

SPR16 Application Note

Testing of Palladium Catalysts for CO/Vinyl Arene Polyketones Synthesis

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The perfectly alternating palladium catalysed CO/vinyl arene copolymerisation is a well known example of a homogeneously catalysed reaction which suffers from deactivation, mainly due to the decomposition of the active species to inactive palladium metal, resulting in catalyst death and limiting the possibility of obtaining high molecular weight polymers.

A series of cationic palladium complexes containing different substituted phenanthroline ligands were prepared from the corresponding neutral chloro derivatives. The catalytic behaviour of a series of complexes in the CO/styrene and CO/*p*-Me-styrene copolymerisations was studied in detail using SPR16 reactors.

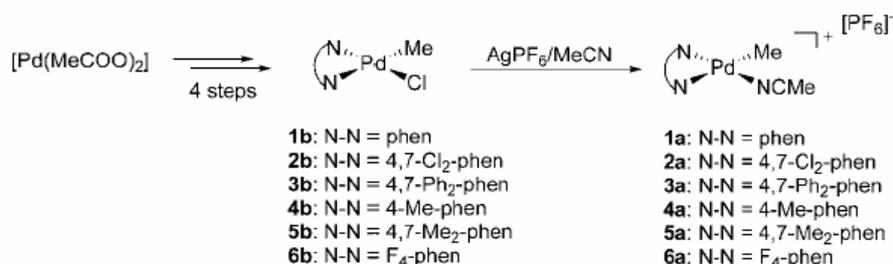


Figure 1: Synthetic pathway of the monocationic palladium complexes 1a-6a

The general procedure for the experiments was as follows: four stainless steel autoclaves of the SPR16 were flushed with argon one time. A 20ml solution of the Pd catalyst and 1,4 benzoquinone in trifluoroethanol was prepared and the reactors were charged with 5ml of the catalyst solution and 3ml of the alkene comonomer. The atmosphere in the reactor was exchanged with carbon monoxide and the reactors pressurised to either 5 or 10 bar. After heating to the desired temperature, the final pressures were adjusted and kept constant throughout the experiment. The carbon monoxide uptake was monitored automatically using the SPR16 pressure sensors and mass flow controller.

Kinetic investigations on this catalytic system were performed using the SPR16, which allows CO uptake to be monitored during the copolymerisation reactions. The tests were performed in the presence of benzoquinone in order to stabilise the active species, at 30°C, under different CO pressures (5 and 10 bar), solvent trifluoroethanol, with alkene to Pd ratios of around 24,000. In all experiments the amount of copolymer obtained at the end of the runs was in good agreement with the value of the CO consumption measured by the instrument.

An example of the results with the SPR16 is shown below:

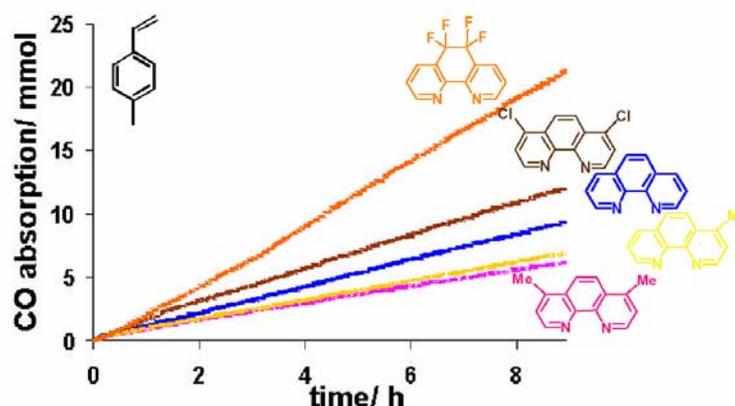


Figure 2: CO/*p*-Methylstyrene copolymerisation: effect of N-N ligand and CO pressure on CO uptake. Catalyst precursor: $[\text{Pd}(\text{Me})(\text{MeCN})(\text{N-N})][\text{PF}_6]$. Reaction conditions: $n_{\text{Pd}} = 0.425 \times 10^{-5}$ mol; $T=30^\circ\text{C}$; styrene $V = 3$ ml; solvent: 2,2,2-trifluoroethanol, $V=5$ ml; $[\text{BQ}]/[\text{Pd}]=5$; $t=9$ h

For all the tested catalysts a linear dependence of CO uptake with time was found and no catalyst deactivation was observed over the investigated range of time, up to 90 hours. The large excess of the aromatic alkene ensures that the reaction is pseudo zero order with respect to the alkene even at long reaction times.

The authors carried out analogous experiments using 1a, 4a and 5a as catalysts in the CO/*p*-Me-styrene copolymerisation at 5 and 10 bar, compared the activity of the two alkenes with different precatalysts, and modified ligands containing electron withdrawing substituents, 4,7-Cl₂-phen and F₄-phen.

On the basis of the catalytic results a clear correlation between the catalytic activity of the complexes and the electron density of the palladium was concluded to exist. In particular, the activity decreases on increasing the electron density on the metal centre, which, in turn, is tuned by substituents.

The study allowed the authors to recognise the (F₄-phen)-Pd complex, $[\text{Pd}(\text{Me})(\text{MeCN})(\text{F}_4\text{-phen})][\text{PF}_6]$ as the best ever catalyst reported for the CO/vinyl arene copolymerisation reaction: it showed very high catalytic activity and productivity, yielding the corresponding polyketones with an M_w value of 1,000,000 and with a degree of stereoregularity of 96% in the *uu* triad.

Original Article

Long-Lived Palladium Catalysts for CO/Vinyl Arene Polyketones Synthesis: A Solution to Deactivation Problems
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