



# Acrolein hydrogenation on PdPt powder catalysts prepared by colloid synthesis

N. Győrffy\*, Z. Paál

*Institute of Isotopes, Hungarian Academy of Sciences, P. O. Box 77, Budapest H-1525, Hungary*

## ARTICLE INFO

### Article history:

Received 2 April 2008

Received in revised form 14 August 2008

Accepted 20 August 2008

Available online 29 August 2008

### Keywords:

Pd

Pt

Bimetallic

Powder catalyst

Acrolein

Hydrogenation

## 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.

© 2008 Published by Elsevier B.V.

## 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)

\* Corresponding author. Fax: +36 1 3922533.  
E-mail address: [gyorffy@iki.kfki.hu](mailto:gyorffy@iki.kfki.hu) (N. Győrffy).

**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

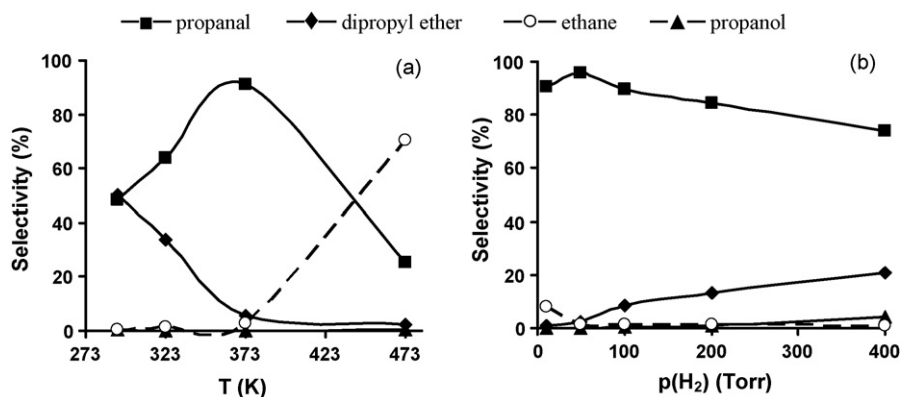


Fig. 1. Selectivity of acrolein hydrogenation on Pd catalyst,  $t = 2$  min: (a) temperature dependence at  $p(\text{Acr}):p(\text{H}_2) = 10:200$  Torr, (b) hydrogen pressure dependence at 323 K.

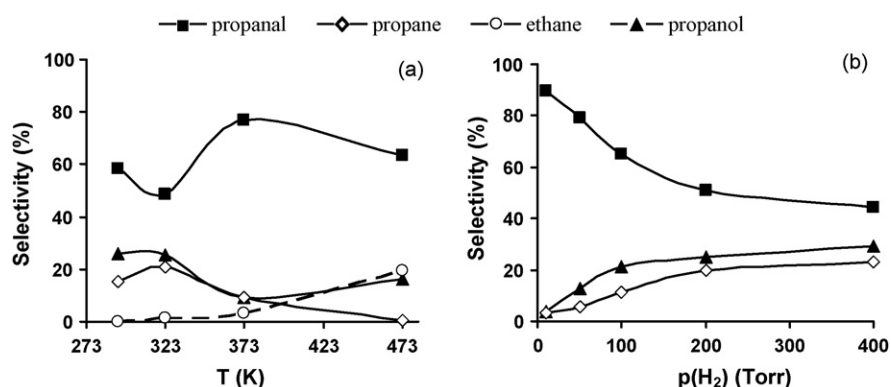


Fig. 2. Selectivity of acrolein hydrogenation on Pt catalyst,  $t = 2$  min: (a) temperature dependence at  $p(\text{Acr}):p(\text{H}_2) = 10:200$  Torr, (b) hydrogen pressure dependence at 323 K.

with higher selectivity on the PdPt pairs and as the surface Pt concentration increased in the sample, the Pt-like character was more and more prevailing; namely the selectivity of propane and propanol increased (Fig. 3). The changes of the amount of PdPt pairs on the surface could be followed with that reaction. The catalysts PdPt 4:1 and PdPt 1:1 formed dipropyl ether with almost the same selectivity. The number of PdPt pairs in these two catalysts might be the same, since the corresponding surface atomic ratios measured by XPS were Pd:Pt = 73:27 and Pd:Pt = 28:72, respectively (Table 1). In the case of PdPt = 1:1, the PdPt pairs on the surface were surrounded with more Pt, and therefore more propanol was formed.

