Journal of Catalysis 292 (2012) 173-180

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Supported Ir–Pd nanoalloys: Size–composition correlation and consequences on tetralin hydroconversion properties

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ARTICLE INFO

Article history: Received 17 January 2012 Revised 3 May 2012 Accepted 13 May 2012 Available online 20 June 2012

Keywords: Nanoalloys Iridium–Palladium Amorphous silica–alumina Ostwald ripening Tetralin Selective ring opening

ABSTRACT

A series of Ir-Pd/SiO₂-Al₂O₃ catalysts has been prepared by incipient wetness co-impregnation of acetylacetonate precursors and treated by reductive thermal decomposition. The decomposition has been followed by combined thermogravimetry, differential thermal analysis, and mass spectrometry, showing a marked difference between the bimetallic and monometallic cases. The catalysts characterization by transmission electron microscopy and single-nanoparticle energy dispersive X-ray spectroscopy reveals that the particles are bimetallic and exhibit a size-composition correlation. More generally, the enrichment of larger particles with the less cohesive element (Pd in the present case) via Ostwald ripening is here claimed to be inherent to the thermal activation treatments used in the preparation of bimetallic catalysts. The catalysts have been tested in the hydroconversion of tetralin, which is considered as a model molecule for gas oil upgrading by selective ring opening. At 350 °C, 4 MPa H₂, and in the presence of ppm amounts of H₂S, hydrogenation, dehydrogenation, and ring-opening/contraction products (ROCPs) are formed. While the activity increases with the Pd content, the selectivity to ROCPs reaches a maximum for the Ir55-Pd45 composition and increases with the sulfur concentration. The structural and catalytic results are combined to propose a qualitative model relying on metal-acid bifunctionality and size-composition correlation. While the particle size drives the number of surface sites, the corresponding surface composition governs the hydrogenation efficiency of these sites. Therefore, by controlling the mean metal composition of the catalyst, it is possible to tune the activity-selectivity balance. © 2012 Elsevier Inc. All rights reserved.

1. Introduction

Going further than aromatics saturation, the selective ring opening of polyaromatic hydrocarbons is a promising route to improve the combustion properties of diesel fuels and consequently reduce undesirable emissions [1]. In order to increase significantly the cetane number, unselective cracking and branching isomerization must be avoided [2]. Ideally, linear paraffins could be formed by the selective opening of all rings. In addition, due to the presence of residual sulfur in pre-hydrotreated fuels, the catalysts must be thioresistant.

Most of researches on selective ring opening have used metal-acid bifunctional catalysts. The role of the metal function is to activate hydrogen for hydrogenation-dehydrogenation steps and possibly favor selective hydrogenolysis of the rings. Hydrogenolysis is known to be catalyzed by noble metals such as Ru, Rh, and Ir. The pioneering work of McVicker et al. has shown the ability of Ir to promote hydrogenolysis of C₆ rings [3]. However, even on Ir, C₆ ring opening is much slower than C₅ ring opening. Thus, the de-

* Corresponding author. *E-mail address:* laurent.piccolo@ircelyon.univ-lyon1.fr (L. Piccolo). sired role of the acid function is to favor contraction of C_6 rings *via* isomerization on Brönsted acid sites, prior to ring opening. Nevertheless, the catalyst acidity should be mild enough to prevent cracking and secondary isomerization. Moreover, through electron transfer, the support acidity provides thioresistance to the metal nanoparticles [1].

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The current strategies in selective ring opening consist in the use of microporous or mesoporous acidic materials loaded with noble metals. However, as a conclusion of several studies using decalin, tetralin, or naphthalene as model molecules [3–17], it remains challenging to obtain both a resistance to poisoning by sulfur, and a high selectivity ratio between C_{10} ring-opening products and $C_{<10}$ cracking products. Moreover, along with ring-opening products, a large proportion of decalin skeletal isomers (or "ring-contraction products") is generally formed. Although less desirable than ring-opening products in terms of cetane number, such compounds could be important intermediates to ring-opening steps in real feedstocks. Indeed, using bifunctional catalysts, several works have obtained significant cetane number enhancements for prehydrotreated light cycle oil feedstocks [10,13,18].

