Supporting information

Efficient Palladium Catalysis for the Upgrading of Itaconic and Levulinic Acid into 2-Pyrrolidones followed by their Vinylation into value added Monomers

Yannik Louven,^a Moritz O. Haus^a Marc Konrad^a, Jan P. Hofmann^b and Regina Palkovits^{a*}

^aInstitut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, Worringerweg 2, Aachen, DE-52074

^bLaboratory for Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

*corresponding author: palkovits@itmc.rwth-aachen.de

Table of Contents

Experimental	1
Catalyst Characterization	1
HAADF-STEM	3
Temperature Programmed Redcution (TPR)	5
X-Ray Photoelectron Spectroscopy (XPS)	5
Catalyst Recycling	7
Absence of Mass Transport Limitations	8
Hydrogenation of Further Dicarboxylic Acids	10
Purification and Identification of Chemicals	10

Experimental

Calculation of Conversion and Yield

.

Conversion and yield for the reductive amidation of itaconic acid are calculated from concentrations determined via HPLC through the assumption of mass conservation within the autoclave. The following definitions are applied for the conversion X and the yield Y_i :

$$X = 1 - \frac{\sum_{non-reduced} n_i}{n_{substrate}(t=0)}$$
(1)

$$Y_i = \frac{n_i}{n_{substrate}(t=0)}$$
(2)

Conversion and yield for the vinylation of 2-pyrrolidones were calculated from concentrations determined via GC. The following definitions are applied for the conversion X_i and the yield Y_i:

$$X = 1 - \frac{n_{substrate}(t=i)}{n_{substrate}(t=0)}$$
(3)

$$Y_i = \frac{n_i}{n_{substrate}(t=0)}$$
(4)

Catalyst Characterization

Methods

Different properties of the utilized Pd-catalysts were characterized by means of ICP-OES, N2-physisorption, HAADF-STEM, CO-pulse chemisorption and temperature programmed reduction (TPR). For ICP-OES measurements an aliquot of the reduced catalyst was dissolved in aqua regia using a microwave digestion vessel. The resulting clear liquid was diluted and measured on a SPECTROBLUE ICP-OES machine. N₂-physisorption was conducted on a QUADRASORB[™] SI (by Quantachrome) after degassing each sample at 150 °C in HV. BET surface areas were calculated from five adsorption points in the range $p/p_0 = 0.05-0.25$ (adsorption branch). TEM images were taken on a FEI Tecnai F20 operated in HAADF-STEM mode. For the determination of palladium particle size distributions, several hundreds of particles per catalyst were evaluated by application of the ImageJ software to the recordings. Several positions on the sample were included for the evaluation to guarantee statistical soundness of the obtained particle size data. For CO-pulse chemisorption, 40mg of dry and reduced sample was weighed into a quartz U-tube, functioning as fixed bed reactor. The filled tube was placed in a Micromeritics AutoChem 2950 HP, where potential passivation layers were removed from palladium by a mild reduction at 200 °C (5 vol.% H₂ in Ar, 30 min). Next, hydrogen was removed by continuously flowing He at 200 °C for 30 min, before cooling down to room temperature and pulsing defined amounts of CO into the He flow. The amount of surplus CO was determined by means of a TCD located at the gas outlet. Dispersion values were calculated from the total amount of adsorbed CO and the metal content of the sample, assuming a stoichiometry of one molecule of carbon monoxide per surface metal atom. For temperature programmed reduction (TPR) 50 mg of dry impregnated sample was weighed into a quartz U-tube, functioning as fixed bed reactor. The filled tube was placed in a ChemBET Pulsar (Quantachrome). To ensure a completely dry sample, the U-tube was heated to 120 °C and kept there for 30 minutes under He-flow. For the TPR measurement a flow of 5 % H₂ in Argon was applied and the Utube was heated from room temperature to 600 °C at a rate of 5 K/min. Hydrogen consumption was detected with a thermal conductivity detector (TCD).

Results

Avg. Pd particle **BET Surface ICP-OES** Metal Dispersion (CO-Pore Pulse) [%] Area Volume Content diameter Material (STEM) [nm] [m² g⁻¹] [ccm g⁻¹] [mg g⁻¹] NORIT A Supra 1866 0.923 -NORIT A Supra (ox.) 1061 0.569 _ -5wt.% Pd/C_Cl_350 1504 1.011 2.40 22.9 44.7 5wt.% Pd/C(ox.) Cl 350 0.527 1.99 25.0 926 51.5 5wt.% Pd/SiO2_Cl_350 222 1.044 39.7 3.57 5.1 5wt.% Pd/Al₂O₃_Cl_350 224 0.723 38.5 3.10 4.7 5wt.% Pd/C(ox.)_Cl_250 0.676 30.1 852 51.1 1.22 5wt.% Pd/C(ox.)_Cl_300 983 0.556 51.0 1.77 29.9 0.704 5wt.% Pd/C(ox.)_Cl_400 888 48.5 2.24 22.6 5wt.% Pd/C(ox.) Cl 450 1165 0.635 48.3 2.67 16.8 5wt.% Pd/C(ox.)_Cl_350_used 588 0.339 39.1 1.92 0.7

Table S1: Physical properties of the supported Palladium catalyst (Pd/C).

