

Surface chemistry with model coordination complexes and organometallic clusters for the preparation of noble metal-based carbon-supported nanoparticles

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Introduction

The present work deals with fundamental investigations of molecular approaches aimed at preparing, step-by-step, noble metal-based carbon-supported catalysts from grafted coordination complexes, or organometallic clusters previously anchored on specifically designed organic spacers. Although activated carbons are extensively used as catalyst supports for many liquid phase applications, tailored surface chemistry of these materials definitely remains a challenge when the functionalization is extended beyond the stage of mere oxidation. In this case, a three-step procedure was first developed to obtain a phosphine-functionalized carbon. Carefully selected Pd coordination compounds and organometallic homo- or heterometallic clusters containing Pd, Pt and/or Ru were then chemically grafted onto the functionalized support, activated under appropriate conditions according to the various precursors used, and converted into supported nanoparticles that were thoroughly characterized in terms of composition, dispersion and particle size. The successive steps were monitored whenever possible by various advanced physico-chemical techniques.

Materials and Methods

The support is an active carbon from NORIT (SX PLUS, 50-100 μm , 940 m^2/g , initial total acidity measured by Boehm's titration : 320 $\mu\text{mol/g}$). The precursors taken as model compounds are either Pd coordination complexes [1] like $[\text{Pd}(\text{OAc})_2(\text{bipy})]$, $[\text{Pd}(\text{O}_2\text{CCF}_3)_2(\text{bipy})]$, $[\text{Pd}(\text{OAc})_2(\text{Et}_3\text{NH})_2]$ and $[\text{Pd}(\text{dba})_2]$, or organometallic clusters corresponding to various stoichiometries : five different homometallic Pd clusters ($[\text{Pd}_4(\text{CO})_5(\text{PPh}_3)_4]$, $[\text{Pd}_{10}(\text{CO})_{12}(\text{PR}_3)_6]$ (R= Bu, Ph), $[\text{Pd}_{12}(\text{CO})_{17}(\text{PBu}_3)_5]$, and a higher nuclearity cluster assumed to be $[\text{Pd}_{24}(\text{CO})_{32}(\text{PPh}_3)_3]$), and two heterometallic Ru-based clusters ($[\text{Ru}_5\text{PtC}(\text{CO})_{14}(\text{COD})]$ and $[\text{Ru}_6\text{Au}_2\text{C}(\text{CO})_{16}(\text{PPh}_3)_2]$). The carbon was first functionalized by reaction with HNO_3 , then further derivatized into amines that were later converted into chelating phosphines as recently published [2]. The catalysts were activated thermally under nitrogen flow and characterized by XPS, XRD, SEM, TEM, DRIFTS/MS, SIMS and CO chemisorption. Some of them were tested for their performance in selective oxidation or hydrogenation processes.

Results and Discussion

The grafting process was first investigated with $[\text{Pd}(\text{OAc})_2(\text{bipy})]$ and its fluorinated analog, $[\text{Pd}(\text{O}_2\text{CCF}_3)_2(\text{bipy})]$. XPS and DRIFTS/MS studies indicated that these two complexes exchange their carboxylate ligands for surface $-\text{COOH}$ groups, resulting in grafted “Pd(bipy)” or “Pd(OAc)_x(Et₃NH)_y” residues. The different Pd clusters of variable nuclearity (4, 10, 12 and 24) were anchored on the non-treated and phosphine-functionalized support and activated thermally at 300°C/1h. While higher metal loadings could be achieved on the non-treated support, the Pd dispersion determined by XPS (Pd/C atomic ratio) was

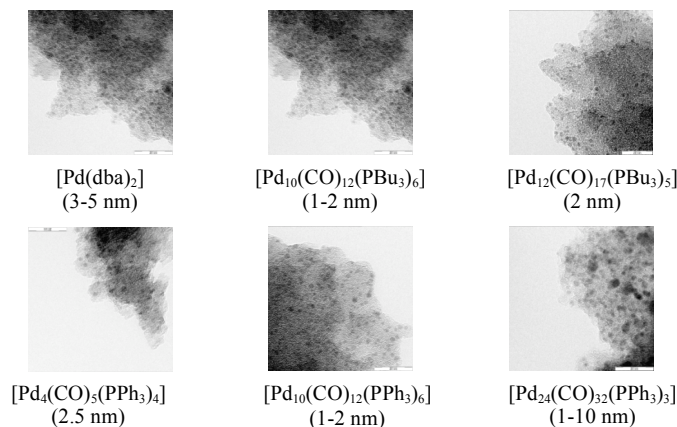
usually higher with the functionalized support. As shown by TEM (Fig. 1), Pd nanoparticles of 1-2 nm in size were obtained with the “Pd₁₀” and “Pd₁₂” clusters, while bigger particles in the range 3-10 nm were obtained with the mononuclear $[\text{Pd}(\text{dba})_2]$ precursor or the “Pd₂₄” cluster.

The grafting mechanism of the “Ru₅Pt” cluster on the functionalized support was demonstrated by SIMS to be a ligand exchange process involving the COD ligand, while the “Ru₆Au₂” cluster was found to decompose and result in a mixture of Ru nanoparticles next to bigger Au particles. XPS showed that the Ru/Pt ratio was retained in the first case, and the formation of mixed-metal particles of 1-2 nm size was proven by TEM/EDXS. The anchoring mechanism was then investigated further by using the $(\text{PPh}_2\text{CH}_2)_2\text{NC}_3\text{H}_7$ ligand to mimic the tethers of the phosphine-functionalized support. After reaction with the “Ru₅Pt” cluster, crystals of $[\text{Ru}_5\text{PtC}(\text{CO})_{14}(\text{PPh}_2\text{CH}_2)_2\text{NC}_3\text{H}_7]$ were isolated, establishing definitely the ligand exchange process occurring at the surface.

Significance and conclusions

Special attention was devoted here to the precursor-support interactions accompanying the incorporation of well-defined metal compounds and clusters on an activated carbon support pre-functionalized with chelating phosphine groups. The strategy was carefully followed throughout the preparation scheme, from the grafting step to the final catalyst, by using a wide panel of advanced techniques and by simulating the surface chemical processes with model systems. The interest of using a phosphine-functionalized carbon support was definitely demonstrated in terms of metal dispersion on the final cluster-derived Pd/C catalysts.

Figure 1. TEM images (and average particle size) of the activated catalysts prepared from different “Pd_n” clusters on the phosphine-functionalized support



References

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