

## Synergistic effects in hydrodechlorination of organic compounds catalyzed by metals\*

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The search for the most suitable hydrodechlorination catalysts should consider both the C-Cl bond strength in a molecule subjected to reaction and the metal-chlorine bond, which should be neither too strong nor too weak. An improvement of Pd- and Pt-based catalysts can be achieved by alloying with metals which bind chlorine even less strongly, e.g. with gold. Addition of platinum to palladium would also be beneficial because of metal-chloride bond energy considerations. Analogous effects occur in the hydrodechlorination of dichlorodifluoromethane and 1,2-dichloroethane, the molecules characterized by stronger carbon-chlorine bonds.

### 1. INTRODUCTION

Recent interest in search for effective catalysts for chlorine removal from harmful organic compounds resulted in a series of papers published in the period of last fifteen years. Catalytic hydrodechlorination (HdCl) offers an exceptional advantage over all oxidative (noncatalytic and catalytic) methods: the carbon skeleton of a chlorine-containing organic molecule is not irreversibly lost (i.e.

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\*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65<sup>th</sup> birthday

not converted to CO<sub>2</sub>), but several useful and less harmful products could be achieved in effect of catalytic transformation.

In this paper we would like to review our results on hydrodechlorination of dichlorodifluoromethane, tetrachloromethane and 1,2-dichloroethane carried out over a number of platinum and palladium-containing systems. The main aim of this presentation is to show how the Sabatier principle [1] works for hydrodechlorination reactions and hydrodechlorination catalysts. It is well known that the Sabatier principle, a qualitative concept in catalysis, states that the interactions between the catalyst and the reactant should be neither too strong nor too weak. If the interaction is too weak, the reactant fails to bind to the catalyst and no reaction takes place. On the other hand, if the interaction is too strong, the catalyst gets blocked by reactant or product. It is commonly accepted that the rate determining step of a large variety of hydrodechlorination reactions is the splitting of the first C-Cl bond [2] of a reacting molecule. Such bond splitting is easier when a binding of chlorine atom and metal surface is stronger. However, a metal-chlorine bond that is too strong would lead to blocking a metal surface with chloride species. In this respect the behavior of the three important catalytic metals, platinum, palladium and gold in hydrodechlorination of different chlorine-containing compounds is analyzed. It will be shown that the combination of two metals results in better catalytic performance, i.e. indicating a number of synergistic effects.

## 2. MATERIAL AND METHODS

Preparation of silica-, alumina- and carbon-supported Pt, Pd, Pt-Pd, Pt-Au and Pd-Au was described in our previous publications [3-8]. In short, aqueous solutions of chloride-containing metal compounds (PdCl<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub> and NH<sub>4</sub>AuCl<sub>4</sub>) were used in incipient wetness (co)-impregnations. Some bimetallic catalysts were prepared by direct redox reaction (Pd-Au [4], Pt-Pd [5]). Final catalyst pretreatment included reduction in H<sub>2</sub>/Ar flow, usually at 400°C for 3 h. Metal dispersion was assessed from CO or H<sub>2</sub> chemisorption, verified by XRD, and, occasionally, by TEM. Palladium containing catalysts were also investigated in the temperature-programmed (palladium) hydride decomposition [4,5]. Such experiments (combined with XRD data) allow us to estimate the degree of metal alloying in supported bimetallic catalysts.

The catalytic conversion of dichlorodifluoromethane, carbon tetrachloride and 1,2-dichloroethane was investigated using a glass flow reaction system [4-8]. After reduction, the catalysts were cooled to the highest reaction temperature (for CCl<sub>2</sub>F<sub>2</sub> – 180°C, CCl<sub>4</sub> – 90°C and 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> – 230°C) and contacted with the reaction mixture, i.e. with a flow of hydrogen + argon and selected chlorine-containing compound provided from a saturator kept at 0°C (CCl<sub>4</sub> and

1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) or supplied from a tank (CCl<sub>2</sub>F<sub>2</sub>). The mass of the catalyst used ranged between 0.1 and 0.4 g, depending on the reaction, in order to not exceed conversion levels beyond 10% (at steady state, for freshly reduced samples). In all kinetic runs, the activities of most catalysts declined with time-on-stream. A typical run lasted ca. 24 h.

