

# Pd-Re/Al<sub>2</sub>O<sub>3</sub>: Characterization and Catalytic Activity in Hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub>

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A series of alumina-supported Pd-Re catalysts were prepared and characterized using X-ray diffraction, chemisorption, and temperature-programmed methods. A different stability of Pd(-Re)-hydride phases was exploited; i.e., the amount and decomposition temperatures of the  $\beta$ -hydride phases for different Pd<sub>x</sub>Re<sub>1-x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were found strongly correlated with  $x$ , suggesting a considerable extent of interaction between Pd and Re in reduced Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. The results from other characterization methods render a similar conclusion. The Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts were tested in the reaction of hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub>. Rhenium appeared inactive in this reaction. Adding Re to Pd/Al<sub>2</sub>O<sub>3</sub> introduces substantial changes in the catalytic behaviour. All Pd-Re bimetallic samples strongly deactivated with time-on-stream, whereas the activity of Pd/Al<sub>2</sub>O<sub>3</sub>, after an initial increase, was fairly stable. Selectivity patterns for the bimetallic samples also differed from that of palladium, showing the increase in the selectivity to methane during the stabilization period. The steady-state activity of Pd-rich (up to 25 at% Re) bimetallic samples was much lower than that of Pd; however, it slightly increased with further Re addition, reaching a mild maximum at 50 at% Re. Such an activity pattern resembles very much the behaviour of alumina-supported Pt-Re catalysts in hydrocarbon conversions. The selectivity towards CH<sub>2</sub>F<sub>2</sub> changed only slightly with the bimetallic composition. X-ray diffraction indicated the presence of carbon dissolved in Pd or Pd-rich phases in spent Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. Differences in lattice parameter of the carbonized phases depended on the nominal composition of Pd-Re, verifying a considerable extent of Pd-Re mixing in the supported catalysts. The results of catalytic screening are compatible with such a conclusion. © 1998 Academic Press

## INTRODUCTION

Catalytic removal of chlorine from organic compounds has recently attracted increasing interest. A special case of this very important technological and environmental issue is the hydrodechlorination of chlorofluorocarbons (CFCs) (1, 2). The necessary phase-out of these ozone-depleting compounds, expressed in the Montreal Protocol, and the use of hydrochlorofluorocarbons (HCFCs) and/or hydrofluorocarbons (HFCs) instead of CFCs launched a

more intensive work on catalytic hydrodechlorination of CFCs. Palladium is unique among the catalytic metals for its activity and selectivity in CFCs hydrodechlorinations, and as a consequence most fundamental work on these reactions has been done with this metal (3–10). Coq and his colleagues (4, 5) thoroughly studied the reaction kinetics of CCl<sub>2</sub>F<sub>2</sub> (CFC-12) hydrodechlorination by palladium supported on different carriers: graphite, alumina, AlF<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, and ZrF<sub>4</sub>. Similarly, the Delft group investigated the catalytic behaviour of Pd/C catalyst (6–9). Choice of support (AlF<sub>3</sub> and carbon appear better than other carriers (4, 5, 11)), metal dispersion (4, 9, 10), catalyst pretreatment and reaction conditions (H<sub>2</sub>/CFC ratio, temperature (3–9)) were found to be important factors in regulating the course of hydrodechlorination. Doping the active phase, i.e. palladium, with another element offers an additional possibility for modifying the activity and selectivity in CFC hydrodechlorination. Various patents confirm such a possibility (12), although fundamental research in this respect is rather scarce (5, 13–15), where palladium was modified with K, Fe, Co, Ag (13), Al, Ti, Zr (5), and Bi, Tl (14, 15).

Although the catalytic behaviour of a palladium catalyst in CFC hydrodechlorination is superior to other supported metals, one may still wish to improve its performance. This may be achieved by matrix isolation of the active metal (Pd) as discrete ensembles by alloying within an inactive metal. The dilution of active Pd sites would alter the rates of different reaction steps, leading to different products, e.g. CH<sub>2</sub>F<sub>2</sub> and CH<sub>4</sub> in CCl<sub>2</sub>F<sub>2</sub> hydrogenolysis. Our choice of rhenium as a metallic modifier of a palladium catalyst was dictated by several reasons. Van de Sandt (16) has recently found that Re is inactive in the reaction of CCl<sub>2</sub>F<sub>2</sub> with H<sub>2</sub>. This result is in line with an earlier finding that rhenium is a very poor catalyst (i.e., even poorer than gold) in hydrodechlorination of methyl chloride (17). Another reason which motivated us to use Re was the fact that a lot is known about how to prepare bimetallic clusters of Re with Pd (or Pt). A simple procedure seems to maintain the hydroxylated surface of a support, facilitating an easy migration of an oxidized rhenium precursor to Pd (or Pt) particles. In an opposite case, i.e. after an intensive support

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drying, oxidized rhenium species would be strongly bound to exposed  $\text{Al}^{3+}$  Lewis acid sites present on the surface of dehydroxylated  $\gamma\text{-Al}_2\text{O}_3$ , and subsequent reduction does not lead to the formation of well-mixed bimetallic Pd(Pt)-Re clusters (18–21). However, it must be recognized that Pd-Re is a difficult system, with a miscibility gap, which, in addition, has only been occasionally studied. Thus, existing data on a solid Pd-Re system (thermodynamics, crystallographic structure) (22) still wait for their verification and/or provision of missing information.

## EXPERIMENTAL

### Catalyst Preparation

The Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts were prepared by successive incipient wetness impregnation of alumina (Alumina Catalyst Shell S618, 240  $\text{m}^2/\text{g}$ , pore volume 0.8  $\text{cm}^3/\text{g}$ , 120–140 mesh, acid washed, and calcined at 550°C for 3 h). First, the alumina was impregnated with a solution of  $\text{Pd}(\text{NO}_3)_2$  to obtain 2 wt% metal loading. The solution of  $\text{Pd}(\text{NO}_3)_2$  was prepared by dissolving Pd wire (specpure from Johnson Matthey, diameter of 0.2 mm) in concentrated  $\text{HNO}_3$  (analytical reagent from POCh, Gliwice, Poland). During impregnation and preliminary drying with infrared lamps a good mixing was assured by the rotary motion of a beaker containing catalyst precursor components. Then, the solid was further dried in an air oven overnight at 90°C. Next, it was precalcined in flowing air (commercial grade purified over zeolite 5A) in a fluidized bed regime ramping the temperature from room temperature (RT) to 350°C at 4°C/min, and kept at this temperature for 2 h. Next, the catalyst was prereduced in flow of  $\text{H}_2$  (prepurified over MnO/SiO<sub>2</sub> trap), maintaining a fluidized bed regime and ramping the temperature from RT to 450°C (at 4°C/min)

and kept at 450°C for 2 h. Finally, the catalyst was purged from  $\text{H}_2$  and cooled down in helium flow to RT, and passivated by several air injections.

Portions of the prereduced and passivated Pd/ $\text{Al}_2\text{O}_3$  were used in preparation of bimetallic Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts. Each portion of 2 wt% Pd/ $\text{Al}_2\text{O}_3$  was impregnated (in the rotating beaker) with an appropriate amount of an aqueous solution of  $\text{NH}_4\text{ReO}_4$  (Puratronic from Alfa Johnson Matthey GmbH, Karlsruhe, Lot S20903, dissolved in redistilled water), dried overnight at 120°C, and left for a sufficient period to pick up moisture from the atmosphere. Finally, the Pd-Re/ $\text{Al}_2\text{O}_3$  were transferred to glass stoppered bottles and kept in a desiccator.

