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Hydrodechlorination of Dichlorodifluoromethane (CFC-12) on Silica-Supported Palladium and Palladium-Gold Catalysts

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Silica-supported palladium and palladium-gold catalysts were screened in the reaction of dichlorodifluoromethane with dihydrogen at 180°C. The Au-containing sample appeared superior as far as the selectivity towards difluoromethane (desired reaction product) is concerned (95% *vs.* ~30% for Pd/SiO_2). A comparative X-ray diffraction study of the catalysts, before and after reaction, confirmed our earlier findings that during the hydrodechlorination massive amounts of carbon originated from CCl_2F_2 dissolve in palladium. However, a similar conclusion cannot be drawn from XRD studies of the Pd-Au/SiO_2 catalyst, because upon entering Pd bulk both gold and carbon may produce analogous shifts of the XRD reflections. For that reason, temperature programmed hydrogenation of carbon deposited in the Pd and a Pd-Au catalyst was used. In contrast to the behaviour of monometallic Pd/SiO_2, only insignificant quantity of carbon was found in the bimetallic Pd-Au/SiO_2 sample subjected to hydrodechlorination. This result supports the idea that a complete hydrodehalogenation of CCl_2F_2 to methane would occur *via* bare carbon adspecies. Thus, one can associate a superior catalytic behaviour of Pd-Au alloy catalysts (selectivity to CH_2F_2 ~95%) with a low abundance of C_1 adspecies.

Key words: dichlorodifluoromethane, catalytic hydrodechlorination, Pd/SiO_2, Pd-Au/SiO_2, carbon removal after reaction, temperature-programmed hydrogen treatment (TPHT), X-ray diffraction (XRD)

Recently we investigated catalytic hydrodechlorination of dichlorodifluoromethane (CFC-12) over a variety of supported palladium-based catalysts [1–8]. Among them special attention was paid to bimetallic Pd-Au catalysts. They appeared exceptional, because very significant enhancement of the selectivity towards difluoromethane (desired reaction product) was achieved for palladium catalyst modified with gold (from ~40% for pure Pd up to 95% for $Pd_{0.60}Au_{0.40}$, Ref. [5]). It should be stressed that such a pronounced synergistic effect could only be obtained when a high degree of mixing between supported Pd and Au was attained [5–8].

In the course of hydrodechlorination, carbon from the molecule of CCl_2F_2 dissolves in palladium [1–11]. Recent work [12] shows that a substantial carbonization takes place at a very early stage of the reaction, when also most important changes in the catalytic behaviour occur. It is known that carbon dissolution in palladium is accompanied by the increase the lattice constant (from ~0.389 nm for Pd up to ~0.399 nm for $PdC_{0.13}$, [13,14]) and bulk carbonization of Pd can be conveniently monitored by X-ray diffraction [8]. However, in the case of possible carbonization of bimetallic

Pd-Au catalysts, such an analysis is problematical. An observed downward shift in the diffraction spectrum would be produced not only by carbon incorporation but also by some changes in the phase composition of Pd-Au bimetal (*e.g.* some phase segregation). The introduction of both carbon and gold to palladium causes noticeable increase in the lattice parameter. In other words, the XRD study of monometallic Pd catalysts subjected to hydrodechlorination should determine the extent of carbiding, whereas such unambiguous tests would not be performed in bimetallic Pd-Au catalysts. As a matter of fact, it is difficult to judge whether any shift in the position of XRD reflections is affected by Pd-Au or Pd-C intermixing effects.

In this work we look at a difference in carbon retention in palladium catalysts doped with gold. Two relevant issues should be considered. First, as it has been mentioned the XRD would give here a rather inconclusive information. Therefore, we applied the Temperature Programmed Hydrogenation (TPH) of carbon present in spent (*i.e.* subjected to reaction) catalysts. It was hoped that the estimation of carbon content in Pd-Au catalysts should allow a more close re-inspection of XRD spectra of these materials, because the shift in XRD reflection caused by carbon doping should be estimated. Then, the degree of Pd-Au alloying in working catalysts could be easily assessed. Second, any difference in the amount of carbon retained in Pd and Pd-Au catalysts would give some information on the reaction mechanism of hydrodechlorination, especially why the gold dopant results in a pronounced increase in the selectivity towards CH_2F_2.