### 3. RESULTS AND DISCUSSION

A number of previous results showed that palladium is a better catalyst than platinum for hydrodechlorination of dichlorodifluoromethane [9]. On the other hand, platinum seems superior in hydrodechlorination of carbon tetrachloride [5,8], whereas gold is only slightly active in both hydrodechlorinations [4,6,7]. Simple consideration of the energies of C-Cl bond in three tested chlorine-containing molecules (Table 1) leads to the following conclusions. First, the molecule of CCl<sub>4</sub> should be more easily deprived of chlorine because the Cl-C bond energy is the lowest. Therefore, it is no surprise that such a respective catalytic reaction takes place at the temperature roughly 100°C lower than for analogous processes for the other chlorine-containing molecules (CCl<sub>2</sub>F<sub>2</sub> and 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) [4-8]. Second, the fact that Pt is better than Pd in catalytic hydrodechlorination of CCl<sub>4</sub>, whereas the opposite is true for hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub> and 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> suggests that a weaker metal-Cl bond is less effective for dissociating Cl-C bond in these compounds. Gold is even less adequate for this process, so activation of Cl-C bond is difficult with this metal. The qualitative situation is presented in Figure 1.

Tab. 1. Dissociation energies of Cl-C bonds in reactants used in this work.

Investigated compound	Considered C-Cl bond	Cl-C bond dissociation energy, kJ/mol	Literature source
CCl <sub>4</sub>	Cl-CCl <sub>3</sub>	305.9±7.5	Ref. [10]
CCl <sub>2</sub> F <sub>2</sub>	Cl-CClF <sub>2</sub>	346.0±13.4	Ref. [10]
1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Cl-CH <sub>2</sub> CH <sub>2</sub> Cl	348.1±9.6	Ref. [11]

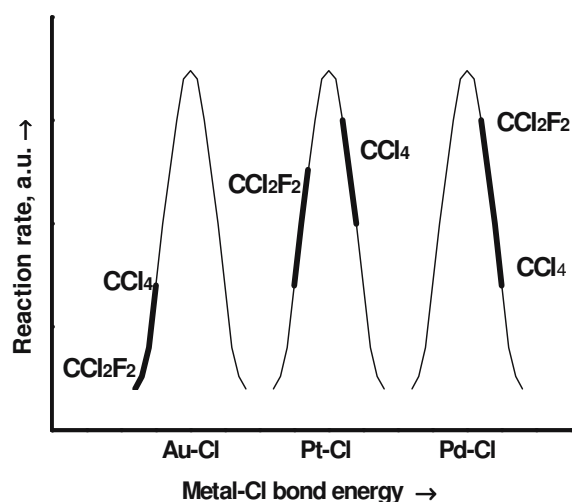


Fig. 1. Suggested volcano-shaped relations between the hydrodechlorination activity of Au, Pt and Pd and metal-chloride bond. For explanation, see text.

Figure 1 shows three volcano-shaped curves for Pd, Pt and Au, and suggested qualitative locations for hydrodechlorination of  $\text{CCl}_4$  and  $\text{CCl}_2\text{F}_2$ . As mentioned, HdCl of  $\text{CCl}_2\text{F}_2$  requires higher energy for splitting the first Cl-C bond than in the case of  $\text{CCl}_4$ , so platinum may not be too active in such a splitting, however for the analogous process with  $\text{CCl}_4$ , this metal would be quite efficient. On the other hand, palladium which binds stronger chlorine atoms than platinum [12,13] should be more active in splitting a stronger Cl-C bond in the molecule of  $\text{CCl}_2\text{F}_2$  (and that of  $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ ). However, in this case and even more drastically in HdCl of  $\text{CCl}_4$  hydrodechlorination, strongly-bound chloride species should block active sites of this metal. Therefore, the HdCl activity of palladium is situated on the decreasing branch of the volcano curve, irrespective of the reacted molecule. Gold binds chloride species much weaker than Pd and Pt, therefore its ability to hydrodechlorinate is poor.