Also, 2 wt% Re/ $\gamma\text{-Al}_2\text{O}_3$  was prepared in a similar manner; i.e. the alumina was impregnated with an appropriate amount of an aqueous solution of  $\text{NH}_4\text{ReO}_4$ . Table 1 shows weight percentages and atomic ratios of Pd and Re in all catalysts studied in this work.

### Catalyst Characterization

Temperature-programmed reduction experiments were performed in a standard apparatus with a Gow-Mac thermal conductivity detector and data acquisition by a micro-computer (23). In order to obtain a good degree of Pd-Re mixing, we wished to avoid the precalcination step before the reduction. As mentioned in the Introduction, precalcination at higher temperatures was found detrimental in the process of formation of bimetallic Pd(Pt)-Re clusters (upon further reduction of Pd(Pt)-Re/ $\text{Al}_2\text{O}_3$ ). In TPR experiments, the temperature of a catalyst sample (0.25 g) was ramped from RT to 400°C at 8°C/min, in a flow of a 10%  $\text{H}_2/\text{Ar}$  (purified by passing over MnO/SiO<sub>2</sub>). After collecting the TPR profile, the sample was kept in  $\text{H}_2/\text{Ar}$  flow at 400°C for 3 h. Such a procedure corresponded to the

TABLE 1  
Characterization of Pd-Re/ $\text{Al}_2\text{O}_3$  Catalysts

Catalyst designation <sup>a</sup>	Metal content		Gas uptake <sup>b</sup>		Gas uptake <sup>c</sup>		H/Pd <sup>d</sup> from DTPR
	Pd, wt%	Re, wt%	H/Pd	CO/Pd	H/(Pd + Re)	CO/(Pd + Re)	
Pd	2.0	—	0.137	0.097	0.137	0.097	0.43
Pd <sub>0.95</sub> Re <sub>0.05</sub>	2.0	0.18	0.118	0.098	0.112	0.093	0.39
Pd <sub>0.90</sub> Re <sub>0.10</sub>	1.99	0.39	0.096	0.101	0.086	0.091	0.36
Pd <sub>0.75</sub> Re <sub>0.25</sub>	1.98	1.15	0.068	0.101	0.051	0.076	0.31
Pd <sub>0.50</sub> Re <sub>0.50</sub>	1.93	3.38	0.050	0.108	0.025	0.054	0.25
Pd <sub>0.25</sub> Re <sub>0.75</sub>	1.81	9.5	0.074	0.205	0.018 <sub>5</sub>	0.051	0.17
Re	—	2.0	0.00 <sub>5</sub>	0.027	0.00 <sub>5</sub>	0.027	—

Note. Nominal weight percentages, metal fraction exposed from  $\text{H}_2$  and CO chemisorptions, and H/Pd ratios from  $\beta\text{-Pd}(\text{-Re})\text{H}$  decompositions calculated from DTPR profiles (Fig. 4).

<sup>a</sup> In the catalyst code, Pd<sub>x</sub>Re<sub>1-x</sub>, x denotes atomic fraction of Pd calculated from the nominal composition of the Pd-Re material in a catalyst.

<sup>b</sup> Irreversible adsorption of  $\text{H}_2$  (at 70°C) and CO (at 20°C) calculated per Pd atom in a catalyst.

<sup>c</sup> As in <sup>b</sup>, but calculated per each metal atom in Pd-Re bimetal.

<sup>d</sup> The amount of hydrogen liberated from decomposition of  $\beta\text{-Pd}(\text{-Re})\text{H}$  phases during DTPR runs (Fig. 2b) calculated per one Pd atom.

pretreatment of Pd-Re catalysts before screening them in CCl<sub>2</sub>F<sub>2</sub> hydrodechlorination.

After TPR runs up to 400°C and reduction at 400°C for 3 h, the samples were cooled down to -50°C, and subsequent TPR runs, now up to 800°C, were performed. Since the sample had already been reduced, the aim of such a study was to monitor hydrogen evolution in the process of β-hydride decomposition. Another reason was to check whether or not hydrogen treatment at 400°C for 3 h leads to complete reduction of Pd-Re precursors. We shall further refer to these experiments as DTPR (difference temperature-programmed reduction).

The experiments of H<sub>2</sub> and CO chemisorption on Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts were performed in a pulse system, with Ar and He as carriers, respectively. To avoid formation of β-PdH, chemisorption of H<sub>2</sub> was carried out at 70°C, using low H<sub>2</sub> pressure. CO chemisorption was done at 20°C.

XRD experiments were performed on a standard Rigaku-Denki diffractometer using Ni-filtered CuKα radiation. An X-ray diffraction camera-gradientless reactor (24) was used for measurements in a controlled atmosphere. After reduction (at the same conditions as used before chemisorption or kinetic runs), samples were scanned by a step-by-step technique. Resulting diffraction profiles originating from the metal phase(s) were obtained by the method of subtraction of the alumina support background profile (25).

All spent (i.e., after kinetic experiments) Pd-Re/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were also investigated by XRD. In this case, the measurements were carried out *ex situ*, i.e. without using the XRD camera-reactor. As previously, the resulting diffraction profiles characteristic of the metal phase(s) were obtained by the method of subtraction of the alumina support background (with Al<sub>2</sub>O<sub>3</sub> pretreated at the conditions of hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub>).

#### Hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub>

The reaction of dichlorodifluoromethane (CFC-12, from Galco S.A., Belgium, purity 99.9%) with hydrogen (purified over MnO/SiO<sub>2</sub>) was conducted in a glass flow system under atmospheric pressure at 140–180°C. Feed partial pressures were 15 and 150 Torr (1 Torr = 133.3 N m<sup>-2</sup>) of dichlorodifluoromethane and hydrogen, respectively, in a helium carrier (also purified by MnO/SiO<sub>2</sub>). The flow of all gases was metered by MKS mass flow controllers and the overall flow rate of the reactant gas mixture was 100 ml/min. The reaction mixture leaving the reactor was introduced via stainless steel tubing onto a gas chromatograph (HP 5890 series II with FID) and analyzed using a 5% Fluorcol/carbopack column (3 m) from Supelco. The results of GC analysis were elaborated using HP Chemstation.

In order to adequately establish changes in a catalytic behaviour, a typical reaction run lasted ~24 h. The first period of reaction involved a 20-h passivation at 180°C.

During this time a catalyst was stabilized in a flow of the reaction mixture. Analyses of the reacting gas were made in 30-min intervals. After getting stable conversions and product distributions, i.e. after ~20 h of time-on-stream, the reaction temperature was being changed and the next experimental points collected. In order to avoid secondary reactions, the overall conversion was kept low, i.e. ≤10%.

## RESULTS

Table 1 shows the results of H<sub>2</sub> and CO chemisorption experiments conducted over the series of Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. It is seen that a gradual introduction of Re suppresses hydrogen uptake, and, simultaneously, increases the consumption of CO.

Figure 1 shows collected TPR profiles of all investigated catalysts. As expected, Re introduction into Pd/Al<sub>2</sub>O<sub>3</sub> causes a gradual increase of hydrogen consumption (positive peaks). Fairly sharp negative peaks indicate evolution of hydrogen from β-PdH decomposition (18, 26–29); they are more distinct for Pd and Pd-rich catalysts.

