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Deactivation of Pd/C catalysts in the hydrodechlorination of the chlorofluorocarbons CFC-115 and CFC-12

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ABSTRACT

The deactivation of Pd/C catalyst in the hydrodechlorination of the two chlorofluorocarbons $CClF_2$–CF_3 (CFC-115) and CF_2Cl_2 (CFC-12) into their corresponding hydrofluorocarbons CHF_2–CF_3 (HFC-125) and CF_2H_2 (HFC-32) has been systematically investigated. Besides Pd/C catalyst, Pd black was used as a model catalyst in order to exclude the effects of carbon support. The results show that Pd/C catalyst is more efficient for the catalytic hydrodechlorination of CFC-115 than that of CFC-12. From the XRD, TEM, and H_2-TPR characterizations, it can be concluded that the deactivation of Pd/C catalysts in the hydrodechlorination of CFC-115 at 673 K, a weight hourly space velocity (WHSV) of 2400 ml g^{-1}(catal.) h^{-1} and a H_2:CFC-115 molar ratio of 2 is mainly attributed to the sintering of the active species Pd particles while the catalyst deactivation in the hydrodechlorination of CFC-12 at 553 K, a WHSV of 1000 ml g^{-1}(catal.) h^{-1} and a H_2:CFC-12 molar ratio of 4 is due to the carbonaceous deposits. Additionally, the deactivation mechanisms of Pd/C catalysts in the two different hydrodechlorination reactions are discussed.

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1. Introduction

The production of ozone-depleting gases such as chlorofluorocarbons (CFCs) has been regulated under "Montreal protocol on substances that deplete the ozone layer" for many years [1–3]. Because hydrofluorocarbons (HFCs) contain no chlorine, they do not contribute to ozone depletion. Consequently, HFCs are not regulated by the Montreal protocol and currently used as substitutes for CFCs. An economical and yet sustainable route to produce HFCs is to insert a catalytic unit, in which CFCs can be converted to their corresponding HFCs, into existing processes for CFC production [4,5]. So far Pd/C has been considered to be the most promising catalyst in the hydrodechlorination due to its excellent activity of Pd species and the inertness of the support activated carbon which shows a good resistance to HCl and/or HF produced in the reaction [5–7].

However, the deactivation of Pd/C catalysts during the hydrodechlorination of CFCs has been found, and generally there are three probable mechanisms for the catalyst deactivation: sintering of Pd particles [8], coking [9–12], and Pd poisoning by chlorine [7,12–14]. The mechanism of the catalyst deactivation may be related to the type of hydrodechlorination. But, to the best of our knowledge, there is no comparison study on the deactivation of the same Pd/C catalyst used in different hydrodechlorination reactions.

In the current study, Pd/C catalyst has been used in the hydrodechlorination of CFC-115 and of CFC-12, respectively, a vast amount of which was produced and used in China before July 2007. The main focus is on investigating the deactivation of a self-developed Pd/C catalyst during the hydrodechlorination of CFC-115 and of CFC-12. Through a comparison study, the deactivation mechanisms will be discussed.

2. Experimental

2.1. Catalyst preparation

2.8 wt.% Pd/C was prepared by a conventional impregnation method with palladium chloride (A.R., Sinopharm Chemical Reagent Co. Ltd., China) as the Pd precursor and commercial activated carbon ($S_{BET} = 1055\ m^2\ g^{-1}$, $V_{total} = 0.50\ cm^3\ g^{-1}$, OVCLS Carbon, Calgon Carbon Corporation, USA) as the support. The filtered solid was first dried in an oven overnight at 323 K. Afterwards *ca.* 2 g of the dried sample was loaded in a fixed-bed reactor where was heated up to 673 K with a rise rate of 10 K/min in a nitrogen flow of 20 ml/min (a nitrogen purity of 99.999%) and then maintained at 673 K for 2 h. After the temperature was cooled down to room temperature, the N_2 flow was switched to a mixture flow

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containing 10 vol.% H_2 in N_2 with a total flow rate of 20 ml/min and then heated up to 623 K with a rise rate of 10 K/min and maintained at 623 K for 3 h. Finally, the temperature was cooled down to room temperature in a nitrogen flow of 20 ml/min.

Palladium black (average crystallite size: 10 nm, purity ≥ 99.9%, Shaanxi Kaida Chemical Engineering Co., Ltd., China) was used as-received as a model catalyst.

