CHEMISTRY LETTERS, pp. 1403-1406, 1983.

AN IMPROVED METHOD TO PREPARE CATALYSTS FOR THE SELECTIVE DECARBONYLATION OF FURAN-2 CARBOXALDEHYDE INTO FURAN

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We are able to produce pure furan and pure carbon monoxide from furan-2 carboxaldehyde using an improved catalyst. This new catalyst (Pd/C - K_2CO_3) is activated by UV irradiation at 254 nm for 1 h.

Many studies were devoted to the decarbonylation of furan-2 carboxaldehyde - an aldehyde obtained by acid hydrolysis of pentoses - in order to produce furan. The more recent papers [1-4] show that this reaction can be selectively performed but the short life time of the various catalysts use hinders any scaling up of the process on an industrial scale.

We reproduced the previously described reactions and decided to use palladium metal deposited on various supports. Some of our results are summarized in Table 1 and show the marked influence of the support.

In the case of carbon as carrier, the yields can be strongly affected according to the commercial origin of the support since the presence of various elements as impurities could induce a lowering of the catalytic activity. Systematic analysis of the catalyst samples collected before and after reaction have shown no significant changes in the composition of heavy elements (palladium, traces of sulfur, chlorine, silicon,..) ; this was also established when the catalytic run was ineffective in decarbonylating the substrate. For this reason we believe that the influence of particle size could be determinant on the catalytic activity of palladium.[5-7]

Palladium is used as catalyst and running the reaction in a flask equipped with a mechanical stirrer and a distillation column to produce selectively pure furan and carbon monoxide. The reaction was carried out at 162°C and the furan distilling off at the column head was condensed and collected.

Table 1. Decarbonylation of furan-2 carboxaldehyde on supported catalysis [a)]

Catalyst 5 % Pd/support	Turnover-rate (h^{-1})
Pd/C	150
Pd/Al_2O_3	30
Pd/$BaSO_4$	3
Pd/$CaCO_3$	7
Pd/silicic acid	traces

a) Conditions :

reactor : 100 ml ; distillation column : 30 cm ; T = 162°C ;
batch process ; reaction time = 5 h ;
furfural/palladium ratio = 50 ml/60 mg of metal ;
the products were analysed by GPC

In order to increase the yield, we used mixtures of the catalyst with alkaline metal salts, in particular K_2CO_3 as previously mentionned in the literature.[8-11)] ESCA revealed the presence of Pd atoms which have adsorbed oxygen as shown by the chemical shifts. Before reaction, when the surface of the catalyst was cleaned by Ar^+ ions on 300 Å no potassium was detected. The same analysis of Pd/C - K_2CO_3 mixture after a catalytic run clearly indicates the presence of potassium alone in the first layers whereas after etching of almost 300 Å (4 kV, 60 Å during 90 s) palladium was again observed. The first observation can be interpreted as the result of the migration of the potassium atoms inside the catalyst and giving rise to active sites with palladium clusters of convenient size. Indeed for other catalytic systems Praliaud and co-workers [12)] have proposed that the enhancement of the catalytic activity, when K^+ ions are added to Ni/SiO_2, is due to an increase of the size of the metallic particles. Deactivation of the catalyst could be the consequence of the formation of a potassium layer which prevents the organic molecules from reaching the active sites and also because the right particules size would be lost.

We have found that UV irradiation (254 nm) of Pd/C catalyst under room conditions for 1 h induces a remarkable increase of activity. Turnovers as high as 4600 g of furan/g Pd were reached but in this case loss of activity was rapidly observed. Addition of K_2CO_3 after irradiation cancels any gain and restores the activity of Pd/C alone.

Moreover we have observed that irradiation of a mixture Pd/C - K_2CO_3 for 1 h yields a good catalyst for this decarbonylation (Table 2). Indeed, after a slight decrease of activity, the production of furan was observed to remain steady. Some preliminary experiments of extended duration revealed that turnovers as high as 13000 g of furan/g of palladium were achieved without any significant deactivation. Such a result has never been reported in the literature and allows *hope for adopting this method to produce furan.*

Table 2.

	Duration (h)	Turn over rate (h^{-1})
Pd/C without irradiation	100	45
Pd/C with UV irradiation (1 h)	53	68
Pd/C + K_2CO_3 (1/1)	105	84
Pd/C + K_2CO_3 (1/1) with UV irradiation (1 h)	53	94

Conditions : reactor : 250 ml ; distillation column : 30 cm ; T : 162°C ; long duration process (the concentrations were maintained almost constant during all the experiments).

Furfural/palladium ratio : 150 ml/45 mg of metal.

Preliminary studies of this catalyst by ESCA have shown that deep penetration of the potassium atoms occur as previously described and after the catalytic cycles were performed for 280 h a layer of potassium surrounding palladium atoms on carbon is formed.

Thus simultaneous addition of K_2CO_3 and UV irradiation cause the palladium atoms to reach a convenient cluster size ; presumably these clusters do not contain potassium atoms at all. In the case of the mixture of Pd/C - K_2CO_3 the irradiation should induce the formation of clusters having a stable size whereas in the case of addition of K_2CO_3 after irradiation diffusion phenomena of K^+ atoms leading to rearrangement of the metallic particles could explain the weak catalytic activity for long time reactions.

We presently focus our attention to gain more insight in the mechanism of this activation.

The authors are grateful to Agrifurane and Co, Agen (France) for financial support and a research grand to P.L.

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(Received December 17, 1982)