In the case of PdPt 1:4, the number of PdPt pairs might be much less, since XPS indicated an atomic ratio of Pd:Pt = 7:93 (Table 1). These fewer PdPt pairs produced dipropyl ether with lower selectivity. On larger contiguous Pt surface the selectivities of propanol and especially propane was similar to those observed on monometallic Pt catalyst (Fig. 3). At high temperature (473 K) acrolein underwent also hydrogenolysis over the bimetallic catalysts and the selectivity of ethane was similar to that observed on monometallic Pd catalyst (Fig. 4). Propanol was also formed on the catalyst PdPt 1:4, as expected for a larger contiguous Pt surface.

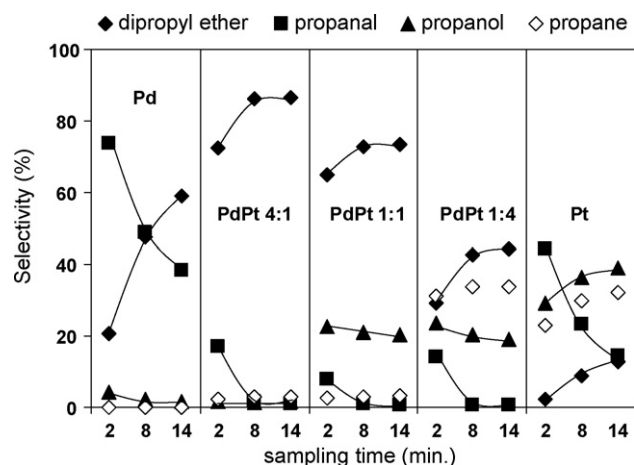


Fig. 3. Acrolein hydrogenation over various catalysts as a function of sampling time at 323 K and at  $p(\text{Acr}):p(\text{H}_2) = 10:400$  Torr.

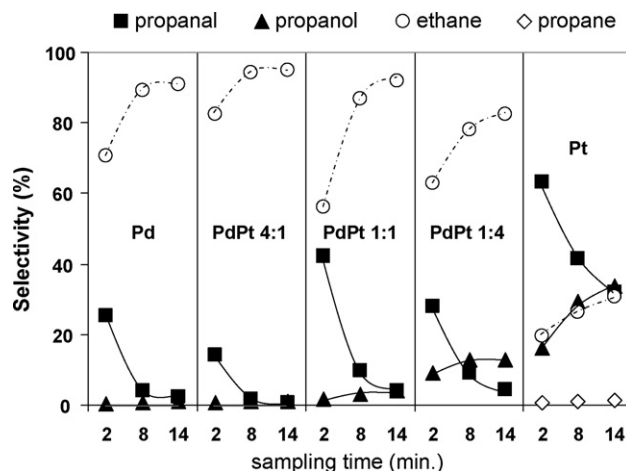


Fig. 4. Acrolein hydrogenation over various catalysts as a function of sampling time at 473 K and at  $p(\text{Acr}):p(\text{H}_2) = 10:200$  Torr.