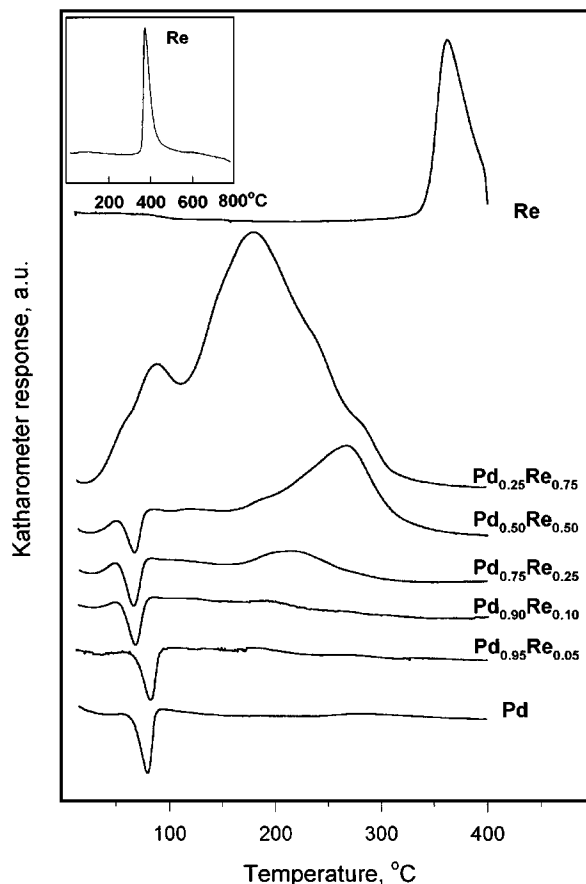


FIG. 1. TPR profiles of Pd-Re/Al<sub>2</sub>O<sub>3</sub> (experiments terminated at 400°C). Inset: complete TPR run for alumina-supported rhenium precursor.

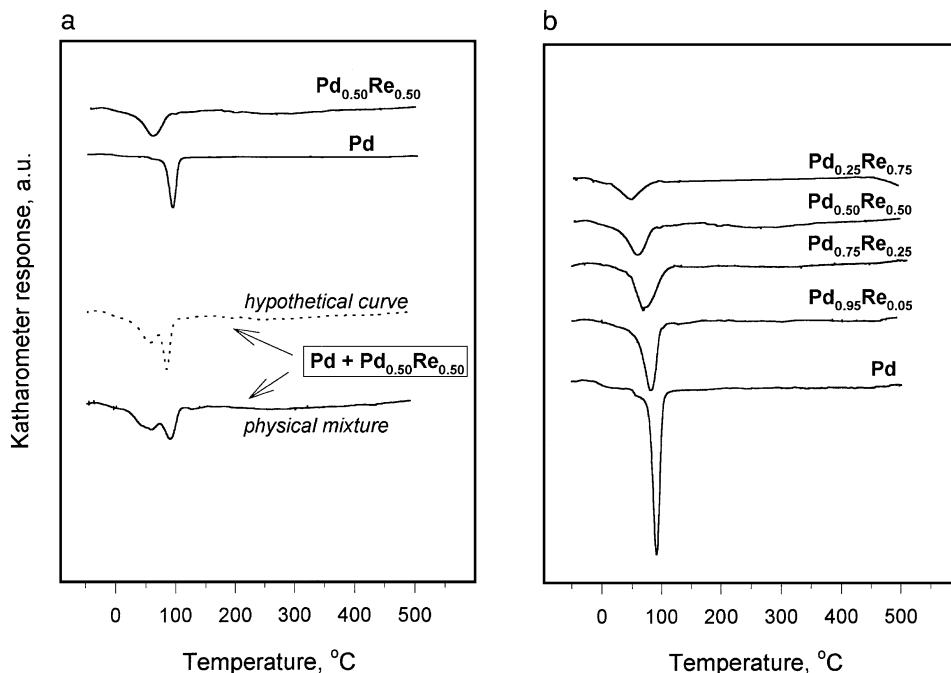


FIG. 2. (a) DTTPR (difference TPR, see text) profiles of alumina-supported  $\text{Pd}_{0.50}\text{Re}_{0.50}$ , Pd and a physical mixture of both catalysts. Dotted line represents the hypothetical DTTPR trace of the mixture, predicted from additive contributions from individual components; (b) DTTPR profiles of alumina-supported Pd and Pd-Re catalysts.

DTTPR runs (see Experimental) showed that prereduction of all samples (except  $\text{Re}/\text{Al}_2\text{O}_3$ ) at  $400^\circ\text{C}$  for 3 h leads to an entire reduction ( $\pm 5\%$ ). The Re precursor, as expected from the shape of its TPR peak in Fig. 1 and from a separately performed TPR experiment at up to  $800^\circ\text{C}$  (Fig. 1, inset) needed further reduction at  $400$ – $800^\circ\text{C}$  (DTTPR profile not shown). Another purpose of carrying out DTTPR runs was to examine changes in intensity, shape, and position of negative peaks indicating  $\beta$ -Pd(-Re)H decomposition. It was inferred, in line with Ziemecki *et al.* (18), that differences in stability of the  $\beta$ -phase caused by the incorporation of Re to Pd can be used in diagnosing the mutual interaction between Pd and Re (= extent of mixing). Figure 2a presents a basis for such expectations: different intensities and positions of the negative peaks for Pd and  $\text{Pd}_{0.50}\text{Re}_{0.50}$  samples are reproduced in the DTTPR profile of a mechanical mixture of these two catalysts. Figure 2b shows the presence of single negative  $\beta$ -hydride peaks, suggesting a better bimetal homogeneity than expected in the physical mixture of Pd and  $\text{Pd}_{0.50}\text{Re}_{0.50}$ . The amounts of hydrogen liberated during  $\beta$ -Pd(-Re)H decomposition calculated per one Pd atom are shown in last column of Table 1. It is thought that if Pd were not interacting with Re, these H/Pd values should not vary with the bimetal composition.

X-ray diffraction profiles of reduced Pd-Re/ $\text{Al}_2\text{O}_3$  are shown in Fig. 3. The overall picture is very complex, since alumina greatly contributes to the XRD spectrum (30, 31). In addition, the strongest Pd (111) reflection coincides

with Re (002). The fact that covalent radii of Pd and Re are similar (0.128 nm) would cause only modest changes in positions of the reflections characteristic of a fcc phase after an initial introduction of Re to Pd. At first glance, the XRD profiles of Pd,  $\text{Pd}_{0.95}\text{Re}_{0.05}$ ,  $\text{Pd}_{0.90}\text{Re}_{0.10}$ ,  $\text{Pd}_{0.75}\text{Re}_{0.25}$ , and  $\text{Pd}_{0.50}\text{Re}_{0.50}$  look very similar; the presence of Re (or Re-rich) hcp phase is evident only for  $\text{Pd}_{0.25}\text{Re}_{0.75}$  (Fig. 3).

Two reduced samples, Pd and  $\text{Pd}_{0.25}\text{Re}_{0.75}$ , cooled down in a hydrogen flow, were also investigated by XRD. Figure 4 shows the resulting XRD profiles. It is evident that larger changes (caused by the formation of the respective  $\beta$ -hydride phase) are better seen for Pd.

Samples of Pd-Re/ $\text{Al}_2\text{O}_3$  used in the reaction of  $\text{CCl}_2\text{F}_2$  hydrodechlorination were also investigated by XRD. A typical XRD profile, after subtracting the background from  $\text{Al}_2\text{O}_3$ , is shown in Fig. 5. The resulting diffraction pattern was decomposed into the sum of analytical Pearson VII-type functions by the method of least square fitting. Figure 5 displays shifts of basic fcc phase diffraction peaks (111 and 200) toward lower angles, indicating an increase in lattice parameter of the fcc phase. Table 2 shows the calculated lattice parameters of this new fcc phase; it is seen that the respective values depend on the nominal bimetal composition.