2.2. *Characterization*

The X-ray diffraction patterns of the fresh and used catalysts were collected on a Philips PW 3040/60 using CuK_α radiation (λ = 0.154 nm) and a step size of 0.033°. The voltage and current were 40 kV and 40 mA, respectively. The temperature-programmed reduction (TPR) experiments were conducted on a Micromeritics AutoChem II 2920 equipped with a TCD detector where the sample cell was loaded with *ca.* 50 mg of the catalyst powder. Prior to the TPR experiments, the sample was pretreated in an Ar flow of 30 ml/min at 573 K for 1 h and then cooled down to room temperature. Afterwards the sample was heated up to 973 K with a temperature ramp of 10 K/min in a mixture flow containing 10 vol.% H_2 in Ar with a total flow rate of 30 ml/min. The transmission electron microscopy (TEM) observations were preformed on a Tecnai G2 F30 S-Twin microscope operating at 200 kV. The samples were diluted in ethanol to give a 1:5 volume ratio and sonicated for 10 min. The ethanol suspension was dripped onto a Cu grid covered with a thin film of carbon.

2.3. *Hydrodechlorination*

The hydrodechlorination of CFC-115 and of CFC-12 was carried out in a fixed-bed reactor where 1.0 g of the catalyst was loaded. The inner diameter of the reactor was about 6 mm. Prior to the catalytic reaction, the catalyst bed was heated up to 623 K with a temperature ramp of 10 K/min in a nitrogen flow of 20 ml/min and then the N_2 flow was switched to a mixture flow containing 10 vol.% H_2 in N_2 with a total flow rate of 20 ml/min and maintained at 623 K for 3 h. After the temperature was set to the desired reaction temperature in a nitrogen flow of 20 ml/min, the N_2 flow was switched to a mixture flow of CFC-115 or CFC-12 and H_2 with a given molar ratio. The effluent gas from the outlet of the reactor was firstly bubbled through a scrubber with 0.5 mol/l NaOH solution to remove any HCl or HF formed during the reaction and then passed through a dry vessel filled with silica gel. The component concentrations of the effluent gas from the scrubber were analyzed using an on-line gas chromatograph-mass spectrometer (Agilent 7890/5975c-GC/MSD) equipped with a 60 m × 0.323 mm GS-GasPro column and a mass selective detector.

3. Results and discussion

3.1. *Hydrodechlorination of CFC-115*

In the hydrodechlorination of CFC-115 over the prepared Pd/C catalyst at 623 K, a weight hourly space velocity (WHSV) of 600 ml g^{-1}(catal.) h^{-1}, and a H_2:CFC-115 molar ratio of 2, the initial conversion of CFC-115 and the selectivity for HFC-125 are only about 60% and 93%, respectively (Fig. 1). Unexpectedly, after a reaction time-on-stream of 120 h, the conversion of CFC-115 is significantly enhanced. A CFC-115 conversion of 97% and a selectivity of 97% for HFC-125 over the developed Pd/C catalyst are achieved. Additionally, the only detected byproduct is CF_3–CH_3 (HFC-143a) with a low selectivity, which is also indicated in Fig. 1. Within a reaction time-on-stream of 300 h under the applied conditions, no decline of both conversion and selectivity is observed, implying that the industrial hydrodechlorination of CFC-115 into HFC-125 over the developed Pd/C catalyst is technically feasible.

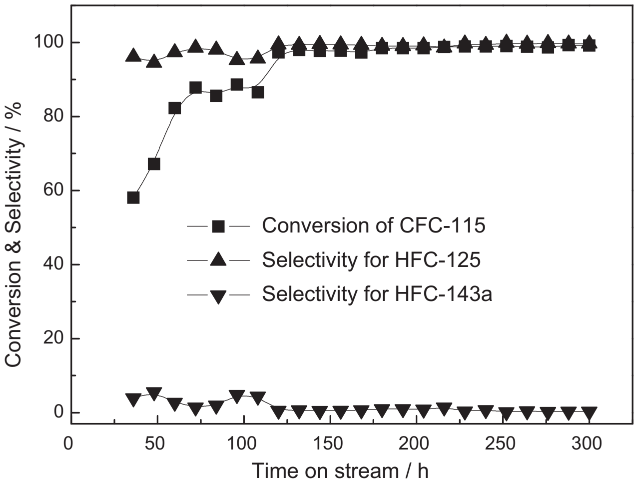

Fig. 1. Hydrodechlorination of CFC-115 over the Pd/C catalyst at 623 K, a total pressure of 1 bar, a weight hourly space velocity (WHSV) of 600 ml g^{-1}(catal.) h^{-1}, and a molar ratio of H_2 to CFC-115 of 2.