The synthesized Pd/C catalysts were subjected to characterization using the methods detailed above (**Table S1**). The results indicate that the nominal and actual palladium loading match well. The slightly lower Pd concentration in the used sample can be explained by adsorbed organic species on the surface, as the mass of the catalyst was higher after the reaction. The ratio of noble metal to substrate used in our reactions is as low 0.1 mol.%, highlighting the activity of palladium for the challenging hydrogenation of imide carbonyls. This is at least partly due to the high surface area of activated carbon, which allows for good dispersion and thus utilization of the noble metal component.

This aspect was further analysed by HAADF-STEM. The recorded images show a uniform distribution of Palladium particles (evidenced by EDX) on the carbon supports. On the oxidic supports several bigger agglomerated particles were found (**Figure S1**). The average Pd particle diameter (d_{avg} .) increased with increasing reduction temperature (**Figure S2**). The particle size distribution is narrow at reduction temperatures between 250 and 350 °C and broadens at 400 and 450 °C. Average Pd particle diameters calculated from CO-pule measurements show a similar trend but the absolute values are 2 - 3 times larger than diameters observed in HAADF-STEM. The difference can be caused by several reasons. Firstly is was assumed that each CO molecule only adsorbs on one Pd atom, but also threefold-hollow site and bridge site adsorption as possible.¹ Furthermore the CO adsorption decreases with increasing Pd particle size as CO-metal interaction is stronger on low-coordinated Pd atoms. That leads to especially high Pd particle sizes calculated from CO pulse for the catalysts made with metal-oxides as support. Here also strong metal support interactions can lower the adsorption of CO.

HAADF-STEM: Exemplary Images and Histograms



Figure S1: HAADF-STEM images of 5 wt.% Pd catalysts on different supporting materials (from top to bottom: SiO₂, AI_2O_3 , activated carbon (A Supra) and oxidised activated carbon (ox. A Supra)). Palladium particles (evidenced by EDX) are visible as bright dots. Multiple STEM images were used for every catalyst to evaluate the average particle size. Pd particle size distribution is shown in histograms on the right. *individual particle size is calculated based on the assumption of (half-)spherical particles. $d_{avg.}$ is given on a number basis.



Figure S2: HAADF-STEM images of 5 wt.% Pd/C(ox.) reduced at 5 different temperatures in a range from 250 to 450 °C. Palladium particles (evidenced by EDX) are visible as bright dots. Multiple STEM images were used for every catalyst to evaluate the average particle size. Pd particle size distribution is shown in histograms on the right. *individual particle size is calculated based on the assumption of (half-)spherical particles. d_{avg.} is given on a number basis.

Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) results of the carbon supported palladium catalysts are displayed in **Figure 3**. Both catalysts have a reduction peak/ shoulder at 180 °C followed by a second peak at 200/ 220 °C. While the first peak is similar for both catalysts, the area of the second signal is bigger for the catalyst prepared with the oxidized support. It can be assumed that the second signal relates to the reduction of surface groups of the supporting material. That would suggest an intense interaction between palladium nanoparticle and supporting material for the catalyst prepared with the oxidized support.



Figure S3: TPR Temperature programmed reduction (TPR) of the Pd/C catalysts with oxidized/unoxidized support.

X-Ray Photoelectron Spectroscopy (XPS)

Table S2: Distribution of palladium species on carbon supported catalysts. Palladium species were assigned to: Pd^{0} (BE(Pd3d_{5/2}) = 335.0-335.3 eV), $Pd^{\delta+}$ (BE(Pd_3d_{5/2}) = 335.9-336.1 eV) and Pd^{0x} (BE(Pd_3d_{5/2}) = 337.4-337.6 eV).

catalyst	Pd ⁰ [%]	Pd ^{δ+} [%]	Pd ^{ox} [%]
5%Pd/C_Cl_350	20	57	23
5%Pd/C(ox.)_Cl_350	14	61	24
5%Pd/C(ox.)_Cl_350 (used)	5	17	79
5%Pd/C(ox.)_Cl_250	0	44	56
5%Pd/C(ox.)_Cl_300	23	52	25
5%Pd/C(ox.)_Cl_350	14	61	24
5%Pd/C(ox.)_Cl_400	50	27	23
5%Pd/C(ox.)_Cl_450	54	36	10



Figure S4: Pd^{3d} Area of the 5 wt.% Pd/C(ox.) catalysts reduced at 5 different temperatures in a range from 250 to 450 °C (top to bottom).



Figure S5: Pd^{3d} Area of 5 wt.% Pd/C(ox.) and 5 wt.% Pd/C.

Catalyst Recycling



Figure S6: Recycling of 5% Pd/C(ox.)_350. Reaction conditions: 220 °C, 50 bar H_2 , 750 RPM, 1 h, 1.5 g itaconic acid, 1.5 g 25% NH₄OH solution, 0.5 g H₂O, 50 mg catalyst.