The situation depicted in a qualitative fashion in Figure 1 suggests that it is possible to search for synergistic effects in HdCl of three investigated Cl-containing compounds:  $\text{CCl}_4$ ,  $\text{CCl}_2\text{F}_2$  and  $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ . It is feasible that alloying with another element should either increase or decrease the metal-Cl bonding. For example, alloying Pt with Pd should be beneficial for HdCl of  $\text{CCl}_2\text{F}_2$  and  $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ . Similarly, alloying Pt with Au should decrease the metal-Cl bond energy, creating a situation which is more favorable for HdCl of  $\text{CCl}_4$ . In both cases, the catalytic behavior of Pt should approach an expected maximum

activity. Similar changes are anticipated for alloying palladium with gold. Figures 2–4 show that, indeed, the Sabatier’s principle works well in such cases.

Since the Cl-C bond energies in 1,2-dichloroethane and dichlorodifluoromethane are comparable (Table 1), the effect of adding some gold or platinum to palladium should be positive. Palladium itself, which is the best catalytic metal in HdCl of both organic compounds, is still “too strong” in binding chloride species. Therefore, an addition of less active metal, such as platinum or gold is very helpful. Figures 2 and 3 demonstrate the synergistic effects for the differently supported Pd-Au and Pd-Pt catalysts.

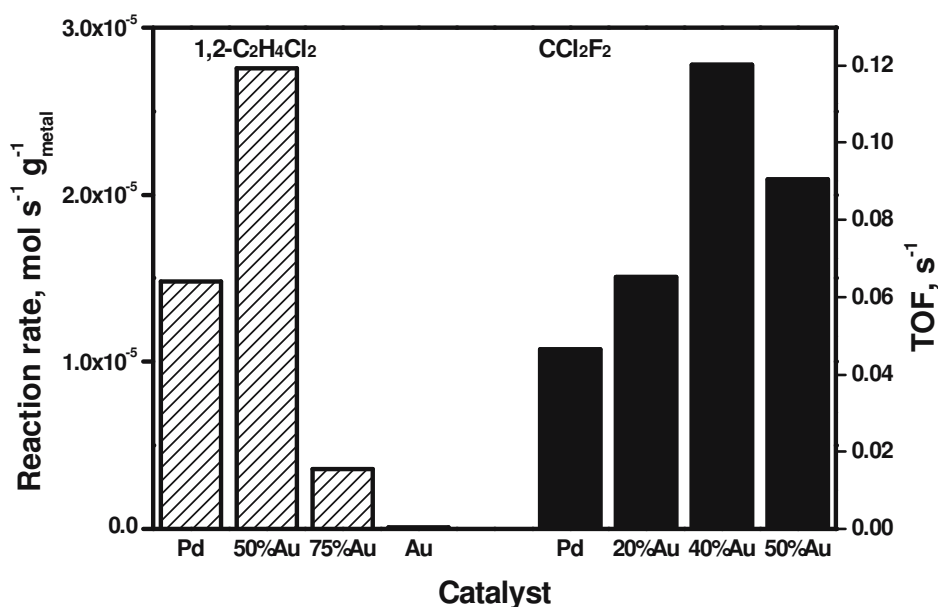


Fig. 2. Catalytic activity of Pd-Au/SiO<sub>2</sub> catalysts in hydrodechlorination of 1,2-dichloroethane at 230°C and Pd-Au/C in hydrodechlorination of dichlorodifluoromethane at 180°C (adopted on Śrębowata [3] and Bonarowska et al. [4], respectively).