From the TEM images (Fig. 2a), one can see that the Pd particles are well dispersed on the support for the fresh Pd/C catalyst. The mean size of the Pd species is about 3.3 nm. After the catalyst used in the CFC-115 hydrodechlorination shown in Fig. 1, the Pd particle size becomes smaller, indicating that a re-dispersion of the Pd species takes place on the surface of the carbon support (Fig. 2b). In order to investigate the catalyst deactivation, the hydrodechlorination of CFC-115 was carried out at a higher temperature of 673 K, a higher WHSV of 2400 ml g^{-1}(catal.) h^{-1}, and a H_2:CFC-115 molar ratio of 2 (these results are not shown here). When the conversion of CFC-115 over the same Pd/C catalyst was declined to 50% of its initial one, the particle size of Pd in the catalyst was analyzed by the TEM technique. Fig. 2c shows the TEM observation, from which it is clearly seen that the Pd particle size in the deactivated catalyst becomes larger, and the mean particle size is about 6.5 nm. Additionally, some large Pd particles with a size of *ca.* 50 nm can be seen, as indicated by the arrow bars. The sintering of active species Pd particles leads to the deactivation of the Pd/C catalyst in the hydrodechlorination of CFC-115.

3.2. *Hydrodechlorination of CFC-12*

In the hydrodechlorination of CFC-12 over the same Pd/C catalyst at 553 K, a WHSV of 1000 ml g^{-1}(catal.) h^{-1}, and a H_2:CFC-12 molar ratio of 4, the initial conversion of CFC-12 is almost 100% even at a lower temperature of 553 K and the selectivity for the desired product HFC-32 is *ca.* 70% in company with the formation of the three byproducts CHCl-CF_2 (HCFC-22), methane, and ethane, see Fig. 3. It can be also seen that at a reaction time-on-steam of about 80 h, the activity starts decreasing and the selectivity for HFC-32 slightly goes down, indicating the occurrence of the catalyst deactivation.

After the Pd/C catalyst used in the hydrodechlorination of CFC-12, the TEM observation clearly shows that the Pd particles are still well dispersed on the carbon support and no aggregation or sintering takes place, see Fig. 4, in comparison with the TEM image of the fresh catalyst shown in Fig. 2a. This indicates that the deactivation of the Pd/C catalyst in the hydrodechlorination of CFC-12 is not due to sintering, different from the case in the hydrodechlorination of CFC-115.

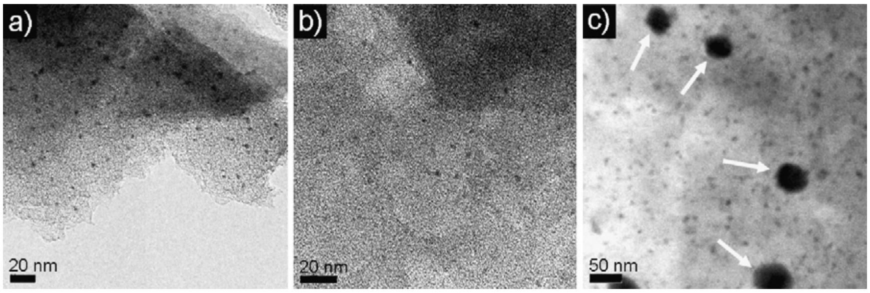

Fig. 2. TEM images of the Pd/C catalyst. (a) Fresh one, (b) used in the hydrodechlorination of CFC-115 without deactivation, and (c) deactivated catalyst after used in the hydrodechlorination of CFC-115.

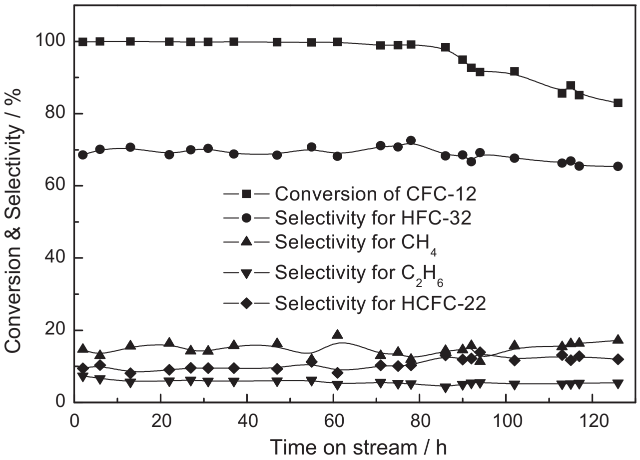

Fig. 3. Hydrodechlorination of CFC-12 over the Pd/C catalyst at 553 K, a total pressure of 1 bar, a WHSV of 1000 ml g^{-1}(catal.) h^{-1}, and a molar ratio of H_2 to CFC-12 of 15.