EXPERIMENTAL

Two silica-supported catalysts were selected for investigation: 2 wt. Pd/SiO_2 and 2.7 wt.% $Pd_{0.60}Au_{0.40}/SiO_2$ (indexes indicate atomic fractions of Pd and Au, respectively, in the metallic phase). Their preparation, pretreatment and characterization by H_2 chemisorption, X-ray diffraction and temperature-programmed (hydride) decomposition studies were described in [12]. Briefly, the monometallic Pd/SiO_2 catalyst was prepared by an incipient wetness impregnation of silica gel (Davison 62, 75–120 mesh, washed with diluted HCl and redistilled water) with an aqueous solution of $PdCl_2$. The $Pd-Au/SiO_2$ catalyst was prepared by direct redox reduction method [15]. Specifically, gold (from an aqueous solution of ammonium chloroaurate) was deposited onto prereduced 2 wt.% Pd/SiO_2. Palladium dispersion (as the H/Pd ratio), measured by hydrogen chemisorption at 70°C was 0.36 for 2 wt.% Pd/SiO_2 and 0.003 for 2.7 wt.% $Pd_{0.60}Au_{0.40}$. The temperature-programmed hydride decomposition and XRD methods revealed a high degree of Pd-Au alloying in the latter catalyst [12]. The reaction of CCl_2F_2 (purity 99.9%) with dihydrogen (99.9%, further purified by MnO/SiO_2) was conducted on both catalysts at 180°C, in a flow system, described elsewhere [1,2,5]. The catalyst performance was stabilized during ~3 h of time-on-stream (TOS). Steady state was defined as a change in conversion of less than 0.1% at a 100 min TOS and a change in product selectivities less than 1% at a 100 min TOS.

After kinetic experiments the catalysts were further investigated by temperature-programmed hydrogen treatment (TPHT) in order to determine species, which can be removed by hydrogen from used catalysts. Progress of TPHT runs, using a 30% H_2/He flow (25 cm^3/min) and a 10°C/min ramp, was followed by a quadrupole mass spectrometer (Dycor-Ametek M200, Pittsburgh, PA). Several masses were monitored during the experiment, namely, $m/z = 2$ (for H_2), 4 (for He), 15, 16 (both for CH_4), 18 (H_2O), 36, 38 (both for HCl), 50 and 85 (both for CCl_2F_2). Major changes in the mass evolution were detected only for $m/z = 15$ and 16, which are suggestive of methane formation via hydrogenation of carbon species left on the catalysts after the reaction.

RESULTS AND DISCUSSION

We used silica-supported Pd and Pd-Au catalysts, although one of inevitable products of CCl_2F_2 hydrodehalogenation is HF, which is detrimental to silica. However, since our approach was to employ the X-ray diffraction and temperature programmed hydrogen treatment of tested Pd-based catalysts, the use of other supports, like alumina or carbon, would not be considered. XRD reflections from alumina overlap the respective reflections from palladium, complicating the phase analysis. In the case of carbon, the temperature-programmed hydrogenation of used catalysts would not differentiate between deposited and support-originated carbon. Use of silica does not suffer the aforementioned problems. In addition, in order to reduce a possible corrosion of the silica support, the kinetic experiments were limited to ~3 h time. Advantageously, such reaction duration led to a steady-state (see Experimental).

The results of kinetic screening of Pd/SiO_2 and $Pd\text{-}Au/SiO_2$ catalysts are shown in Fig. 1. Stable catalyst performance was achieved after two hours of time on stream. The monometallic catalyst showed a higher activity (per g_{cat}) than $Pd\text{-}Au/SiO_2$. On the other hand, the bimetallic sample displayed a superior selectivity (~95%) towards CH_2F_2, which is a desired reaction product (as a potential substitute for ozone-depleting CCl_2F_2). In the case of 2 wt.% Pd/SiO_2 methane was the predominating product (~70%). The remaining (minor) products like $CHClF_2$, CH_2ClF, $CClF_3$ made less than 2% of all the products.

