



# Acrolein hydrogenation on PdPt powder catalysts prepared by colloid synthesis

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## ABSTRACT

Acrolein was hydrogenated over unsupported Pd, Pt and PdPt bimetallic catalysts with different Pd:Pt atomic ratios. The formation of saturated aldehyde (propanal) by C=C bond hydrogenation was the main reaction on each catalyst. Maximum conversion values were reached at 293 K over each palladium containing catalyst and at 473 K on Pt. Palladium and platinum behaved differently in secondary reactions. Dipropyl ether was formed in the presence of Pd, while under the same conditions – low temperature (323 K) and high hydrogen pressure (400 Torr) – propane and propanol were produced on the Pt catalyst. The selectivity patterns of bimetallic catalysts were different from those of monometallic ones: under the same conditions dipropyl ether showed a higher selectivity on the PdPt pairs. As the surface Pt concentration increased, the Pt-like character was more and more prevailing; namely the selectivity of propane and propanol increased. At high temperature (473 K) acrolein underwent hydrogenolysis over each catalyst. The selectivity of ethane was higher when Pd was present.

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## 1. Introduction

Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to their corresponding alcohols has a great industrial importance [1,2]. The reaction can lead to three types of products: the C=C double bond is hydrogenated to give a saturated aldehyde or the C=O double bond is involved, yielding an unsaturated alcohol and finally total hydrogenation can occur resulting in a saturated alcohol. From an industrial viewpoint, the most important product is the unsaturated alcohol and this compound is the most difficult to obtain. Several studies were devoted to the improvement of the selectivity towards the unsaturated alcohol. These revealed that forcing the molecule to a preferential adsorption through the C=O group or hindering the adsorption through the C=C bond will increase the selectivity of the unsaturated alcohol. Enhanced selectivity can be obtained in particular by choosing the proper supports, such as  $ZrO_2$  [3],  $TiO_2$  [4], and activated carbon [5]; by using bimetallic catalysts, such as PtNi [6,7,8], PtSn [9], RhSn [10], and RuSn [11,12]; or by poisoning the C=C bond adsorption sites [13]. Interaction of Pt with subsurface Ni promoted the reaction to unsaturated alcohol in studies carried out with single crystals [7] or deposited films [8]. Increasing the chlorine content and adding Re to Ir/ $\gamma$ - $Al_2O_3$  catalysts improved the formation of cinnamyl alcohol in liquid

phase hydrogenation of cinnamaldehyde [14], while unsaturated alcohol was produced with selectivities up to 99% over 5% Pt/K-10 (montmorillonite) [15]. Metals which are usually active in catalytic hydrogenation have different efficiencies in hydrogenation of C=O and C=C double bond [1,2]. Early studies showed that unpromoted metals had specific selectivities to unsaturated alcohols: iridium and osmium were rather selective; palladium, rhodium and nickel were unselective or slightly selective; platinum, ruthenium and cobalt were moderately selective [16]. Delbecq and Sautet [17] showed by theoretical calculation that the metal selectivities can be rationalized in terms of the different radial expansion of their *d* bands; they found that the larger the band, the stronger the four-electron repulsive interaction with the C=C bond and the lower the probability of its adsorption. Indeed, the *d*-band width increases in the series Pd < Pt < Ir < Os which accounts well for the experimental selectivities. When the adsorption of C=O and C=C bonds takes place together, the kinetic factor plays an important role: generally speaking, a C=C bond hydrogenates more easily and more rapidly than a C=O bond. Carbonyl groups are usually hydrogenated over platinum, while no hydrogenation has been reported over palladium for aliphatic aldehydes. In contrast, Pd was more efficient in the hydrogenation of alkenes than Pt.

The present paper deals with the catalytic properties of Pt, Pd, and PdPt powders of different compositions in acrolein hydrogenation. In our previous papers we described the preparation of PdPt powders and their characterization by XPS, UPS, TEM, EDS [18] as well as catalytic tests in hydrogenative ring-opening (HRO)

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**Table 1**

Catalyst composition and temperature dependence of the conversion of acrolein hydrogenation over various catalysts

Catalysts	Atomic ratio (XPS) <sup>a</sup>	mg	Conversion (%)			
			Temperature (K)			
			293	323	373	473
Pd	100:0	55	97.6	97.6	96.2 ± 0.7	94.2
PdPt 4:1	73:27	48	97.6	97.0	94.8 ± 0.6	91.7
PdPt 1:1	28:72	50	98.1	97.9	97.6 ± 0.7	96.1
PdPt 1:4	7:93	49	95.9	94.5	93.0 ± 0.2	88.1
Pt	0:100	55	77.9	88.7	93.2 ± 2.5	96.0

<sup>a</sup> Data taken from Ref. [18].

reactions of methyl-ethyl-cyclopropane (MECP) [19]. PdPt catalysts were used for hydrogenation of phenyl aldehydes [20] and Pd with different transition metal components for selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde [21]. The ring opening of MECP was a valuable tool to recognise the formation of alloy structure during preparation and its further homogenising in their subsequent redox treatments of the catalyst system in question. With this reaction we did not observe large differences between the bimetallic samples of various compositions. Since palladium and platinum have different behaviour in the hydrogenation of C=O and C=C bonds [17], we chose acrolein hydrogenation as a test reaction for additional characterization of our PdPt bimetallic catalysts.