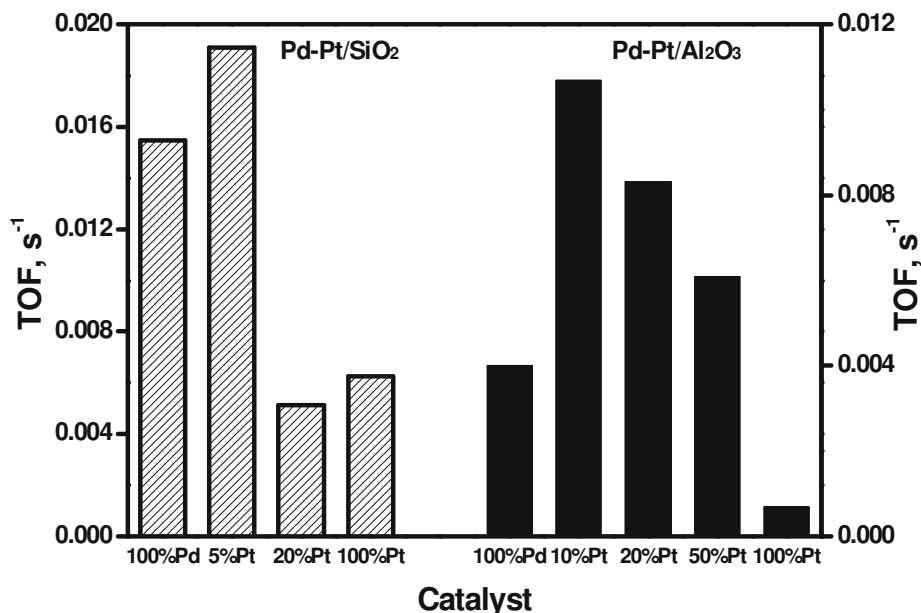


Fig. 3. Synergistic effect in hydrodechlorination of  $\text{CCl}_2\text{F}_2$  on supported Pd-Pt/SiO<sub>2</sub> catalysts at 180°C (left side – silica supported [5], right side – alumina-supported catalysts [8]).

In this respect, application of Pt-Au catalysts in hydrodechlorination of  $\text{CCl}_2\text{F}_2$  (and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ ) does not seem very useful. Further weakening of metal-Cl bond by adding gold reduces the hydrodechlorination capability of platinum. Conversely, the beneficial effect could be achieved from alloying platinum with palladium (Figure 3). However, the catalytic performance of platinum in  $\text{HdCl}$  of  $\text{CCl}_4$  is greatly improved by adding gold (Figure 4).

#### 4. CONCLUSIONS

The selection of the most suitable  $\text{HdCl}$  metallic catalysts depends on the strength of the C-Cl bond in a molecule subjected to reaction and on the metal-chlorine bond, which should be not too strong and not too weak. A relatively weak C-Cl bond in  $\text{CCl}_4$  (~306 kJ/mol) does not require a high dechlorination potential, thus Pt is a better catalyst than Pd in  $\text{CCl}_4$  reaction. In addition, an improvement of Pt-based catalysts can be achieved by alloying with metals which bind chlorine even less strongly than Pt (i.e. with Au). In contrast, Pd is a better catalyst than Pt for hydrodechlorination of a stronger C-Cl bond (~350 kJ/mol), present in  $\text{CCl}_2\text{F}_2$  and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ . However, a good performance

of Pd can be improved further by alloying it with less active Pt (or Au), as a result of weakening of the metal-chlorine bond.

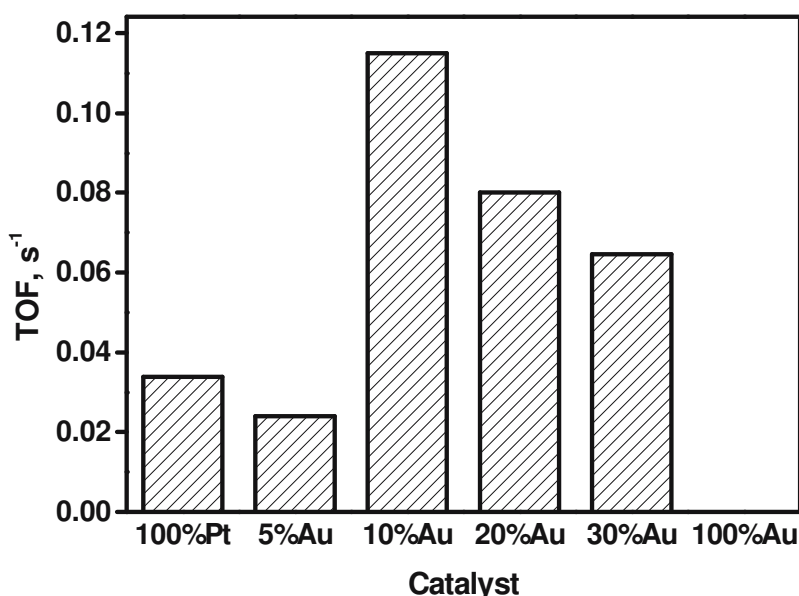


Fig. 4. Synergistic effect in  $\text{CCl}_4$  hydrodechlorination on Pt-Au/ $\text{Al}_2\text{O}_3$  catalysts at  $90^\circ\text{C}$  (based on Legawiec-Jarzyna [6] and [7]).

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