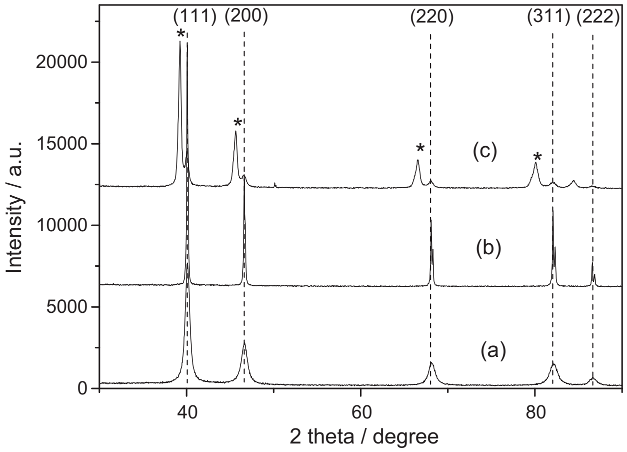

Fig. 5. XRD patterns of the Pd black. (a) Fresh one, (b) after deactivated in the hydrodechlorination of CFC-115, and (c) after deactivated in the hydrodechlorination of CFC-12.

3.3. XRD analysis of Pd black

To exclude the effect of carbon support, Pd black was used as the model catalyst for the hydrodechlorination at the same conditions as that over the Pd/C catalyst. The deactivation of the Pd black can easily take place in the hydrodechlorination of both CFC-115 and CFC-12. From the XRD patterns (Fig. 5a), five well-resolved diffraction peaks can be observed for the fresh Pd black. After the Pd black catalyst used in the hydrodechlorination of CFC-115, the five diffraction peaks are still preserved (Fig. 5b) but the diffraction peaks become sharper, indicating that the crystal size of Pd becomes larger. On the other hand, after the Pd black used in the hydrodechlorination of CFC-12, the shifts of the diffraction peaks to lower angles can be seen (Fig. 5c, marked with asterisks), which are attributed to the formation of palladium carbide [15,16]. Moreover, it should be pointed out that the carbon in the formed palladium carbide comes from the reactant.

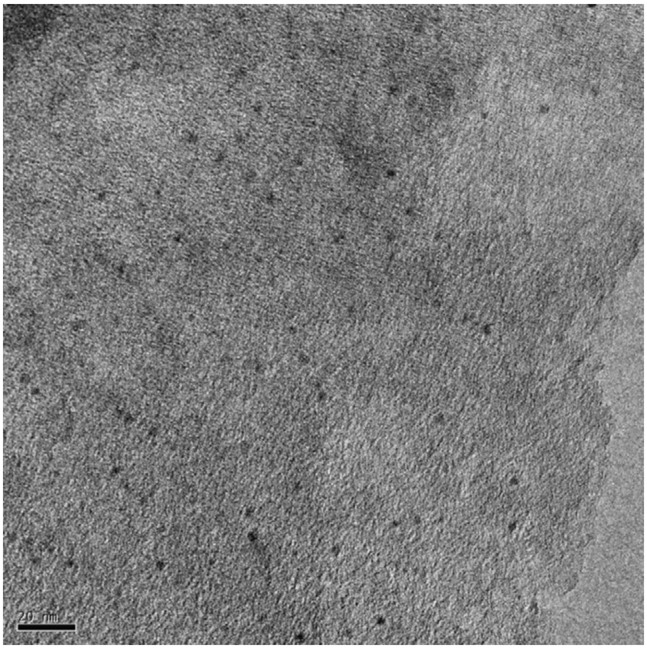

Fig. 4. TEM image of the deactivated Pd/C catalyst after used in the hydrodechlorination of CFC-12.