The results of catalytic screening of Pd-Re/ $\text{Al}_2\text{O}_3$  in  $\text{CCl}_2\text{F}_2$  hydrodechlorination are shown in Figs. 6 and 7 (time-on-stream behaviour) and Table 2 (steady-state values).

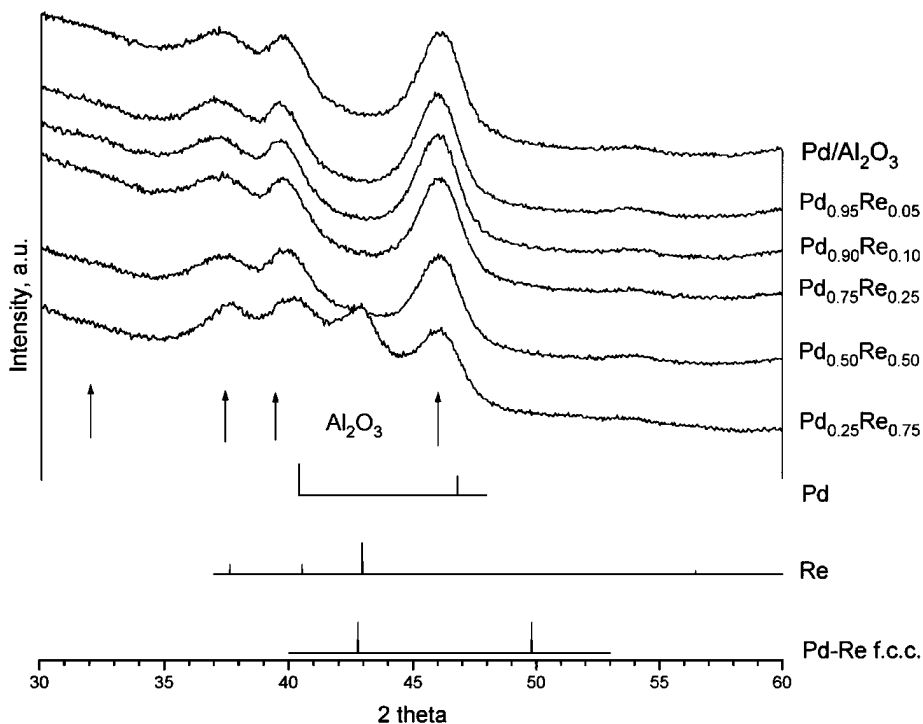


FIG. 3. XRD spectra of prereduced alumina-supported Pd and Pd-Re catalysts. Bottom histogram for fcc phase of Pd-Re is taken from Tylkina *et al.* (45).

## DISCUSSION

### *Temperature-Programmed Reduction and Chemisorption Study of Pd-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>*

Figure 1 shows TPR profiles of Pd-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst precursors. The appearance of fairly sharp negative peaks for all Pd-rich samples (up to 50 at% Re) manifests decomposition of  $\beta$ -hydride phases (18, 26–29). It should be recalled that the Pd/Al<sub>2</sub>O<sub>3</sub> precursor has been prereduced before introducing NH<sub>4</sub>ReO<sub>4</sub>. For Re-rich samples hydrogen consumption is high, especially for Pd<sub>0.25</sub>Re<sub>0.75</sub>. It should be said that Re loading in this catalyst is 4.75 times higher than in the Re/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 1). The reduction of the latter catalyst starts at  $\sim$ 350°C and is certainly not completed at 400°C (Fig. 1); Fig. 1 shows the course of a separate TPR experiment carried out up to 800°C. DTTPR experiments up to 800°C, showed that all samples, but Re, are entirely ( $\pm$ 5%) reduced after reduction at 400°C for 3 h. At these conditions, 2 wt% Re/Al<sub>2</sub>O<sub>3</sub> was reduced only in 75%.

The presence of negative peaks in DTTPR profiles showing decomposition of  $\beta$ -hydride phases will be discussed later.

The results of chemisorption measurements shown in Table 1 should be treated with some concern. Before discussing these data one should be aware of difficulties associated with the problem of determining the metal dispersion in Re-based catalysts. Hydrogen chemisorption, a generally accepted method in metal dispersion measure-

ments for supported platinum metals, is not easily permissible in the case of rhenium (32), because the amount of irreversibly chemisorbed hydrogen is too small and chemisorption stoichiometry is not very certain: H/Re<sub>s</sub> = 1 (33) or  $\frac{1}{2}$  (34). The first disadvantage complicates use of the pulse technique in measuring H<sub>2</sub> chemisorption on Re. Kubicka and Okal (35) found that after very careful reduction of Re/Al<sub>2</sub>O<sub>3</sub> at 550–800°C, hydrogen pulse chemisorption at 300°C produces proper metal dispersion data. So drastic experimental conditions were not acceptable by us. First, we wanted to avoid very high temperature reduction of alumina-supported catalysts, since such a pretreatment can lead to metal–alumina interactions (31, 36) and modify catalytic activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (37), due to the increase of Lewis acidity (38). Second, H<sub>2</sub> chemisorption at 300°C could not be useful for palladium-based catalysts: independent experiments with Pd-Re/Al<sub>2</sub>O<sub>3</sub> (not shown in the Results) demonstrated that the hydrogen uptake at 300°C is 4–5 times lower than at 70°C (a useful temperature for studying Pd catalysts (39–41)). Moreover, a vast majority of H<sub>2</sub> adsorbed at lower temperature is desorbed at 300°C in Ar flow. H<sub>2</sub> chemisorption experiments conducted at 70°C show that the addition of Re to the Pd precursor leads to a gradual decrease in hydrogen consumption, calculated in moles of H per one bulk Pd mole (Table 1). At the same time, CO chemisorption becomes more and more meaningful. Both facts suggest an interaction between Pd and Re, i.e. the formation of bimetallic Pd-Re clusters.

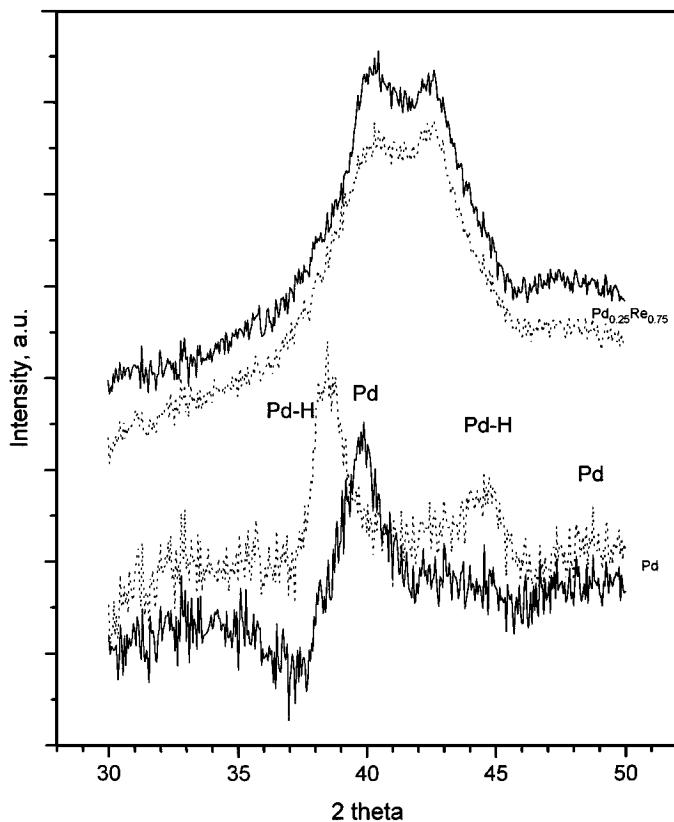


FIG. 4. XRD spectra, after alumina background subtraction, of Pd (bottom part) and  $\text{Pd}_{0.25}\text{Re}_{0.75}$  (top part) after reduction (solid line) and after cooldown to room temperature in  $\text{H}_2$  flow (dotted line). Fcc (111) and (200) reflections from the metal and hydride phases are indicated.

