Pd-nanosalts-catalyzed polymerization of ethylene and CO

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Abstract: Thermoplastic polyketones have been synthesized from CO and ethylene in the presence of Pd-nanosalts. By employing nano-sized catalysts, reactor fouling issue of polyketone polymer was resolved. In this study, we present a synthetic methods for the generation of Pd-nanosalts from Pd catalyst precursors and ammonium-tethered carboxylic acids, and the synthesis of polyketones using Pd-nanosalts.
Keywords: C1 resource, CO, ethylene, Pd-nanosalts.

1. Introduction

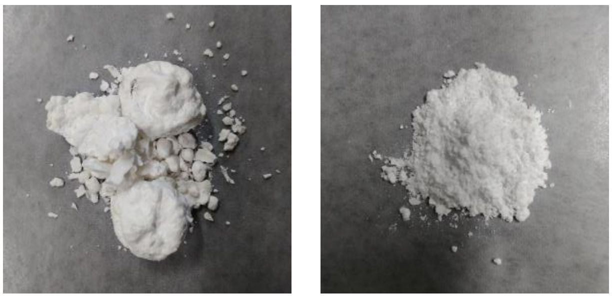
Polyketones are attractive in the polymer industry due to high impact strength and chemical resistance, and are considered as a promising materials to convert C1 gas (CO) to useful chemicals. The main disadvantage of the synthesis of polyketones is the reactor fouling where polymers are adhered to the reactor. In order to resolve the problems related to the reactor fouling, excessive strong acids and heterogeneous materials are added during the process. Based on our previous research on developing heterogeneous catalysts for polyketones, we found out that heterogenous seed-type catalysts may play an important role for antifouling polyketone synthesis. Therefore, we came up with an idea to generate the heterogeneous catalysts *in situ* from homogeneous catalyst precursors, which will be presented in this presentation.

2. Experimental

[1,3-Bis(di-*o*-methoxyphenylphosphino)propane]Pd$(OAc)_2$, i.e., [(domppp)Pd$(OAc)_2$] was prepared by the synthetic procedure reported in the literature.[4] An autoclave (70 mL) was charged with methanol(10 mL), [(domppp)Pd$(OAc)_2$] (1.5 mg, 2.0 μmol) and A salt(Betaine hydrochloride) (0.23 mg, 1.5 μmol). The air in the autoclave was replaced with ethylene gas 10 bar with stirring. And then, the autoclave was vented. The autoclave was recharged with ethylene gas 25 bar and subsequently charged with CO gas to 60 bar. The reaction mixture was stirred (500 rpm) and heated at 90 ℃ for 15 hours. After the reaction, the autoclave was cooled to room temperature, then unreacted gases were vented. The product was filtered with methanol and washed dichloromethane and diethyl ether, which were dried in oven at 65 ℃.

3. Results and discussion

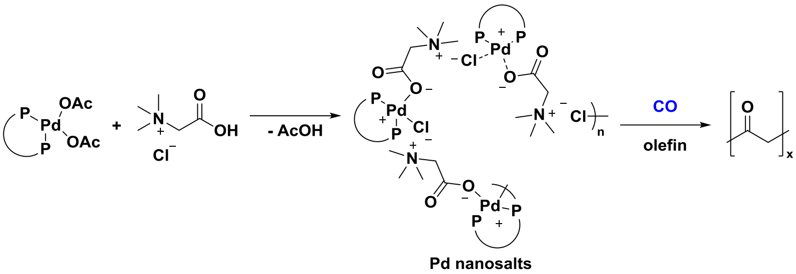
The use of *p*-TsOH with [(domppp)Pd$(OAc)_2$] showed good activities (21 kg/g of Pd). But the reactor fouling was observed. In contrast, when we used A salt with [(domppp)Pd$(OAc)_2$], the reaction showed 22 kg/g of Pd activities without reactor fouling (Figure 1). Furthermore, the polymer showed good bulk density (0.32 g/mL).



(a) **(b)**

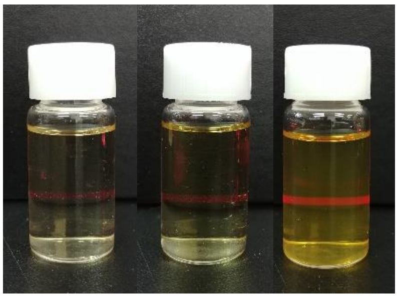
Figure 1. Photographs by the polymerization using (a) *p*-TsOH with reactor fouling. (b) A salts without reactor fouling.

Strong acids such as trifluoroacetic acid (TFA), and *p*-toluenesulfonic acid (*p*-TsOH) are mainly used for the synthesis of polyketones. In comparison, it is not effective to add weak acids such as normal carboxylic acids. In the case of ammonium-tethered carboxylic acids, the acidity becomes stronger due to the positively charged ammonium group. It is used as an anionic ligand capable of coordination to palladium ions. Ammonium-tethered carboxylic acids can replace the acetate ligands of palladium ions, which afford stable Pd-nanosalts (Scheme 1). As a result, stable Pd-nanosalts are used to synthesize polyketones without reactor fouling.



Scheme 1. Pd-nanosalts catalyzed polymerization of ethylene, CO.

To probe the formation of Pd-nanosalts, the colloidal properties of solutions containing Pd catalyst only, Pd catalyst with A salt, and only A salt were compared (Figure 2). Tyndall phenomenon was observed with solutions containing Pd catalysts regardless of A salt. Even with the solution of only A salt. Tyndall phenomenon was observed, but it was not accurately analyzed by DLS. However, the solutions containing Pd catalysts with A salts were clearly analyzed by DLS. Based on these results in the presence of ammonium-tethered carboxylic acids, the colloidal Pd-nanosalts are formed and they prevent reactor fouling.



(a) **(b)** **(c)**

Figure 2. Tyndall phenomenon observation (a) only A salts, (b) only Pd catalyst, (c) Pd catalyst with A salts.

4. Conclusions

In conclusion, the carboxylic acid with a positively charged ammonium groups interacts with palladium ions to form stabilized nanosalts. The average particle size of the nanosalts were analyzed by DLS Studies, and the colloidal properties of the solutions were observed through Tyndall phenomenon. By using *in situ* generated heterogeneous Pd-nanosalts from homogeneous precursor, reactor fouling of polyketone polymers was completely prevented.

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