Figure S7: HAADF-STEM images of the 5wt.% Pd/C(ox.)_350 (a) prior to and (b) after reaction.



Figure S8: Pd^{3d} Area of the fresh (b) and recycled (a) catalyst.

Nature of the Catalytic Active Species

Methods

To proof the heterogeneous nature of the catalyst a hot filtration test was performed. Therefore the reaction was stopped after 1 hour reaction time, the catalyst was separated from the reaction solution and the solution was fed back into the autoclave and the reaction was continued for another hour.

Results

The concentration of 3- and 4-methyl-2-pyrrolidone increased after removal of the catalyst by 3 % from 46.1 mol% to 49.4 mol%. This small change can be caused by the error of the HPLC method. Thereby, the heterogeneous nature of the catalytically active species is confirmed.

Absence of Mass Transport Limitations

Methods

The absence of mass transfer limitations was asserted by testing for the influence of (i) stirring intensity and (ii) catalyst loading on the outcome of reductive amidation experiments. Experimental procedures and other parameters were as discussed in the main text.

Results

The stirring speed was found to have negligible influence on the reaction outcome (Figure S9 a). Minor variations in the determined yield and conversion levels for the displayed experiments can be caused by the chosen HPLC method. Since stirring intensity contributes to better mass transfer between the gas and liquid phases as well as between the bulk liquid and the catalyst grain, mass transfer limitations at these interfaces are unlikely. Further evidence is derived from a variation of catalyst loading (Figure S9 b), while keeping the product of the former with the reaction time constant. Under the assumption of a purely catalytic reaction, with a first order kinetics with respect to the catalyst, equal outcomes are expected for these experiments. Reduced yields, on the other hand, would indicate a suboptimal use of catalyst and thus likely mass transfer limitations. In reality, a slight increase in yield and productivity for the 1 h and 0.30 mol% catalyst loading experiment was found.



Figure S9: Influence of **a**) stirring speed and **b**) catalyst loading of Catalyst 2 (5% Pd/C) on the reductive amidation of itaconic acid. Reaction conditions: 2 h, 750 rpm, 37.5 mg catalyst, 220 °C, 50 bar H₂, 1.5 g itaconic acid, 1.5 g NH₄OH solution and 0.5 g H₂O)

Hydrogenation of Further Dicarboxylic Acids

The reductive amidation of further dicarboxylic acids was tested to investigate if the same intermediated are formed and the reaction proceeds via the same reation path. The conversion of maleic acid and succinic acid lead to lower yields but the same intermediates are found (**Table S3**). For comparison the conversion of itaconic acid is shown in the table as well (entry 3).

Entry	Substrate	Yield	Conversion	Productivity	c(Acid)	c(Monoamide)	c(Diamide)	c(Imide)	c(Pyrrolidone
		[%]	[%]	[mol/mol/h]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]
1	Maleic Acid	37.3	57.8	119.7	10.1	16.8	7.9	7.5	37.3
2	Succinic Acid	37.1	59.5	118.4	11.2	16.5	7.0	5.9	37.1
3	Itaconic Acid	78.3	85.0	256.4	3.2	6.9	1.6	3.4	78.3

Table S3: Reductive amidation of different dicarboxylic acids. Reaction conditions: 220 °C, 50 bar H₂, 2 h, 0.15 mol% Pd.

Purification and Identification of Chemicals

Methods

¹H-NMR spectra were recorded on a Brucker Avance III (400 Hz) at room temperature. DMSO-d6 was used as NMR solvent.

Results

Mixtures of 3- and 4-methyl-2-Pyrrolidone as well as 5-methyl-2-pyrrolidone were synthesized as described before from itaconic and levulinic acid, respectively. Afterwards the desired products were obtained through distillation at reduced pressure (ca. 0.03 mbar, 64-67 °C (3/4MP), 60-64 °C (5MP) top end). The ¹H-NMR spectra of the purified pyrrolidones (**Figure S10 and S11**) are in line with expectations and show good purities.

The synthesized pyrrolidones were then vinylated with acetylene in the presence of KOH as catalyst. The desired products were obtained thorough distillation at reduced pressure (ca. 0.03 mbar, 28-32 °C (3/4MNVP), 30 °C (5MNVP). The ¹H-NMR spectra of the purified pyrrolidones (**Figure S12 and S13**) are in line with expectations and show good purities.



Figure S10: ¹H-NMR spectrum of 3- and 4-methyl-2-pyrrolidone from the reductive amidation of itaconic acid.



Figure S11: ¹H-NMR spectrum of 5-methyl-2-pyrrolidone from reductive amination of levulinic acid.



Figure S12: ¹H-NMR spectrum of 3 and 4-methyl-N-vinyl-2-pyrrolidone from vinylation with acetylene.



Figure S13: ¹H-NMR spectrum of 5-methyl-N-vinyl-2-pyrrolidone from vinylation with acetylene.

Literature

1 J. B. Giorgi, T. Schroeder, M. Bäumer and H.-J. Freund, *Surface Science*, 2002, **498**, 71-77.