We have recently shown that Ir supported on amorphous silicaalumina (ASA) is thioresistant and active in tetralin hydrogenation,



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ring contraction, and ring opening [16,19]. The selectivity to ringopening/contraction products (ROCPs) is roughly proportional to the acid/metal site number ratio. Thus, a low-loaded (<1 wt.%) Ir catalyst supported on an acidic ASA (40 wt.% silica in our case) was found to be an optimal combination in terms of selectivity to ROCPs (>50%) and cracking products (<10%). However, the selectivity to ring-opening products remained low (<10%) [16].

Palladium exhibits excellent properties in terms of hydrogen activation and thioresistance [20]. In an attempt to further improve the catalytic performances of our ASA-supported system, we have investigated the structural and catalytic properties of Ir-Pd/ASA bimetallic catalysts obtained by co-impregnation of ASA with acetylacetonates. Transition-metal acetylacetonates have proven to be efficient precursors to prepare contaminant-free supported catalysts with a high degree of metal dispersion and thermal stability [21]. However, unlike for other Pd-based bimetallic systems [22] such as Cu-Pd [23,24], Mn-Pd [25], Pt-Pd [26], Ni-Pd [27,28], and Co-Pd[29], the synthesis of Ir-Pd catalysts by combining acetylacetonates has never been attempted to our knowledge. In the bulk phase, similar to that of Ir-Pt, the phase diagram of Ir-Pd presents a miscibility gap below 1500 °C at 50 at.% composition and ranging from ca. 11 to 98 at.% Pd at 500 °C [30]. This may increase the difficulty to obtain Ir-Pd nanoalloys with respect to the abovementioned Pd-based ones.

Besides, few catalytic studies have been devoted to the Ir-Pd system. Recently, Persson et al. synthesized a number of Pd-based bimetallic catalysts for methane combustion. Ir-Pd/ γ -Al₂O₃ was prepared by impregnation using IrCl₃ and Pd(NO₃)₂ precursors, but separate particles were obtained [31]. López-De Jesús et al. prepared Ir-Pd/ γ -Al₂O₃ catalysts from IrCl₃ and PdCl₂ for liquidphase hydrogenation of benzonitrile and evidenced a nanoparticle size-composition correlation [32]. Using a colloidal method, Shen et al. synthesized Ir-Pd/C catalysts and observed a positive effect of Ir addition to Pd for ethanol oxidation in alkaline media [33]. Similarly to our study, Rocha et al. investigated tetralin hydroconversion over a dealuminated HY zeolite loaded with Ir-Pd particles, which were obtained from $(NH_4)_3$ IrCl₆ and Pd $(NH_3)_4$ Cl₂ precursors [34]. Nevertheless, no ROCPs were formed on this catalyst, and the hydrogenation activity was found comparable to that of a reference Pd-Pt catalyst. For the selective opening of one-ring or two-ring hydrocarbons, several other combinations of noble metals have been reported: Ir-Pt [6,10,11,35], Pd-Pt [5,14], Os-Ru [5,9] Pd-Rh [13], and Pt-Rh [36]. However, a frequent limitation of the works dealing with bimetallic catalysts is the poor direct investigation of the nanoparticles structure, allowing determining whether they are themselves bimetallic or whether monometallic particles coexist [37-39].

In this article, we will show how the size and composition of ASA-supported Ir–Pd nanoparticles affect the activity–selectivity balance in high-pressure tetralin hydroconversion.