For calculation of turnover frequencies one needs reliable metal dispersion data. Table 1 shows a serious disagreement between the results of hydrogen and CO chemisorption. Engels and Lehmann (42) showed that BET surface areas of Pd-Re powders reduced at  $400^\circ\text{C}$  were correlated much better with CO sorption capacity than with  $\text{H}_2$  results. Thus, in calculation of reaction rates (Table 2 and Fig. 7) the TOF values are determined on the basis of  $\text{CO}/(\text{Pd} + \text{Re})$  ratios taken from Table 1.

TPR of palladium catalysts usually exhibits a characteristic, fairly sharp negative peak attributed to evolution of hydrogen in the phase transformation  $\beta\text{-PdH} \rightarrow \text{Pd} + \frac{1}{2}\text{H}_2$  (18, 26–29). Such a peak is quite well separable from very shallow (almost invisible) minimum indicating desorption of chemisorbed hydrogen (26). It should be recalled that the process takes place at a definite, not too low partial pressure of  $\text{H}_2$ , resulting from the composition of flowing  $\text{H}_2/\text{Ar}$  mixture (here, 10%  $\text{H}_2/\text{Ar}$ ). When one is working with supported Pd-based bimetallic catalysts, the process of easy formation/decomposition of  $\beta\text{-PdH}$ , and the known dependence of the extent of hydride formation on the degree of Pd alloying, offers an exceptional occasion to monitor alloying in supported Pd-based systems. Ziemecki *et al.* (18) em-

ployed this method for monitoring changes in Pd-Re/ $\text{Al}_2\text{O}_3$  induced by different pretreatments. The absence of Pd hydride decomposition recognized in TPR spectrum and its verification by an *in situ* XRD study clearly indicated interaction between Pd and Re, especially when supported on nondehydroxylated alumina (18). It should be stressed that the stability of the  $\beta\text{-Pd}(\text{+another metal})\text{H}$  system depends on the concentration of the other metal, e.g.,  $\beta\text{-PdH}$  is more stable than  $\beta\text{-PdAgH}$  and hydride stability would decrease with increase of Ag content (43). In TPR profiles, when Pd is alloyed with another metal, the respective  $\beta$ -hydride decomposition peak should shift toward lower temperatures. In catalyst probing with this method, the appearance of two (or more) hydride decomposition peaks in TPR would indicate the presence of two (or more) different (bi)metal phases capable of forming individual hydride phases. On the other hand, the presence of one, relatively sharp, hydride decomposition peak would speak for a respectable alloy homogeneity. Figure 2a displays the basis for such a diagnosis. The top profile presents the DTPR profile for  $\text{Pd}_{0.50}\text{Re}_{0.50}$ , middle—for Pd, and bottom—for the physical mixture of those two catalysts. In addition, in Fig. 2a, a dotted line presents a hypothetical DTPR profile of the mixture, calculated from contributions of individual components.

DTPR profiles of Pd-Re/ $\text{Al}_2\text{O}_3$  samples show the presence of one hydride decomposition peak (Fig. 2b). This finding clearly suggests the presence of only one hydride phase in our Pd-Re bimetallic catalysts. It should also be noted that the hydride decomposition peak shifts gradually towards lower temperatures (and becomes smaller) with the increase of Re content. We assume that in the case of negligible interactions between Pd and Re, the hydride peak should not shift. Therefore, the simultaneous presence of, say, pure palladium and Pd-rich alloy phase (capable of hydride formation) in our Pd-Re/ $\text{Al}_2\text{O}_3$  is not likely. Another indication that we do not deal with the separated bimetal components is the fact that the H-to-Pd ratios in decomposing  $\beta$ -hydride phases (DTPR profiles) are not constant but exhibit a consistent decrease with increasing the Re content (Table 1).

However, this method for probing pure Re and Re-rich phases is not appropriate since Re forms the respective hydride only under very high pressures of hydrogen (44).

#### X-Ray Diffraction Study of Pd-Re/ $\text{Al}_2\text{O}_3$

*In situ* XRD studies of reduced Pd-Re/ $\text{Al}_2\text{O}_3$  also demonstrate some formation of Pd-Re alloys. It must be stressed that alumina-supported Pd alloys are not ideal samples for XRD study. This is related to the fact that the XRD profile from  $\text{Al}_2\text{O}_3$  is very intense, compared to an overlapping signal from the metal phase (30, 31). If one considers the possibility of the presence of several alloy phases (due to, e.g. alloy inhomogeneity) and serious XRD

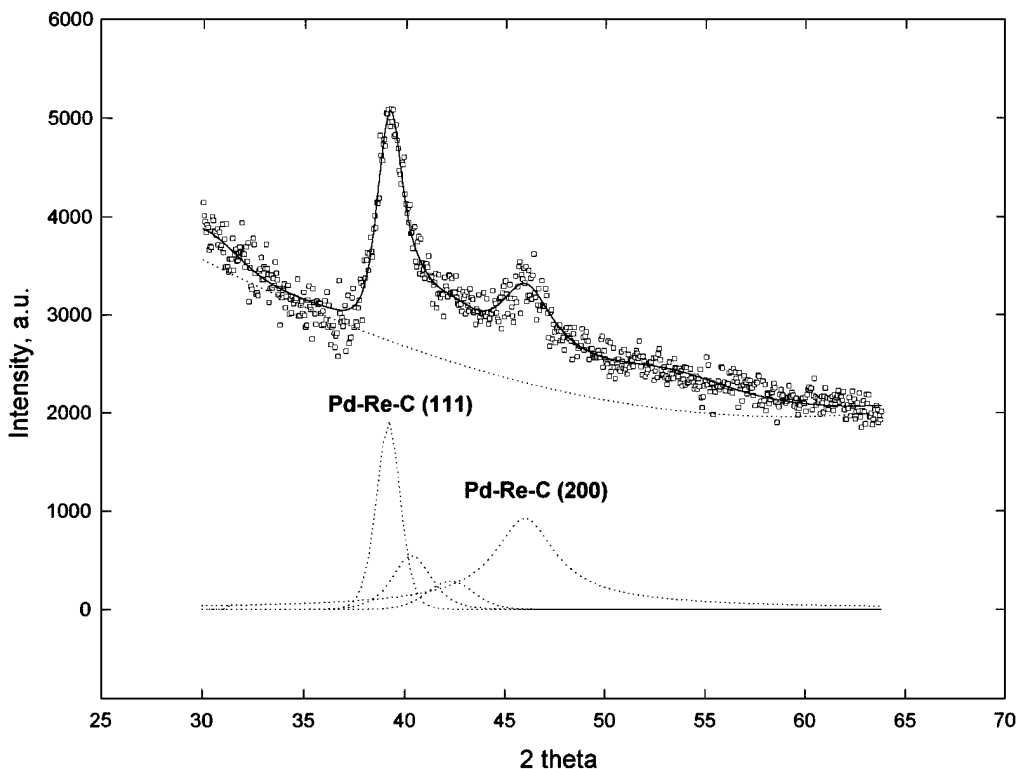


FIG. 5. XRD spectrum of Pd<sub>0.75</sub>Re<sub>0.25</sub> used in CCl<sub>2</sub>F<sub>2</sub> hydrodechlorination. A shift of fcc phase towards lower angles is marked with peak assignment to a Pd-Re-C phase.

