palladium catalysts. TEM images of the monometallic and the bimetallic palladium catalysts before and after the reactions are shown in Fig. 7. TEM images of the Pd/C catalyst before the reaction (A) and the bimetallic palladium catalyst before (C) and after (D) the reactions show Pd particles of about 2 nm with good dispersion, but the image of the Pd/C catalyst after the reaction (B) shows sintering of Pd particles (about 15 nm). In comparing (B) and (D), the sintering of the catalysts was markedly decreased in the bimetallic palladium catalysts. Therefore, from this result we can confirm that the bimetallic components maintain good dispersion of Pd particles.

## 4. XPS Study

C 1s core level XPS spectra of the monometallic and bimetallic palladium catalysts are compared in Fig. 8. The convoluted component is assigned as follows. The component at 284.6 eV is ascribed to the carbon [Bonzel et al., 1980]. The binding energy component centered at 286.04 eV is attributed to the C-OH species, which is likely to be formed during washing with acid solution. The highest B.E. component at 290-291 eV can be attributed to the C-F species [Albers et al., 1992], which is formed during washing with HF solution.

Fig. 9 shows the Pd 3d core level XPS spectra of the monometallic and bimetallic palladium catalysts. The curve-fitted spectra of all the catalysts show two overlapping peaks at 335.83 and 337.57 eV, indicating the presence of Pd 3d$_{5/2}$. The peak at 337.57 eV also indicates the presence of a Pd-F species. The intensity of the B.E.

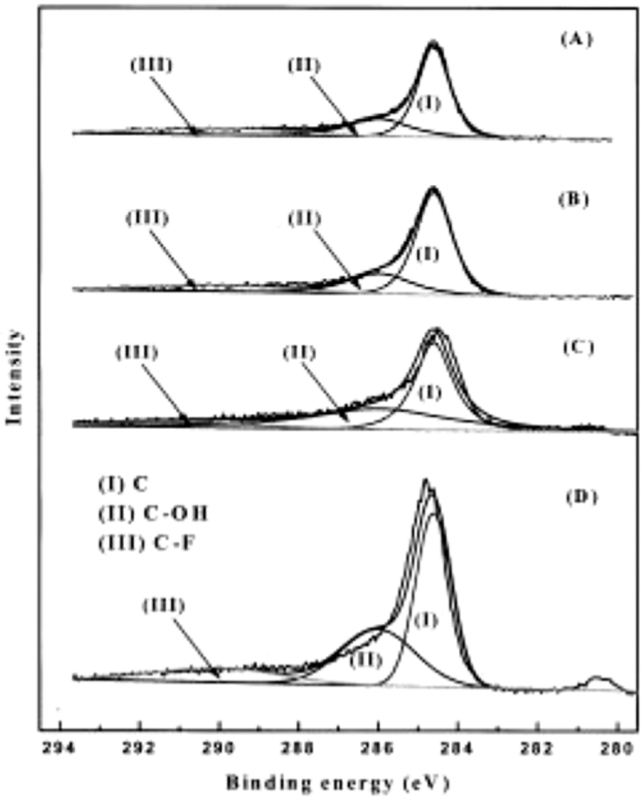


**Fig. 8. XPS spectra of C 1s for the Pd/C and Pd-Ru/C. A: Pd(1 wt%)/C catalyst before the reaction; B: Pd(1 wt%)/C catalyst after the reaction; C: Pd(1 wt%)-Ru(0.5 wt%)/C catalyst before the reaction; D: Pd(1 wt%)-Ru(0.5 wt%)/C catalyst after the reaction (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=320 °C (time on stream≈25 h), reduction temp.=450 °C (for 5 h), H$_2$/CFC-12 feed ratio=6).**

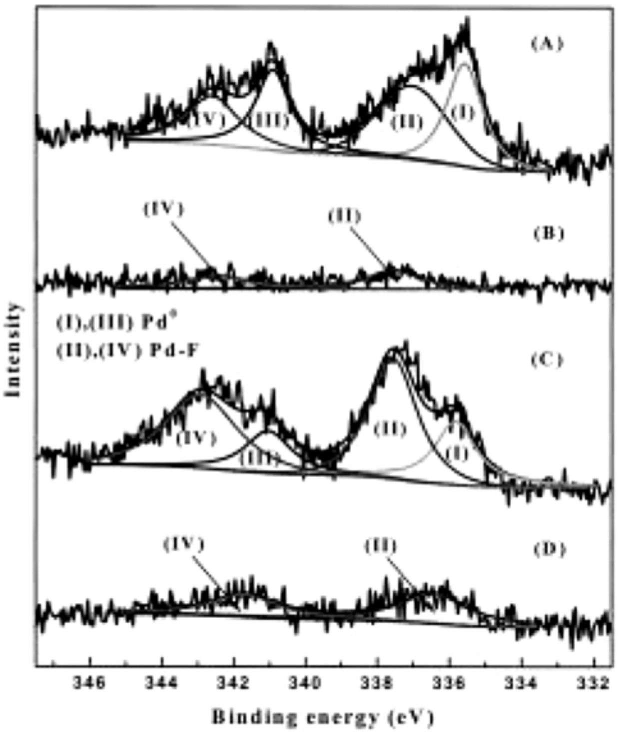


**Fig. 9. XPS spectra of Pd 3d$_{5/2}$ for the Pd/C and Pd-Ru/C. A: Pd(1 wt%)/C catalyst before the reaction; B: Pd(1 wt%)/C catalyst after the reaction; C: Pd(1 wt%)-Ru(0.5 wt%)/C catalyst before the reaction; D: Pd(1 wt%)-Ru(0.5 wt%)/C catalyst after the reaction (Condition: amount of catalyst used=1 g, P=101.3 kPa, reaction temp.=320 °C (time on stream≈25 h), reduction temp.=450 °C (for 5 h), H$_2$/CFC-12 feed ratio=6).**

side-positioned Pd species, 335.83 eV, decreased after the hydrogenolysis. The peak was also observed in the monometallic and the bimetallic palladium catalyst after the reaction. These results indicate that the electron-deficient species found in the Pd $3d_{5/2}$ XPS spectra may be that of the Pd bound to fluorine.

Coq et al. [Coq et al., 1993] reported that halogens migrate to alumina and found the formation of Pd-C, but they failed to show the presence of Pd-F. However, in this research work the formation of Pd-F over all catalysts was identified by the XPS analysis.

## CONCLUSION

From the hydrogenolysis of CFC-12 over bimetallic palladium on the activated carbon catalysts, the following conclusions were obtained.

(1) The catalytic activity of the bimetallic palladium catalysts (Pd-Bi/C, Pd-Ru/C) was improved compared with that of the monometallic palladium catalyst. The bimetallic palladium catalysts showed much higher conversion rates (more than 99% of it was converted) than the monometallic palladium catalyst (<92%), and it was not significantly deactivated even at high temperatures (>320 °C), while the monometallic palladium catalyst was apparently deactivated as the reaction temperature increased.

(2) The results of TEM, XRD, XPS and $H_2$ chemisorption analyses showed that the sintering of the catalysts was markedly decreased by bimetallic components, such as Bi and Ru.

(3) The formation of Pd-F over the Pd/C catalyst was identified by XPS analysis in this research work.

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