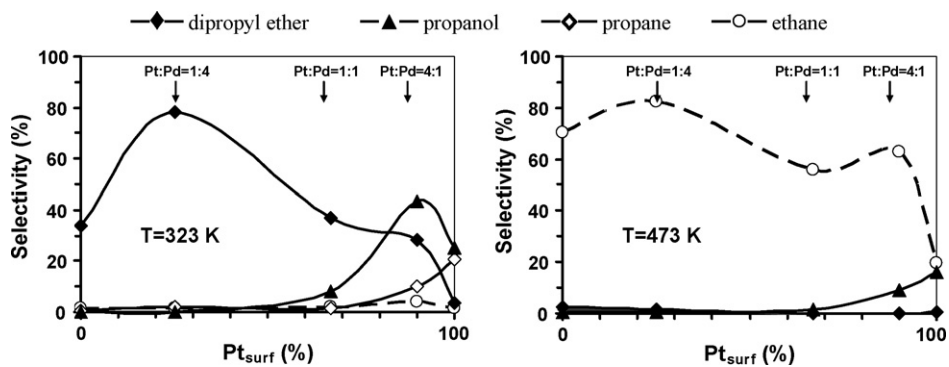
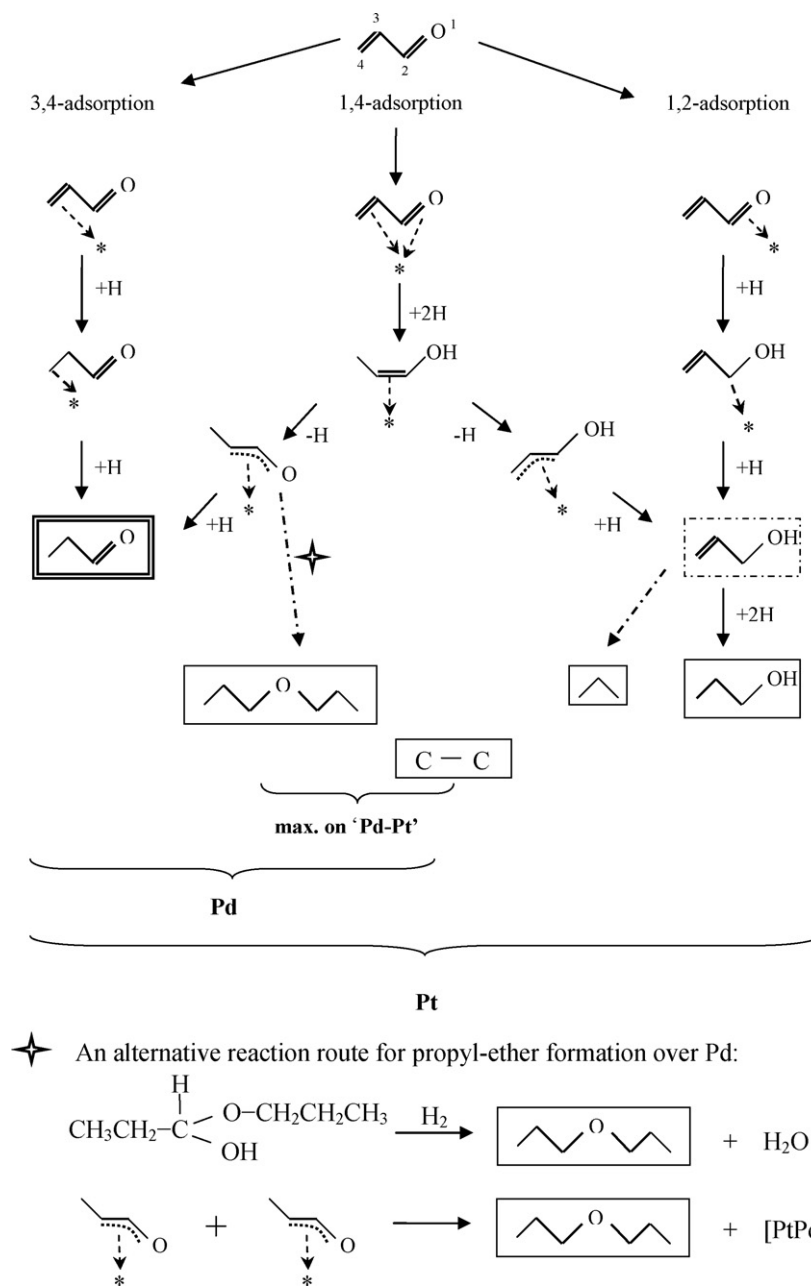


Fig. 5. Selectivity of secondary products of acrolein hydrogenation as a function of surface Pt content at 323 K and 473 K [p(Acr):p(H<sub>2</sub>) = 10:200 Torr, t = 2 min].



Scheme 1. Different adsorption modes of acrolein and the assumed main reaction pathways.