2. Experimental

2.1. Materials and catalyst preparation

Amorphous silica–alumina (ASA, commercial name SIRAL) was supplied by Sasol (Germany), following a patented preparation procedure [40,41]. SIRAL-40, containing 40 wt.% silica, was chosen as a support for its optimal performances, in correlation with its Brönsted acidity [19]. The powder, received in hydrated form, was activated by heating at 550 °C in air for 3 h. It resulted in dehydration and transformation of the alumina part from AlO(OH) (boehmite) to γ -Al₂O₃. For SIRAL-40, the average oxide grain size, BET surface area, pore volume, and pore diameter were 50 µm, 500 m² g⁻¹, 0.90 mL g⁻¹, and 6.4 nm, respectively. The catalysts were prepared

Table 1

Metal composition of the samples, as determined by ICP-OES.

Sample	Pd content/metal content	Metal weight/catalyst weight
name	(at.%)	(wt.%)
Ir/ASA	0	0.96
Ir89–Pd11/ASA	11	1.04
Ir55–Pd45/ASA	45	0.91
Ir11–P89/ASA	89	1.02
Pd/ASA	100	0.85

by incipient wetness (co-)impregnation of the supports with Ir acetylacetonate, Ir(acac)₃, and/or Pd acetylacetonate, Pd(acac)₂. These precursors (Sigma–Aldrich, purity 97%) were dissolved in toluene, using the concentration needed to obtain a metal loading of 1.0 wt.%. After maturation during 2 h at room temperature, the samples were dried at 120 °C overnight and reduced in an H₂ flow at 350–500 °C for 6 h. In the case of Ir/ASA, we have shown that the catalysts must be treated by direct H₂ reduction of acac-impregnated ASA, without pre-calcination, to avoid particle agglomeration [42].

The compositions of the so-called Ir(100-x)-Pd(x)/ASA sample series (x in at.%), as determined from inductively coupled plasma–optical emission spectrometry (ICP-OES, Activa – Horiba Jobin Yvon), are reported in Table 1. Prior to each activity measurement, the samples were further exposed *in situ* to an H₂ flow for 2 h at 350 °C.

2.2. Materials characterization techniques

The TG–DTA–MS (thermogravimetry–differential thermal analysis–mass spectrometry) system is described in the electronic Supplementary material file.

The carbon-replicated samples were observed by high-resolution transmission electron microscopy (HRTEM). The microscopes used were Jeol 2010 (200 kV, LaB_6 filament, 0.19 nm resolution), 2010F (200 kV, FEG, 0.19 nm resolution), and 2100F (200 kV, FEG, Cs-corrected probe, 0.11 nm STEM resolution). They were all equipped with energy dispersive X-ray spectroscopy (EDS). Scanning TEM (STEM) was performed with the 2100F. Atomic-level high-resolution high-angle annular dark field (HAADF, Z-contrast) and bright field images were recorded.

Size histograms were obtained from the statistical treatment of the micrographs, by analyzing more than 300 particles. The metal particle size was averaged over the metal surface distribution $n_i d_i^2$, which is more relevant to catalysis than the number distribution n_i (n_i is the number of particles in the diameter range d_i). The "surface-weighted mean size" $\langle d \rangle_{surf}$ is given by $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

2.3. Catalytic testing and product identification

The experiments were carried out in a gas-phase flow fixed bed catalytic microreactor described in details elsewhere [16]. The standard reaction conditions for tetralin hydroconversion were H₂ 4 MPa, tetralin 6 kPa, and 350 °C. The H₂S concentration was varied between 0 and 200 ppm. The catalyst weight and the mass flow rate were adjusted for conversion control (contact time range 2-20 s).

For the catalytic tests at fixed tetralin conversion (48–56%), the catalyst weight was varied (50, 40, 20, 10, and 7 mg for increasing Pd contents), while the total flow rate was kept in the range 160–200 mL min⁻¹, and the H_2S concentration was 100 ppm.

