

Catalytic hydrodechlorination of chloroform to olefins with Pd supported on activated carbons obtained by chemical activation of lignin

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Introduction

Olefins are one of the most important compounds in petrochemical industry because of their use on many syntheses. The most common process to produce them is steam cracking. This process requires high temperatures and high pressure, and thus a high energy consumption. New alternative technologies have appeared in the recent years to reduce this energy consumption. One of the most interesting is catalytic hydrodechlorination (HDC) of chlorinated volatile organic compounds (CIVOCs), which is also useful for the treatment of these dangerous CIVOCs in gas streams. The purpose of this study is the obtention of light olefins by HDC of chloroform (CLF) with Pd catalysts supported on activated carbons obtained by chemical activation of lignin with different activating agents.

Materials and Methods

Five activated carbons were synthesized as supports by chemical activation of lignin using FeCl₃, ZnCl₂, H₃PO₄, NaOH and KOH as activating agents. In the case of activation with FeCl₃, ZnCl₂, H₃PO₄, lignin samples were physically mixed with an activating agent: precursor mass ratio, equal 3:1 and dried for 24 h at 60 °C. The impregnated samples were heat-treated in a tubular furnace under continuous N₂ flow (200 Ncm³·min⁻¹) at 500 °C in the case of H₃PO₄ and ZnCl₂ and 800 °C for FeCl₃. The activation temperature was reached at 10 °C·min⁻¹ heating rate and maintained for 2 h. In the case of NaOH and KOH- activations, lignin was previously carbonized at 500 °C at the same aforementioned conditions and then activated at 800 °C using an activating agent:lignin mass ratio of 4:1. After cooling down to room temperature, the samples were washed with a 0.1M HCl aqueous solution, rinsed with distilled water until neutral pH of the washing water and finally filtered and dried for at 60 °C overnight. Pd was deposited on the activated carbons by incipient wetness impregnation, with a PdCl₂ 1M HCl aqueous solution, to obtain a nominal 1.0 wt.% of Pd, been finally dried overnight in an oven at 70°C. The catalysts were denoted as follow: FeCPd, ZnCPd, PCPd, NaCPd and KCPd. The catalysts were characterized by several techniques as N₂ adsorption-desorption at -196°C, X-ray photoelectron spectroscopy (XPS), X-ray diffraction spectroscopy (XRD), transmission electronic microscopy (TEM) and temperature programmed desorption (TPD).

The HDC experiments were performed in a continuous flow reaction system (Micro-Activity by PID) described elsewhere, using a quartz fixed bed reactor micro-reactor. The catalyst was previously reduced “in situ” under a H₂ flow (50 Ncm³·min⁻¹) at 300 °C for 2 h. The operating

conditions were atmospheric pressure, total flow rate of $100 \text{ Ncm}^3 \cdot \text{min}^{-1}$, an inlet chloroform concentration of 1000 ppmv with a H_2/CLF molar ratio of 50:1. The reactor outlet was coupled to a gas chromatograph (Varian 450-GC), equipped with a FID detector.

Results and Discussion

The five catalysts showed complete CLF conversion at the initial time at 300°C although different deactivation profiles were obtained after 50 hours of time on stream. FeCPd catalysts showed a fast deactivation which activity decreased by 60 % after 3 hours of experiment. Meanwhile KCPd, NaCPd and PCPd showed a constant similar deactivation profile, ZnCPd showed full conversion at the end of the experiment. The evolution of selectivity to olefins with time on stream is represented in Figure 1, where FeCPd showed the highest selectivity to ethylene and propylene (63 %) followed by ZnCPd (57 %). Figure 2 represents the relation between $\text{Pd}^{\text{n+}}/\text{Pd}^0$ ratio studied by XPS and the total amount of $\text{CO}+\text{CO}_2$ desorbed, obtained by TPD. FeCPd and ZnCPd catalysts presented the lowest amount of surface groups (specially quinones and carbonyls) and the highest Pd^0 proportion, the two catalysts that performed the highest selectivity to olefins.

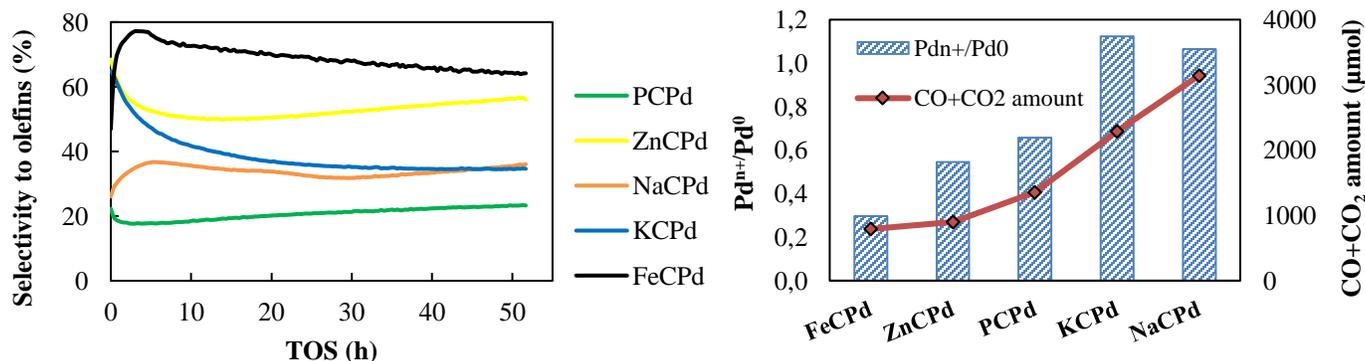


Figure 1. Selectivity to olefins vs time on stream (300°C , $\tau=0.2 \text{ kg h mol}^{-1}$, H_2/CLF molar ratio 50)

Figure 2. Influence of the chemical agent activators on the Pd electron deficiency and $\text{CO}+\text{CO}_2$ desorbed at 300°C

Conclusions

It seems that the presence of carbonyl and quinones groups on catalytic surface promote the complete hydrogenation of reaction intermediates, as they favour strong adsorption of reactants. The sintering of Pd and the accumulation of chlorinated species on the surface, observed by XPS and TEM of the used catalysts after long experiment, produced the different deactivation profile.

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References

1. Amghizar I., Vandewalle L.A., Van Geem K.M., Marin G.B. (2017) New Trends in Olefin Production. *Engineering* 3, 171–178.