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Understanding of the structure activity relationship of PtPd bimetallic catalysts prepared by surface organometallic chemistry and ion exchange during the reaction of iso-butane with hydrogen

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ABSTRACT

Well-defined silica supported bimetallic catalysts Pt_{100-x} Pd_x were prepared by Surface Organometallic Chemistry (SOMC) and Ionic-Exchange (IE) methods. For all investigated catalysts, *iso*-butane reaction with hydrogen under differential conditions led to the formation of methane and propane, n-butane, and traces of *iso*-butylene. The total reaction rate decreased with increasing the Pd loading for both catalysts series as a result of decreasing turnover rate of both isomerization and hydrogenolysis. In the case of Pt_{100-x} $Pd_{x\mathbf{(SOMC)}}$ catalysts, the experimental results in combination with DFT calculations suggested a selective coverage of Pt (1 0 0) surface by agglomerated Pd atoms like "*islands*", assuming that each metal roughly keeps its intrinsic catalytic properties with relatively small electron transfer from Pt to Pd in the case of Pt-rich sample and from Pd to Pt in the case of Pd-rich sample. For the PtPd catalysts prepared by IE, the catalytic behavior could be explained by the formation of a surface alloy between Pt and Pd in the case of Pd-rich sample and by the segregation of a small amount of Pd on the surface in the case of Pt-rich sample, as demonstrated by TEM, EXAFS and DFT. The catalytic results were explained by a structure activity relationship based on the proposed mechanism of C—H bond and C—C bond activation and cleavage for *iso*-butane hydrogenolysis, isomerization, cracking and dehydrogenation.

1. Introduction

Over the last half century, a tremendous amount of research has been devoted to the study and exploration of a variety of bimetallic catalysts using different combinations of transition and noble metal catalysts in order to improve their catalytic performance (activity, stability, selectivity, and lifetime) for a wide range of catalytic processes [1,2]. The better catalytic behavior observed in the case of heteronuclear systems with respect to their homonuclear analogues has been and still is an intriguing subject and numerous theories have been put forward to explain the synergetic effect observed between the two metals. In particular, the study of bimetallic catalysts containing Pt and Pd has been the subject of a sheer number of reports [3–22]. Such studies have been motivated by the excellent catalytic behavior of these systems in processes such as, oxygen reduction reaction (ORR) [3–7,23], hydrogenation of aromatics [10,11,14,15,24–27] and electro-catalytic oxidation of oxygenates such as ethanol [17,18,28] and formic acid [19–21].

According to recent Density Functional Theory (DFT) studies conducted by Norskov and coworkers [22], the d-band center position (with respect to the Fermi level) of a catalyst can play an important role in determining the catalytic behavior since this parameter is directly related to the adsorption energies of the reactants on a catalyst as well as their activation energy. Indeed, the position of the d-band center has been found to depend on both the strain and the electronic coupling present in the catalyst. In the case of ORR for example, it was claimed that the small compressive strain resulting from the small lattice mismatch between Pt and Pd (it is noteworthy that Pt and Pd exhibit the same face-centered cubic (FCC) and a minor lattice mismatch of only 0.77%) and the electronic coupling between these two metals causes a

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downshift in the d-band center and therefore reduces the binding strength of adsorbed reaction intermediates, such as O and OH [29]. This was claimed to yield an enhancement in the surface coverage of O_2 on the Pt surface and thus an improvement in the ORR catalytic activity of PdPt bimetallic catalysts.

The promoting effect of such electronic coupling between Pt and Pd during the electro-catalytic oxidation of HCOOH [30] and hydrogen over PtPd bimetallic catalysts in the presence of CO [31] has been elucidated. For example, Arenz *et al.* [30] demonstrated that Pd atoms either on the surface or in the surface of Pt (1 1 1) single crystals exhibit three to five times higher activity than Pt atoms for the electro-oxidation of formic acid at 0.4 V. Using FTIR, the authors claim that the presence of Pd would reduce the adsorption of CO intermediates that acts as a poison for Pt monometallic catalysts during the dehydration of HCOOH. Later, Somorjai *et al.* [32] confirmed the results obtained by Arenz *et al.* [33] using Pd/Pt nanoparticles synthesized by localized overgrowth of Pd on cubic Pt seeds during the electo-oxidation of formic acid. Meanwhile, the cyclic voltammetry experiments conducted recently by de Bruijin *et al.* [31] reveal that upon CO saturation only a lower fraction of surface sites is poisoned in the case of PtPd bimetallic catalysts. This resulted in a better catalytic activity of PtPd compared to Pt during the electro-catalytic oxidation of hydrogen in the presence of CO.

PtPd catalysts have been also extensively investigated in the hydroprocessing of petroleum middle distillate fractions due to their interesting catalytic performance during the hydrogenation of aromatics at relatively low temperatures required to overcome thermodynamic limitations [10,11,34]. Indeed, it is well known that supported Pt noble metal catalysts do exhibit a high activity for the hydrogenation of aromatics at relatively low temperatures (250–300 °C) compared to the NiMo and CoMo hydrotreating sulfide catalysts [35]. However, Pt catalysts tend to strongly deactivate during the hydrogenation of real feedstock due to the presence of sulfur. Interestingly, PtPd catalysts were reported to be more tolerant to sulfur [10,15,25–27]. One possible explanation for the promoting effect of Pd is the formation of "electron-deficient Pt" resulting from the electronic coupling between Pt and Pd that yield to lesser interaction of sulfur (probably as H_2S) with the Pt active centers. In another study, the increased sulfur tolerance of PtPd was attributed to the electron transfer from Pt to Pd, which would increase the Pd-S bond strength resulting in a Pd-S shell and a sulfur-free Pt core [34,36].