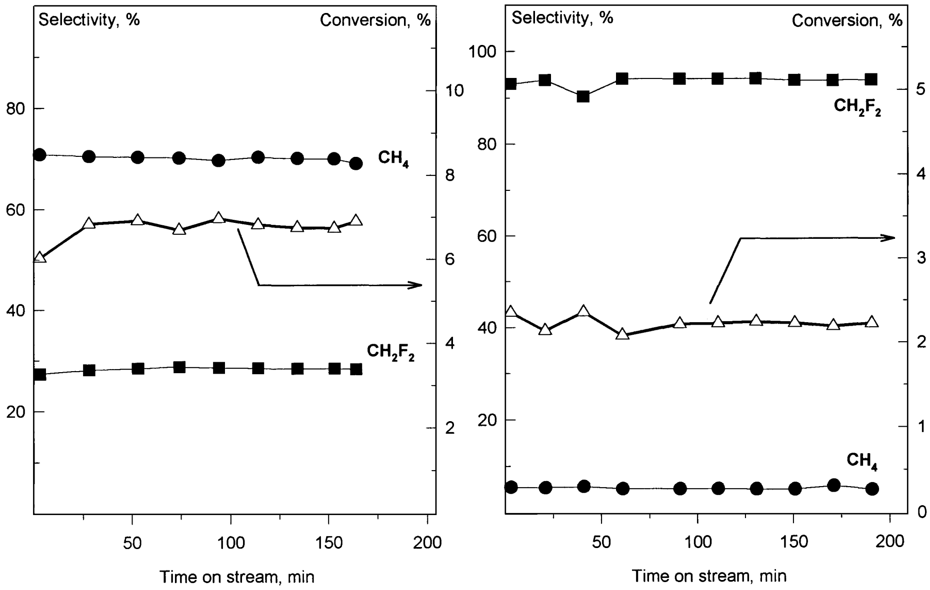

Figure 1. Time-course of CCl_2F_2 hydrodechlorination at 180°C: left section – 2 wt.% Pd/SiO_2 (0.164 g), right section – 2.7 wt.% $Pd_{0.60}Au_{0.40}/SiO_2$ (0.278 g). Conversion (triangles) and selectivities towards major products: methane (circles) and difluoromethane (squares) are indicated.

Characterization of freshly reduced and spent catalysts was carried out by X-ray diffraction. Fig. 2 presents the XRD profiles of both catalysts prior to and after the hydrodechlorination tests. It is seen that there is a great difference between the XRD spectra of the fresh and spent Pd/SiO_2 samples. Clearly, the reaction of CCl_2F_2 generates a new diffraction peak, shifted towards lower diffraction angles compared to the (111) reflection of Pd. This indicates a partial transformation of palladium to a Pd-C solid solution [13,14], the phenomenon being commonly observed in studies of the Pd catalysts subjected to hydrodechlorination of carbon-containing compounds [1–11]. In contrast, the XRD profile from the Pd-Au/SiO_2 suffers from very insignificant changes. Likewise, the XRD profile after the temperature programmed hydrogen treatment (used for coke removal after the reaction) is not much changed compared to the previous two XRD spectra. However, both Au and C, when alloyed with palladium, cause a similar shift in the XRD reflections. Hence, the XRD examination cannot answer the question of possible carbonization of the Pd-Au catalyst in the course of CCl_2F_2 hydrodechlorination.

The results of temperature programmed hydrogen treatment (TPHT) studies are presented in Fig. 3. It is clear from this figure that much more methane is produced by the monometallic Pd/SiO_2 catalyst, than by bimetallic Pd-Au/SiO_2. This means that