reflection broadenings (due to small alloy particles), difficulties are even worse. This is exemplified in Fig. 3. The XRD profiles are very complex. All profiles belonging to Pd and Pd-Re, but Pd<sub>0.25</sub>Re<sub>0.75</sub>, look similar. In the case of Pd<sub>0.25</sub>Re<sub>0.75</sub>, the spectrum shows an additional peak at 42.5°, originating, most probably, from Re (hcp). Difficulties in interpretation (peak assignment) are enlarged by the fact that Tytkina *et al.* (45) reported the existence of a Pd-Re fcc phase characterized by smaller, compared with Pd and Re, lattice parameter (0.366 nm), resulting in (111) reflection also at ~42.5° (Fig. 3). Such a contraction in lattice parameter is in line with EXAFS data for Pd-Re/Al<sub>2</sub>O<sub>3</sub> (46): interatomic distance in Pd-Re is shorter than for pure metals (0.267 vs 275 nm). Summing up, it is hardly possible to use the XRD profiles in Fig. 3 for making an ultimate conclusion as to the extent of mixing of the bimetal phase. Ziemecki *et al.* (18), investigating Pd-Re/Al<sub>2</sub>O<sub>3</sub> by XRD, faced similar problems.

More information allowing the assessment of the degree of interaction between Pd and Re come from XRD studies of the catalysts which were transformed into a  $\beta$ -Pd(Re)H phase. Figure 4, exhibiting XRD patterns after alumina background subtraction, shows the effect of a prolonged, low-temperature hydrogen pretreatment of two catalysts: Pd and Pd<sub>0.25</sub>Re<sub>0.75</sub>. In the case of the first sample, large shifts of (111) and (200) reflections towards lower angles

(Fig. 4, bottom) manifest a typical transformation of Pd into palladium hydride. For Pd<sub>0.25</sub>Re<sub>0.75</sub>, change in the XRD profile is modest (Fig. 4, top), showing that this catalyst does not contain any (or has only very little) Pd-rich phase able to form a  $\beta$ -hydride phase. Since this catalyst contains appreciable amounts of Pd, the conclusion must be that a significant quantity of Pd interacts with Re.

The Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts after catalytic screening in CCl<sub>2</sub>F<sub>2</sub> hydrodechlorination were also studied by XRD. Most of the catalysts showed significant shifts of the (111) and (200) reflections towards lower angles (Fig. 5). Such a shift was previously interpreted by carbon incorporation to the Pd lattice (7, 8, 10). In the present study, these shifts were gradually smaller with increasing Re content in Pd-Re. Table 2 shows lattice parameter of this new Pd(-Re)C phase. The lattice parameter for pure Pd sample agrees extremely well with that calculated earlier for carburized Pd samples with maximum carbon content of ~13 at% (47, 48). To explain the differences observed between lattice parameters calculated from both reflections for the Pd-Re catalysts, the following reasoning can be used. In the case of the Pd-Re system a possibility of the formation of different intermetallic alloys cannot be ruled out. Although the crystallography of the Pd-Re system was not intensively studied, nevertheless, fcc Pd-Re phase was reported (45). The Pd (111) reflection is superimposed with those from

TABLE 2  
Hydrodechlorination of  $\text{CCl}_2\text{F}_2$  on Pd-Re/ $\gamma$ - $\text{Al}_2\text{O}_3$  Catalysts

Catalyst <sup>a</sup>	Reaction temp., °C	Selectivity, <sup>b</sup> %				TOF, <sup>c</sup> s <sup>-1</sup>	E <sub>a</sub> , kJ/mol	Lattice parameters for fcc structure (nm) from	
		CH <sub>4</sub>	CH <sub>2</sub> F <sub>2</sub>	CHClF <sub>2</sub>	CH <sub>2</sub> ClF			(111) peak	(200) peak
Pd	180	18.1	73.6	5.6	1.0	0.0531	62.7 ± 0.7	0.3995	0.3999
	170	16.4	75.2	6.4	0.6	0.0369			
	160	15.0	76.2	7.7	0.2	0.0246			
Pd <sub>0.95</sub> Re <sub>0.05</sub>	180	25.1	68.7	4.7	—	0.0184	60.0 ± 0.5	0.3982	0.3945
	170	22.8	70.9	4.9	—	0.0128			
	160	20.6	72.5	5.5	—	0.0089			
Pd <sub>0.90</sub> Re <sub>0.10</sub>	180	24.5	68.4	4.9	0.9	0.0141	62.1 ± 0.5	0.3990	0.3913
	170	22.3	70.7	5.0	0.8	0.0096			
	160	20.3	73.4	5.5	—	0.0066			
Pd <sub>0.75</sub> Re <sub>0.25</sub>	180	19.4	73.8	4.0	0.5	0.0167	58.7 ± 0.5	0.3930	0.3897
	170	17.6	76.1	4.4	—	0.0117			
	160	15.6	78.0	4.7	—	0.0081			
Pd <sub>0.50</sub> Re <sub>0.50</sub>	180	12.2	81.2	3.4	0.7	0.0194	57.6 ± 0.6	0.3993	0.3939
	170	11.0	82.9	3.4	0.5	0.0137			
	160	9.9	84.6	3.9	—	0.0096			
Pd <sub>0.25</sub> Re <sub>0.75</sub>	180	12.6	77.7	4.0	1.1	0.0087	57.5 ± 0.6	0.3878	0.3820
	170	11.4	80.3	3.7	0.7	0.0061			
	160	10.5	81.9	3.9	—	0.0043			
Re	180	negligible activity after 20 h time-on-stream (CClF <sub>3</sub> ~40%, CHClF <sub>2</sub> ~52%)							

Note. Steady-state turnover frequencies (TOFs), product selectivities, apparent activation energies (E<sub>a</sub>s), and lattice parameters of fcc structures in spent catalysts.

<sup>a</sup> For the catalyst code see Table 1.

<sup>b</sup> Minor products: C<sub>2</sub>H<sub>6</sub>, CClF<sub>3</sub>, CH<sub>3</sub>Cl, and CH<sub>2</sub>F-CH<sub>2</sub>F (Σ% < 5%).

<sup>c</sup> Assuming metal dispersion measured by CO chemisorption (CO/(Pd + Re) from Table 1).

Re and Re-rich solid solution phase(s). Therefore any shift caused by carburization will be shadowed by those reflections. On the other hand, the Pd (200) reflection, although less intense than the (111), is fairly isolated from the Re reflections and thus this reflection will reflect more clearly the possible changes caused both by alloying and carburization. Because interatomic distances in Re and Pd are very close to each other (~0.275 nm), the alloying of these two metals should not produce significant displacements of respective peaks in the XRD spectra. However, depending on the Re content, carbon incorporation should be different. Table 2 shows that this is actually the case, confirming our earlier speculations as to a considerable extent of Pd-Re interactions in the Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts.