3.4. H_2-TPR results of Pd black

From the H_2-TPR profiles (Fig. 6), the fresh Pd black shows an evolution of hydrogen at about 360 K, attributed to the formed palladium hydride. For the catalyst deactivated in the hydrodechlorination of CFC-115, the evolution of hydrogen shifts to a higher temperature of about 368 K. This accounts for the enlargement of the Pd particle size. In contrast, for the catalyst deactivated in the hydrodechlorination of CFC-12, besides the evolution of hydrogen, a consumption of hydrogen at temperatures between 600 and 900 K appears. This broad peak could be ascribed to the consumption of hydrogen because of the reduction of the formed palladium carbide by hydrogen as well as of the deposited carbonaceous materials reacted with hydrogen [16].

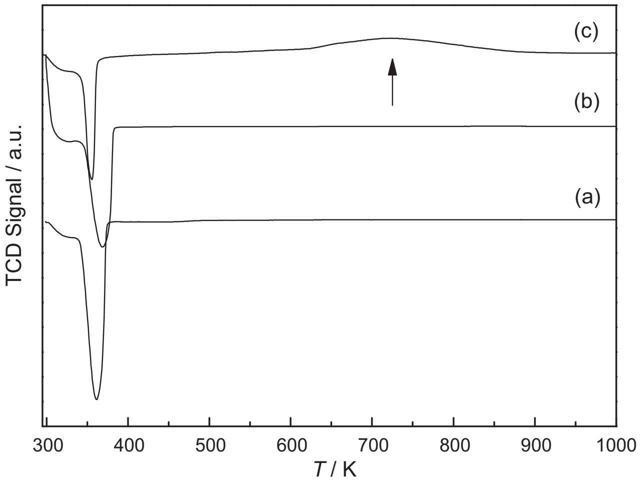

Fig. 6. H_2-TPR profiles of the Pd black. (a) Fresh one, (b) after deactivated in the hydrodechlorination of CFC-115, and (c) after deactivated in the hydrodechlorination of CFC-12.

3.5. Deactivation mechanisms of Pd/C in the hydrodechlorination

Generally, in the case of hydrodechlorination over Pd supported catalysts, the deactivation could be due to the carbonaceous deposits, sintering of the active phase, loss of active phase, and poisoning of the active phase [17].

In the current study, no palladium carbide is formed after either Pd/C or Pd black catalysts used in the hydrodechlorination of CFC-115, confirmed by the XRD and TPR characterizations. From the TEM characterization of the fresh and deactivated catalysts, it can be concluded that the sintering of Pd particles results in the deactivation of Pd/C in the hydrodechlorination of CFC-115, which is in agreement with the observation by Moon et al. [18].

After the Pd/C catalyst used in the hydrodechlorination of CFC-12, the TEM observation shows that the sintering of the active species Pd particles does not take place. On the other hand, palladium carbide and/or carbonaceous materials are formed after the Pd/C or Pd black catalyst used in the hydrodechlorination of CFC-12. van de Sandt et al. [16] reported that the formed palladium carbide could play a promotion role in the hydrodechlorination of CFC-12. However, the current study shows that the catalyst deactivation is always accompanied with the formation of palladium carbide, whatever the Pd/C or Pd black is used. Moreover, the BET surface area, especially the microporous surface area, of the deactivated Pd/C catalyst after used in the hydrodechlorination of CFC-12 is dramatically decreased, compared to that for the fresh catalyst, indicating the carbonaceous deposits.

It has been reported that in the hydrodechlorination of CFC-12, $^*CF_2$ radical could be the most abundant surface intermediate [19,20]. The desorption of $^*CF_2$ assisted with hydrogen would give HFC-32 and the further surface reaction of the formed radicals with hydrogen could finally lead to the formation of CH_4 and even C_2H_6 as byproducts. In addition, the ratio of the desorption rate to the surface reaction rate could determine the productivity of the desired product HFC-32. However, the deep surface reaction between the formed radicals could lead to the carbonaceous deposits as well as to the formation of palladium carbide, resulting in the catalyst deactivation [8]. While in the hydrodechlorination of CFC-115, the desorption rate of the assumed surface intermediate $^*CF_2{-}CF_3$ assisted with hydrogen could be much faster than the further surface reaction rate between the surface intermediates. Consequently, the carbonaceous deposits hardly take place.

4. Conclusions

The deactivation of Pd/C and Pd black catalysts in the hydrodechlorination of CFC-115 and of CFC-12 has been investigated. The results show that the sintering of Pd particles leads to the deactivation of the Pd/C catalyst in the hydrodechlorination of CFC-115 while the carbonaceous deposits and the formation of palladium carbide are the causes for the catalyst deactivation in the hydrodechlorination of CFC-12.

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