The gas composition at the reactor outlet was determined by online gas sampling and gas chromatography (GC). The GC-FID was a HP 5890 II equipped with a HP-1 column ($25 \text{ m} \times 0.2 \text{ mm} \times$ $0.5 \mu\text{m}$). In a typical catalytic test, at least 50 isomers of C₁₀ aromatic and saturated compounds are formed and can hardly be separated and identified, except by (post-reaction) comprehensive twodimensional gas chromatography ($GC \times GC$) [16,43,44]. The corresponding instrument is described in the Supplementary file.

3. Results

The reductive thermal decomposition of the metal precursors has been studied by TG–DTA–MS. The results are reported in the Supplementary file. To summarize the most significant features (Fig. S1), Ir(acac)₃ and Pd(acac)₂ decompose essentially in to light alkanes (methane and C₂₊ alkanes) at *ca*. 350 °C with low exothermicity, while the mixture decomposes exothermically to methane at 475 °C. Thus, mixing the two precursors somewhat hinders the decomposition process, and the bimetallic case is far from being a superposition of the single-metallic ones. Instead, the results suggest a strong interaction between Ir and Pd species.

3.1. Structural characterization of the metal nanoparticles by TEM-EDS

Fig. 1 shows STEM images of the Ir55–Pd45 sample. The nanoparticles are well-dispersed and essentially exhibit a truncated octahedral shape, as expected for thermally equilibrated fcc particles in the considered size range (see also Ref. [16] for Ir). However, some particles exhibit rough facets and, besides, small clusters and even isolated Ir atoms have been evidenced by STEM–HAADF.

Fig. 2a–e shows the particle size distributions corresponding to the series of Ir(100-*x*)–Pd(*x*)/ASA catalysts (x = 0, 10, 50, 90, and 100) derived from conventional TEM image analysis. For x = 50, the histogram for the sample reduced at 550 °C (instead of 350 °C for the other samples) after impregnation is also reported (Fig. 3c, R550). This shows that the additional 200 °C do not affect significantly the characteristics of the final catalyst, contrary to what TG–DTA–MS would have suggested (Fig. S1). This is explained by the isothermal reduction of the solids during 8 h prior to the catalytic tests, at variance from the TG conditions.

Strikingly, the distribution gradually shifts to larger sizes and becomes wider as *x* increases. These trends are summarized in Fig. 2f. For monometallic Ir and Pd catalysts, the mean particle sizes are 1.5 nm (full width at half-maximum 0.6 nm) and 4.5 nm (FWHM 2.5 nm), respectively. As TG–DTA–MS ones, these TEM results suggest an interaction between Ir and Pd species during the preparation process, and the formation of bimetallic particles.



Fig. 1. STEM images of the C-replicated Ir55–Pd45 sample. A high-resolution HAADF image of a *ca.* 3-nm-sized particle is shown in insert.

In order to determine the individual particle composition, we have performed EDS with various probe diameters (2–100 nm) on the Ir–Pd samples. Bimetallic particles have been hardly detected in the Ir89–Pd11 and Ir11–P89 samples, which is not surprising with regard to their composition. However, the nanoparticles in the Ir55–Pd45 sample are bimetallic, as shown by Fig. 3. Interestingly, the Pd content of the nanoparticles increases roughly linearly with their size. Consistently with the size histogram of Fig. 2c, the nanoparticle size ranges between 1 and 5 nm. According to Fig. 3, these sizes correspond to Pd contents of *ca*. 0 and 100 at.%, respectively. Only the particles with intermediate size (3.0 ± 0.2 nm) have the composition of the overall sample (45 at.% Pd from ICP) within $\pm 5\%$ in standard deviation. Accurate measurements on two Ir55–Pd45 samples using, for each one, two different spectrometers, were all consistent with this behavior.