In addition to the electronic effect, Pd was claimed to play an important role in the stabilization of Pt nanoparticles against sintering due to the tendency of Pd to segregate on top of Pt. Because Pt has a relatively higher surface energy (2550 mJ/m^2) compared to Pd (2100 mJ/m^2), one would expect migration/segregation of Pd on Pt when sufficient thermal energy is applied. Several previous experimental and theoretical investigations confirmed the tendency of Pd to segregate on the surface of Pt in PtPd bimetallic catalysts prepared using several techniques and different precursors [37–40].

Most early investigations dealing with PtPd bimetallic formulations used classical impregnation, co-precipitation and ion-exchange techniques for the preparation of such catalysts. However, in this case, it is always very hard to unambiguously establish any structure-activity correlation. This is mainly due to the low ability of these techniques to control the particle size distribution, shape, type of bimetallic structure, and composition at the nanoscale level.

To further improve the catalytic behavior of PtPd bimetallic catalysts and get more insights into the structure-activity relationship, several synthesis protocols have being recently developed and adopted for the preparation of well-defined PtPd nanostructures (e.g. alloys, dendrites, core-shells, alternating multi-shells, and atomic monolayers). For example, co-chemical reduction [41,42] and galvanic replacement combined with co-reduction [43,44] have been used to generate alloys and dendritic nanostructures, whereas seed-mediated over-growth has been successfully used to produce core-shell and multi-shell nanostructures [45,46]. Meanwhile, catalysts with Pt monolayer on Pd have been prepared by a combination of electrochemical deposition and galvanic replacement [47].

Since early 1980's, a new approach as been developed and used to successfully prepare various bimetallic catalysts. This strategy consists in the selective and careful deposition/decomposition of an adequate organometallic precursor of a metal M' on the surface of a pre-reduced metal M nanoparticle supported or not (in the presence or absence of gaseous or adsorbed hydrogen). The concept that is derived from the Surface Organo-Metallic Chemistry on oxide is very simple: an organometallic compound has usually a higher reactivity with the surface of a zero-valent nanoparticle of metal than with its oxide support. This concept constitutes the backbone of what we call today "Surface Organometallic Chemistry on Metals" (SOMC/M) [48]. This protocol can yield different bimetallic or plurimetallic nanostructures where, for example, the second metal M' is deposited as partially decomposed $M'R_x$ on top of the first metal M, leading to species that we can write as $M_y(M'R_x)$. This organometallic fragment can be studied by itself for understanding elementary steps of heterogeneous catalysis on metals, or it may be further totally decomposed thermally or under hydrogen. The second metal M' was shown to be transformed to naked-adatoms on top of the first metal M [49]. In other cases, formation of bulk alloys has also been observed during the deposition/decomposition process. In many cases, SOMC/M has led to bimetallic nanostructures (e.g. Rh-Sn [50,55], Ni-Sn [56,57], Ni-Pt [58,59] and Pt-Sn [60–63]) with well-defined particle size distribution and composition. Bimetallic catalysts prepared using SOMC/M were often demonstrated to exhibit better catalytic performance for several catalytic reactions. For example with the system PtSn, in which Sn as main group element is inactive, the selectivity in *iso*-butane hydrogenolysis and isomerization is explained at the molecular level by the proximity of two platinum atoms favoring dimetallacyclobutane whereas this proximity is progressively canceled when Sn atoms are progressively diluting Pt atoms.

In the present study, we intend to use this strategy for the preparation of well-defined PdPt nanocomposites supported on silica, where Pd is deposited on top of Pt. Several catalysts with different Pd/Pt atomic ratios have been prepared and evaluated for the catalytic hydrogenolysis/isomerization of *iso*-butane. The latter reaction was chosen due to its well-known structure-sensitive character, which would allow us to get more insight into the effect of Pd addition on the catalytic performance of Pt. All catalysts have been thoroughly characterized using Electron microscopy, elemental analysis, XAS, H_2 chemisorption, and FT-IR CO chemisorption. DFT calculations have been used to determine the most energetically stable structure of Pt-Pd nanoparticles with respect to temperature, presence/absence of H_2, method of preparation, Pd/Pt atomic ratio. Meanwhile, the catalytic performance of these catalysts will be compared to the activity of samples prepared using the ion-exchange technique. Finally, we will attempt to correlate the catalytic activity/selectivity during the hydrogenolysis of *iso*-butane to the structure of prepared catalysts. Detailed information about the experimental and computational methods used in this work is given in the Supporting Information.

2. Catalysts preparation

Samples in this work were prepared by three different methods: (1) prepared bimetallic PdPt/SiO_2 by classical ion exchange [64] (2)