#### 4. Discussion

Fig. 5 compares the catalysts at the same hydrogen pressure (200 Torr) at lower and higher temperatures (323 and 473 K). The figure contains only the secondary products. Dipropyl ether typical of Pd was also formed over bimetallic catalysts, small amount of Pt promoting its formation. Propanol, which was typical of Pt, was only formed on sites with high Pt contents; synergistic effects of small amount of Pd can be seen at 323 K. The situation was the same with propane which was formed on bimetallic catalyst with high Pt-contents only. The higher reactivity of C=O bond on Pt (1 1 1) confirmed also theoretically [28] was not valid on our dispersed Pt catalyst.

Differences between catalysts can be explained by the various adsorption behaviours on the metal components. The formation of propanal and allyl alcohol can be explained by the Horiuti–Polanyi mechanism (Scheme 1): the associative adsorption of C=C and C=O double bonds followed by hydrogenation, such as 1,2 and 3,4 hydrogen addition. The occurrence of 1,4-diadsorbed species for  $\alpha,\beta$ -unsaturated aldehydes was suggested by several authors [3,4]. The 1,4 hydrogen addition on adsorbed acrolein gives an enolic species, which transforms to  $\pi$ -allylic systems after hydrogen abstraction. The  $\pi$ -allylic species is readily hydrogenated to allyl alcohol, which can be hydrogenated further easily and rapidly. Marinelli and Ponec [29] showed that hydrogenolysis of allyl alcohol to propane is very easy, easier than hydrogenolysis of propanal. According to our results this reaction pathway was typical of Pt. Unsaturated allyl alcohol was not detected under the reaction conditions applied (like that reported for the PtNi bimetallic system [7,8]), since it could have been transformed to propanol and propane because of the high conversion. Another reaction pathway of the  $\pi$ -allylic system leads to oxo  $\pi$ -allylic species, which could be hydrogenated to propanal. This pathway was typical of Pd. Hydrogen dissolves at low temperature in Pd, and therefore two oxo  $\pi$ -allylic species adsorbed on the surface might desorb as an ether, while the surface of Pd might be oxidized. This possible reaction is shown in the last line of Scheme 1. It has been shown in our earlier paper, that Pd sample was significantly oxidized after oxygen treatment [19]. Low amounts of PdO appeared in the presence of much Pt [19]. Results on the bimetallic catalysts showed that the reaction pathway typical of Pd resulting in dipropyl ether also took place over the PdPt pairs (Fig. 5). In the case of PdPt 4:1 XPS indicated Pt enrichment near to the surface suggesting that the bulk is likely Pd-like, so hydrogen may also dissolve in the bulk. Supposedly the dissolved hydrogen and the PdPt sites act together and induce the enhanced activity of the catalyst producing dipropyl ether (323 K) and ethane (473 K). Hydrogen dissolving capacity of the Pd bulk decreased with increasing Pt content, therefore the Pd-like character decreased in the 1:1 and 1:4 catalysts. The higher dipropyl ether formation on PdPt 4:1 may have been due to reactions not accompanied by Pd=O formation. In the case of PdPt 1:4 we could observe propane, which is only typical of sites with high Pt content.

#### 5. Conclusions

Unsupported Pd, Pt and PdPt bimetallic catalysts were prepared in different atomic ratios using methods of colloid chemistry. They were tested in acrolein hydrogenation. In the reaction three types

of products can be formed: the C=C double bond is hydrogenated to give a saturated aldehyde (propanal) or the C=O double bond is involved, yielding an unsaturated alcohol (allyl alcohol) and finally total hydrogenation can occur resulting in a saturated alcohol (propanol). The formation of propanal by C=C bond hydrogenation was the main reaction on each catalyst. The catalysts showed different behaviour in secondary reactions. Under the same reaction conditions – low temperature (323 K) and high hydrogen pressure (400 Torr) – the formation of dipropyl ether was observed over Pd, while propane and propanol were produced on Pt catalyst. The selectivity pattern on bimetallic catalysts was different from that observed on monometallic ones: dipropyl ether was also formed, but the selectivity was higher 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 (Fig. 3). At high temperature (473 K) acrolein underwent hydrogenolysis over each catalyst. The selectivity of ethane was similar over Pd and the bimetallic catalysts and was lower only on monometallic Pt (Fig. 4). The differences between catalysts can be explained by the various adsorption behaviour on the metal components. Surface–subsurface interactions between the atoms of the two metals [7,8] are possible, but could not be detected in our dispersed catalysts. The different reaction pathways are summarized in Scheme 1.