#### Catalytic Behaviour of Pd-Re/ $\gamma$ - $\text{Al}_2\text{O}_3$ in $\text{CCl}_2\text{F}_2$ Hydrodechlorination

The catalytic behaviour of investigated samples allows us to classify our catalysts in three groups: Pd/ $\text{Al}_2\text{O}_3$ , Re/ $\text{Al}_2\text{O}_3$ , and all Pd-Re/ $\text{Al}_2\text{O}_3$  bimetallic catalysts. Re was essentially inactive after several minutes of time-on-stream, its initial activity was not significant either, in harmony with

other data (16, 17). Consequently, in the following discussion we shall only concentrate on Pd and Pd-Re samples.

The main differences between the catalytic behaviour of Pd and Pd-Re bimetallic samples concern time-on-stream behaviour (evolution of activity and selectivity), steady-state activity, and activation energy in  $\text{CCl}_2\text{F}_2$  hydrodechlorination.

Figure 6 (top) shows changes in overall conversion with time-on-stream for all catalysts. It is seen that the activity of palladium increases at the initial stage of the reaction and then is fairly stable. On the contrary, the activities of all bimetallic samples sharply decline with time-on-stream. The initial activity is strongly correlated with Re content: the more rhenium, the higher the initial activity. Since, as was said earlier, rhenium does not show any activity, the behaviour of Pd-Re bimetallic samples cannot be described by assuming that separate Pd and Re particles operate as active phases of the Pd-Re catalysts. However, the high activity of Pd-Re alloys does not last long; sample deactivation is not directly related to rhenium content, because, as will be discussed later, at steady-state, Pd<sub>0.50</sub>Re<sub>0.50</sub> is more active than other Pd-Re samples.



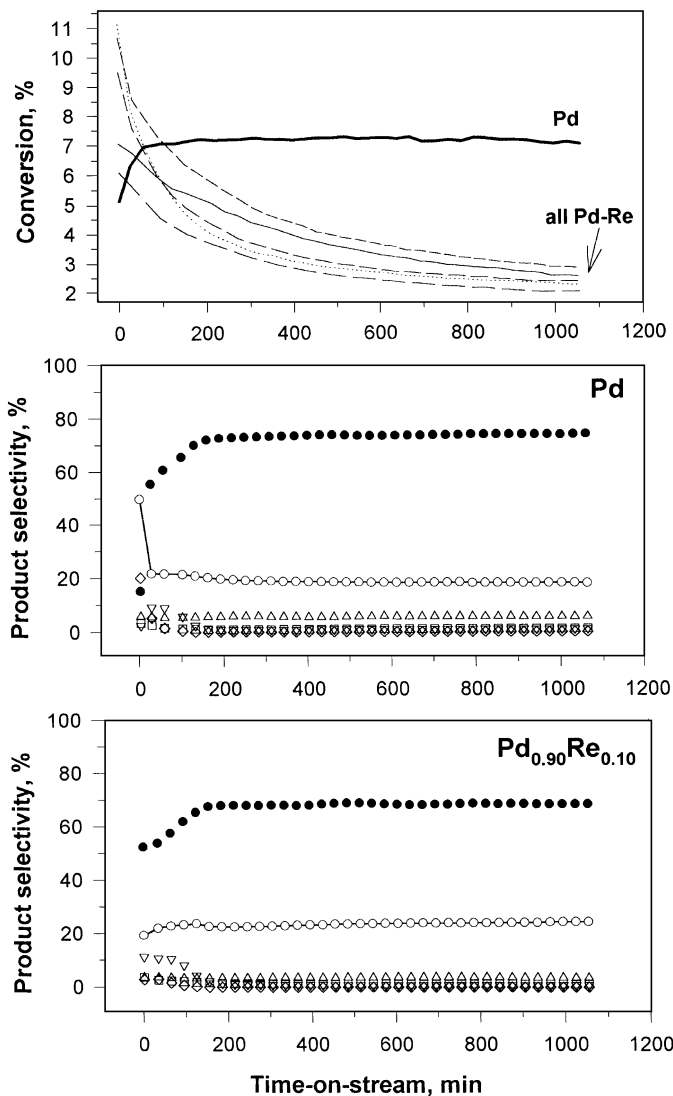


FIG. 6. CCl<sub>2</sub>F<sub>2</sub> hydrodechlorination over Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. Upper part shows the effect of time-on-stream on overall conversion over Pd (—), Pd<sub>0.95</sub>Re<sub>0.05</sub> (— · —), Pd<sub>0.90</sub>Re<sub>0.10</sub> (— · — · —), Pd<sub>0.75</sub>Re<sub>0.25</sub> (— · — · —), Pd<sub>0.50</sub>Re<sub>0.50</sub> (— · — · — · —), and Pd<sub>0.25</sub>Re<sub>0.75</sub> (· · · · ·). Middle and bottom parts show the effect of time-on-stream on product selectivity for two indicated catalysts: CH<sub>2</sub>F<sub>2</sub> (filled circles), CH<sub>4</sub> (empty circles), CHClF<sub>2</sub> (empty triangles), CH<sub>2</sub>ClF (empty reversed triangles), CH<sub>3</sub>Cl (empty squares), and CH<sub>2</sub>Cl<sub>2</sub> (empty diamonds).

The product selectivity also experiences noticeable changes (Fig. 6). Pd/Al<sub>2</sub>O<sub>3</sub> produces a lot of methane and less CH<sub>2</sub>F<sub>2</sub> at the initial stage, however, after several minutes, CH<sub>2</sub>F<sub>2</sub> production increases at the expense of methane. The bimetallic samples behave differently; the formation of CH<sub>4</sub> slightly increases with time-on-stream, at the cost of CH<sub>2</sub>F<sub>2</sub>.

Numerous literature data show that hydroconversion of various alkanes (n-butane, cyclopentane (49), 2,2-dimethylbutane (50)) on Pt-Re/Al<sub>2</sub>O<sub>3</sub> often displays a pronounced maximum in the catalytic activity at 75–80% Re.

The appearance of such a maximum was regarded as an indication for ligand effect in alloying or synergistic action of mixed ensembles (for discussion, see (51)). No matter which explanation is plausible here, the presence of such an effect, especially if it is very pronounced, suggests that we do not deal with a physically mixed bimetal components; i.e. the extent of alloying should be significant. The results of catalytic screening Pd-Re/Al<sub>2</sub>O<sub>3</sub> (Fig. 7) show a similar activity pattern as in the case of Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalysts reported in alkane conversions. This result indicates that, similarly to Pt-Re alloys, Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts must exhibit a considerable degree of alloying.