## 2. Experimental

Pd, Pt and PdPt bimetallic particles were prepared by a method of colloid chemistry, as described in our previous paper [18]. The catalysts were tested in acrolein hydrogenation at different temperatures and hydrogen pressures. The catalytic experiments were carried out in a closed-loop glass reactor. A CP 9001 gas chromatograph with a 50 m CP-Sil 5CB capillary column (at constant temperature, i.e. 303 K) and an FID detector were attached to the system [22]. A standard acrolein pressure of 10 Torr (1 Torr = 0.133 kPa) was used and the hydrogen pressure was varied between 10 and 400 Torr. The reaction temperatures ranged from 293 to 473 K. The samplings took place after 2, 8 and 14 min. In the test reaction the following products were formed: ethane (ret. time 2.27 min), propane (2.34 min), propanal (2.93 min), propanol (3.72 min) and dipropyl ether (4.43 min).

## 3. Results

All catalysts were very active in acrolein hydrogenation. The conversion data are shown in Table 1 as a function of temperature. Bimetallic catalysts containing Pd and Pt showed slightly decreasing activity with increasing temperature. The opposite effect was observed in the case of Pt; the activity was lower at 293 K and increased monotonically at higher temperatures. In spite of the

short contact time, the conversion was very high in each case. At least 3 parallel runs were carried out (not necessarily on the same day); as an example, the standard deviations are shown for the runs carried out at 373 K.

The catalysts could also be characterized by the products formed in secondary reactions. The overall activity showed a positive hydrogen order on all samples (Table 2). The activities of the catalysts were compared at different temperatures as a function of hydrogen pressure. Bimetallic catalysts were more active than monometallic ones at 323 K and 10 Torr hydrogen pressure, but this difference disappeared at 373 K. The activities of Pd containing catalysts were unaffected by increasing hydrogen pressure (above 50 Torr), as opposed to continually increasing activity over Pt at both temperatures with higher  $p(\text{H}_2)$ .

The formation of the saturated aldehyde (propanal) by C=C bond hydrogenation was the main reaction on each catalyst. On Pt the carbonyl group was hydrogenated, while this was not observed over Pd with aliphatic aldehydes [23]. Pd was, however, much more active in alkene hydrogenation than Pt. Unsaturated allyl alcohol was not detected under the reaction conditions applied. The catalysts showed different behaviour in secondary reactions. Dipropyl ether and propanal was formed with the same selectivity over Pd at 293 K and 200 Torr hydrogen pressure (Fig. 1). With increasing temperatures the selectivity of dipropyl ether decreased and ethane became the main product at 473 K, while higher hydrogen pressure at 323 K favoured the formation of dipropyl ether. This product was not formed over Pt catalyst, except at high hydrogen pressure, but with a selectivity as low as 3%. Pt produced, in turn, propanol and propane with high selectivity when conditions were favourable for their formation, i.e. high hydrogen pressure, low reaction temperature (Fig. 2). During acrolein hydrogenation, Pt black and Pt/SiO<sub>2</sub> catalysts gave small amounts of propane [24]. More propane was detected over Pt black (mean particle size of Pt 15.8 nm) than over Pt/SiO<sub>2</sub> (mean particle size of Pt 4.1 nm), which is in agreement with the finding that the occurrence of hydrogenolytic reactions requires larger surface ensembles of Pt atoms [25]. Over Pt catalyst ethane was also formed, but its selectivity was smaller over Pt than over Pd at 473 K.

The two monometallic catalysts behaved differently in secondary reactions: the formation of dipropyl ether was observed over Pd, while Pt catalyst produced propane and propanol under the same conditions. As far as we know, the formation of dipropyl ether has not been reported under analogous conditions. Hydrogenation of cyclohexanone dissolved in ethanol over pre-reduced palladium oxide resulted in reduction of the carbonyl group, but the preferred end product was ether (ethoxycyclohexane), rather than cyclohexanol [26]. In a comparative study of Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> in vinyloxirane transformations in the presence of hydrogen, dibutyl ether as secondary product was observed over Pd [27].

The selectivity patterns of bimetallic catalysts were different from those of the monometallic ones. At low temperature (323 K) and high hydrogen pressure (400 Torr) dipropyl ether was formed

**Table 2**

Conversion of acrolein on Pd, Pt and PdPt 1:4, 1:1 and 4:1 catalysts as a function of hydrogen pressure at 323 and 373 K

	Conversion (%)									
	323 K					373 K				
	$p(\text{H}_2)$ (Torr)					$p(\text{H}_2)$ (Torr)				
	10	50	100	200	400	10	50	100	200	400
Pd	38.9	98.7	98.4	98.5	98.5	98.0	98.3	98.7	97.7	98.2
PdPt 4:1	95.3	96.9	96.8	96.7	98.1	94.8	95.5	94.9	94.8	95.5
PdPt 1:1	59.1	93.9	90.2	94.7	94.1	92.3	95.3	95.7	96.1	96.9
PdPt 1:4	67.8	93.1	92.1	93.3	94.7	89.6	89.5	88.5	92.9	93.5
Pt	42.5	74.2	79.2	81.4	87.1	54.4	80.0	85.0	88.1	93.2

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