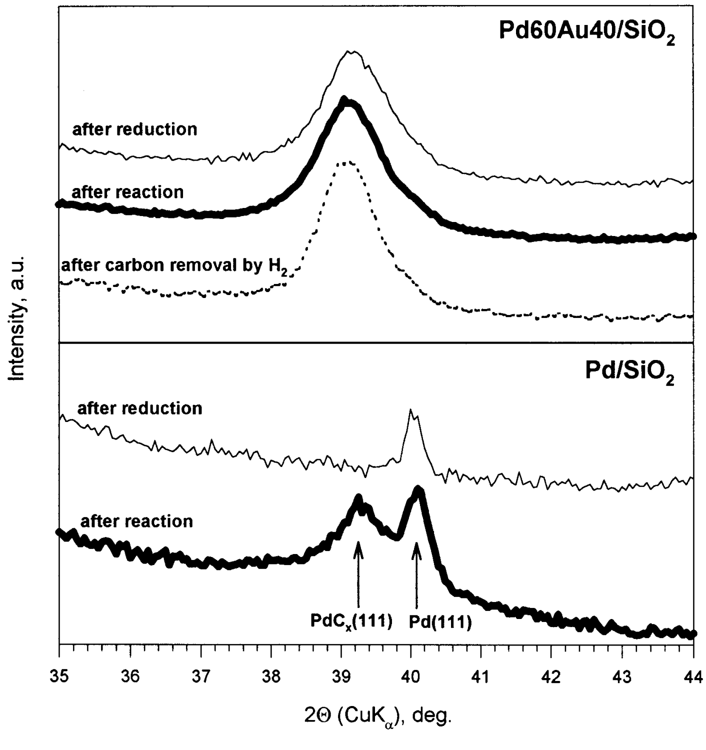

Figure 2. XRD profiles of silica-supported Pd and Pd-Au catalysts, before (thin lines) and after reaction (thick lines). Additionally, the XRD profile for the PdAu/SiO_2 catalysts after temperature programmed hydrogen treatment is shown (dotted line).

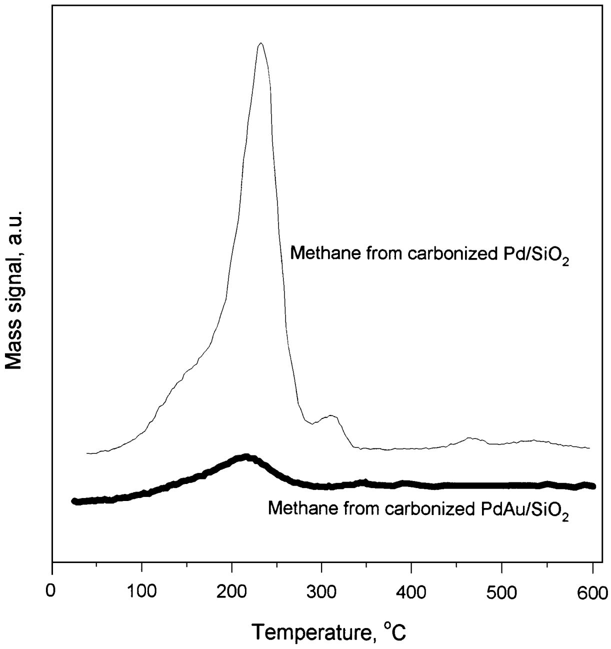

Figure 3. Temperature-programmed hydrogen treatment (TPHT) of 2 wt.% Pd/SiO$_2$ (thin line) and 2.7 wt.% Pd$_{0.60}$Au$_{0.40}$/SiO$_2$ (thick line) catalysts, which were subjected to CCl$_2$F$_2$ hydrodechlorination. M/z 15 was selected for presentation, because methane liberation observed by monitoring m/z 16 is somewhat misrepresented due to evolution of water.

in the latter case the catalyst picks up much larger amounts of carbon in the course of CCl$_2$F$_2$ hydrodechlorination. Only negligible amounts of carbon are found in the 2.7 wt.% Pd$_{0.60}$Au$_{0.40}$/SiO$_2$ catalyst. It should be kept in mind that this bimetallic catalyst showed a much higher selectivity towards CH$_2$F$_2$ (~95%) than the monometallic Pd/SiO$_2$ (~30%). Since CH$_4$ and CH$_2$F$_2$ contribute to >98% of the reaction products, an excessive formation of one of them strongly suppress the selectivity towards the other one. In this case, large amounts of produced methane (undesired product) are responsible for the low selectivity to CH$_2$F$_2$. On the other hand, as was previously suggested [1,2,12], the methane formation from CCl$_2$F$_2$ may result, at least in part, from an easy hydrogenation of bare carbon (C$_1$) species present in the palladium catalyst. In the case of Pd-Au catalysts, the presence of mixed Pd-Au ensembles reduces the surface (and bulk) carbiding. In addition, the Pd-Au alloying weakens the binding of CF$_2$ adcarbenes, which are commonly accepted to be the reaction intermediates [1–11,16,17]. This would be an advantageous factor in avoiding undesirable defluorination to C$_1$ adspecies, and, in effect, the methane formation. Finally, our finding that only negligible amounts of carbon are retained in the 2.7 wt.% Pd$_{0.60}$Au$_{0.40}$/SiO$_2$ indicates that the XRD pattern of the post-reaction sample (shown as a thick line in the upper part of Fig. 2) convincingly reflects the composition of the Pd-Au bimetal in this catalyst.

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