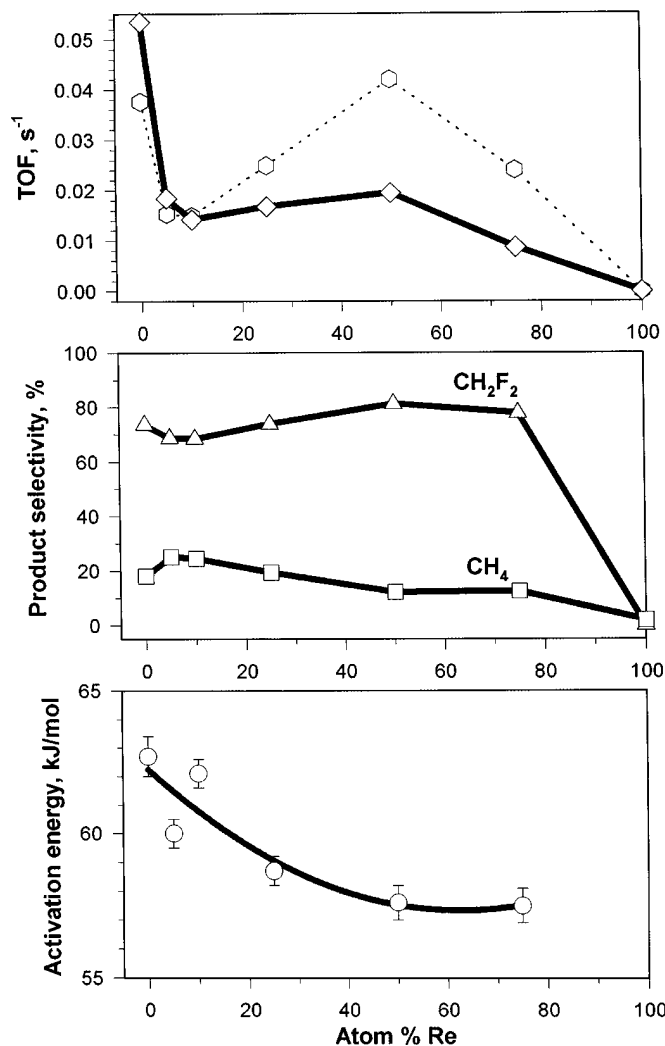


FIG. 7. CCl<sub>2</sub>F<sub>2</sub> hydrodechlorination over Pd-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. The effect of nominal bimetal composition on: turnover frequency (top part, diamonds joined with thick solid line represent TOFs calculated on the basis of metal dispersion from CO chemisorption, hexagons joined with dotted line represent points calculated using metal dispersion from H<sub>2</sub> chemisorption); main product selectivity (middle part, CH<sub>2</sub>F<sub>2</sub>—triangles; CH<sub>4</sub>—squares), and apparent energy of activation (bottom part).

The selectivity towards  $\text{CH}_2\text{F}_2$  (a desired product of  $\text{CCl}_2\text{F}_2$  hydrodechlorination) shows moderate variations with Pd-Re bimetal composition, with some increase in selectivity for Re-rich bimetallic samples (Fig. 7). Figure 7 also shows that apparent energy of activation decreases with increasing Re content. These results are also compatible with our conclusion as to substantial interactions between Pd and Re in  $\text{Al}_2\text{O}_3$ -supported catalysts.

The large production of methane in the reaction of  $\text{CCl}_2\text{F}_2$  with  $\text{H}_2$  suggests either stepwise exchange of halogens for hydrogen (52), or, as we suggest, a total stripping of halogens to form bare  $\text{C}_1$  units, which can further be either hydrogenated off to  $\text{CH}_4$  or incorporated in the catalyst. A massive formation of a Pd-C solution documented by XRD (previous subsection) is in harmony with the known propensity of this metal to dissolve carbon provided by organic molecules (7, 8, 10, 47, 48, 53). It seems likely that the formation of the Pd-C phase has an effect on the catalytic performance of supported Pd catalysts (10). The fate of halogen species stripped off from the CFC molecule also seems important. In the case of the alumina-supported Pd catalyst, we accept the suggestion of Coq *et al.* (5), who proposed that halogens migrate to alumina and modify the metal-support interface in such a way that interfacial Pd atoms become electron-rich, resulting in better selectivity towards partly dehalogenated species (to  $\text{CH}_2\text{F}_2$  compared to  $\text{CH}_4$ ). The time-on-stream behaviour of 2 wt% Pd/ $\text{Al}_2\text{O}_3$ , where the catalyst becomes gradually more active and, especially, selective towards  $\text{CH}_2\text{F}_2$ , is in line with such a supposition.

The time-on-stream behaviour of bimetallic Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts suggests that the introduction of Re to Pd brings about important changes. A strong deactivation for all bimetallic samples is caused either by coke or, as we suggest, by halogen species. At the initial stage, rhenium or Pd-Re mixed sites, precovered with hydrogen after the reduction, are very active, giving a lot of hydrodechlorination products. Halogens, which left the  $\text{CCl}_2\text{F}_2$  molecule, are released as HF and HCl, but can also be strongly bound to Re or Re-Pd mixed sites (Re is supposed to bind halogens more strongly than Pd does). In effect, scavenging of halogens from Re by alumina must be more difficult, therefore halogen coverage of the Pd-Re surface seems higher than in the case of pure Pd. This high halogen surface coverage slows down the overall rate, although it does not drastically change the selectivity pattern. This increase in the selectivity towards  $\text{CH}_4$  during catalyst passivation resembles very much the behaviour of Pd/graphite and Pd black in the studies of Coq *et al.* (4, 5).

Finally, a comment concerning the increase in  $\text{CH}_4$  selectivity with time-on-stream for Pd-Re catalysts is suggested. Because dissolution of carbon in Pd-Re catalysts rich in Pd was documented by XRD (previous subsection), it is also possible that some part of the produced methane on Pd-Re

would originate from hydrogenation of subsurface carbon, accumulated at the very fast initial stage of the reaction. The initial rate of  $\text{CCl}_2\text{F}_2$  conversion is much higher than the steady-state rate. The formation of  $\text{C}_1$  units at the initial reaction stage may be faster than their hydrogenation to  $\text{CH}_4$ . This presumably leads to drastic catalyst coking and carbon incorporation in the metal. After passing over the initial period, the reaction considerably slows down, and a part of the "excessively" accumulated carbon can be hydrogenated off and removed as methane.

## CONCLUSIONS

The preparation of the Pd-Re/ $\text{Al}_2\text{O}_3$  system using incipient wetness impregnation yielded bimetallic catalysts characterized by a considerable extent of mixing. Such a conclusion follows from the characterization by X-ray diffraction, chemisorption, and temperature-programmed methods. In diagnosing bimetal homogeneity, a different stability of Pd(-Re)-hydride phases has been exploited, i.e. the amount and decomposition temperatures of the  $\beta$ -hydride phases for different  $\text{Pd}_x\text{Re}_{1-x}/\text{Al}_2\text{O}_3$  catalysts are found strongly correlated with  $x$ , suggesting significant interaction between Pd and Re in reduced Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts. The results of catalytic screening of Pd-Re/ $\text{Al}_2\text{O}_3$  in  $\text{CCl}_2\text{F}_2$  hydrodechlorination are compatible with such a conclusion. Adding Re (inactive in this reaction) to Pd/ $\text{Al}_2\text{O}_3$  introduces substantial changes in the catalytic behaviour. All Pd-Re bimetallic samples strongly deactivated with time-on-stream, whereas the activity of Pd/ $\text{Al}_2\text{O}_3$ , after an initial increase, was fairly stable. The selectivity pattern for the bimetallic samples also differed from that of palladium, showing the increase in the selectivity to methane during the stabilization period. The steady-state activity of Pd-rich (up to 25 at% Re) bimetallic samples was much lower than that of Pd, however, further addition of Re caused a slight increase in activity. Such an activity pattern resembles very much the behaviour of alumina-supported Pt-Re catalysts in hydrocarbon conversions. The selectivity towards  $\text{CH}_2\text{F}_2$  changed only slightly with the bimetal composition. X-ray diffraction indicated the presence of carbon dissolved in Pd or Pd-rich phases in spent Pd-Re/ $\text{Al}_2\text{O}_3$  catalysts. Differences in lattice parameter of the carbonized phases depended on the nominal composition of Pd-Re, verifying a considerable extent of Pd-Re mixing in the supported catalysts.

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