#### References

- [1] G.V. Smith, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic Press, San Diego, 1999.
- [2] M. Bartók, Á. Molnár, in: S. Patai (Ed.), *Heterogeneous Catalytic Hydrogenation, The Chemistry of Functional Groups, Suppl. A3: The chemistry of double-bonded functional groups*, Wiley, Chichester, 1997, pp. 843–908.
- [3] B. Coq, F. Figueras, P. Geneste, C. Moreau, P. Moreau, M. Warawdekar, *J. Mol. Catal.* 78 (1993) 211.
- [4] M.A. Vannice, B. Sen, *J. Catal.* 115 (1989) 65.
- [5] F. Coloma, A. Sepulveda-Escribano, J.L.G. Fierro, F. Rodriguez-Reinoso, *Appl. Catal. A* 150 (1997) 165.
- [6] C.G. Raab, J.A. Lercher, *Catal. Lett.* 18 (1993) 99.
- [7] L.E. Murillo, A.M. Goda, J.G. Chen, *J. Am. Chem. Soc.* 129 (2007) 7101.
- [8] L.E. Murillo, J.G. Chen, *Surf. Sci.* 602 (2008) 919.
- [9] Z. Poltarzewski, S. Galvagno, R. Pietropaolo, P. Staiti, *J. Catal.* 102 (1986) 190.
- [10] P. Reyes, M.C. Aguirre, J.L.G. Fierro, G. Santori, O. Ferretti, *J. Mol. Catal. A* 184 (2002) 431.
- [11] S. Galvagno, A. Donato, G. Neri, R. Pietropaolo, G. Capannelli, *J. Mol. Catal.* 78 (1993) 227.
- [12] B. Coq, F. Figueras, C. Moreau, P. Moreau, M. Warawdekar, *Catal. Lett.* 22 (1993) 189.
- [13] I. Kun, Gy. Szöllösi, M. Bartók, *J. Mol. Catal. A* 169 (2001) 235.
- [14] P. Reyes, C. Rodriguez, J. Fernandez, G. Pecchi, J.L.G. Fierro, *React. Kinet. Catal. Lett.* 74 (2001) 127.
- [15] Gy. Szöllösi, B. Török, L. Baranyi, M. Bartók, *J. Catal.* 179 (1998) 619.
- [16] P. Gallezot, D. Richard, *Catal. Rev., Sci. Eng.* 40 (1998) 81.
- [17] F. Delbecq, P. Sautet, *J. Catal.* 152 (1995) 217.
- [18] B. Veisz, L. Tóth, D. Teschner, Z. Paál, N. Györfly, U. Wild, R. Schlögl, *J. Mol. Catal. A* 238 (2005) 56–62.
- [19] N. Györfly, L. Tóth, M. Bartók, J. Ocskó, U. Wild, R. Schlögl, D. Teschner, Z. Paál, *J. Mol. Catal. A* 238 (2005) 102–110.
- [20] L. Xiuli, L. Baozong, C. Manhuan, D. Yukou, W. Xiaomei, Y. Ping, *J. Mol. Catal. A* 284 (2008) 1.
- [21] Z. Yuankui, L. Shijian, X. Yun, Y. Daorong, *Appl. Catal. A* 192 (2000) 247.
- [22] D. Teschner, D. Duprez, Z. Paál, *J. Mol. Catal. A* 19 (2002) 201.
- [23] R.L. Augustine, *Catal. Rev., Sci. Eng.* 13 (1976) 285.
- [24] C. Hoang-Van, O. Zegaoui, *Appl. Catal. A* 164 (1997) 91.
- [25] J.H. Sinfelt, *Adv. Catal.* 23 (1973) 91.
- [26] S. Nishimura, T. Itaya, *Chem. Commun.* (1967) 422.
- [27] M. Bartók, A. Fási, F. Notheisz, *J. Catal.* 175 (1998) 40.
- [28] D. Loffreda, F. Delbecq, F. Vigné, P. Sautet, *J. Am. Chem. Soc.* 128 (2006) 13.
- [29] T.B.L.W. Marinelli, V. Ponec, *J. Catal.* 156 (1995) 51.