3.2. Catalyst performances in tetralin hydroconversion

The three bimetallic catalysts and the two monometallic ones have been assessed in tetralin hydroconversion at 350 °C with up to 200 ppm H₂S in the feed. Fig. S2 in the Supplementary file shows $GC \times GC$ chromatograms acquired in the same conditions for Ir/ ASA and Pd/ASA. In addition to tetralin (reactant), naphthalene (dehydrogenation product), and cis and trans decalins (hydrogenation products), five categories of C_{10} products appear on both images: methyl-indans ("aromatic ring-contraction products," the four position isomers), alkyl-benzenes ("aromatic one-ring-opening products," mostly *n*-butyl-benzene), decalin skeletal isomers ("saturated ring-contraction products," the largest family, including dimethyl-bicyclo-octanes and methyl-bicyclo-nonanes), alkylcycloalkanes ("saturated one-ring-opening products," mostly *n*-butyl-cyclohexane and *n*-pentyl-cyclopentane), and C₁₀ paraffins ("saturated two-ring-opening products," mostly n-decane). Paraffins are visible only in the case of low-metal-loaded catalysts [46]. A deeper analysis of the products distribution was performed in Refs. [16,44,46]. In the present paper, in order to facilitate the presentation of the catalysis results, the products issuing from ring opening and ring contraction have been gathered together in a same family, so-called ROCP. Note that the fraction of ring-opening products is less than ca. 10% of the ROCPs at half-conversion [16]. The amounts of hydrocarbons with more (alkylation products) or less (cracking products) than 10 carbon atoms are negligible for the 1 wt.% metal-loaded catalysts considered herein, even at 100% conversion (Fig. S3).

The results in terms of selectivity to ROCPs and total activity, for fixed sulfur content (100 ppm H_2S) and isoconversion (*ca.* 50%), are presented in Fig. 4. As shown by Fig. 4a, the activity increases with the Pd content. The corresponding turnover frequency (TOF, *i.e.*, tetralin consumption activity normalized by the number of surface metal atoms calculated from the size distribution, Fig. 4b) increases from $7.6 \times 10^{-2} \text{ s}^{-1}$ (Ir catalyst) to 1.1 s^{-1} (Pd catalyst). Fig. 4b reveals that the selectivities to ROCPs of the bimetallic catalysts are higher than those of the monometallic ones (14% for Ir and 16% for Pd). The maximum, 22%, is obtained for the Ir55–Pd45 sample. Note that the selectivity of such bifunctional catalysts can be improved by increasing the acid/metal site number ratio, but this comes along with cracking and alkylation [46].

The results for variable sulfur contents are reported in the Supplementary file (Figs. S3 and S4). Briefly, the Pd content has no significant effect on the catalysts thioresistance, that is, the deactivation kinetic order with respect to H₂S is similar for all the catalysts (tetralin conversion rate proportional to $C_{H22}^{-0.7\pm0.2}$). However, the selectivity of Pd-rich catalysts is strongly affected by the sulfur content of the feed. Going from Ir/ASA to Pd/ASA, it is observed that the dehydrogenation of tetralin vanishes and the selectivity to ROCPs becomes dependent on the sulfur content. When the H₂S concentra-



Fig. 2. (a-e) Surface-weighted particle size histograms for the Ir-Pd/ASA series. In the case of the Ir55-Pd45 sample, the reductions at 350 °C (standard treatment) and 550 °C are compared. (f) Center and full width at half-maximum (FWHM) of the size distributions vs. Pd content.

tion increases from 0 to 200 ppm, the naphthalene/decalins selectivity ratio increases for Ir, while the ROCPs/decalins one increases for Pd. The behavior of Ir–Pd is different from those of both Ir and Pd: Dehydrogenation is significant, and the selectivity to ROCPs is positively sulfur-dependent (see the Supplementary file for details).

4. Discussion

4.1. Metal-dependent particle size and size-dependent particle composition

Recently, López-De Jesús et al. have synthesized $Ir-Pd/\gamma-Al_2O_3$ catalysts by impregnation of chlorinated precursors and calcination-

reduction [32]. As in our case, the authors have observed an increase in the particle size with the Pd content. They have ascribed this correlation to a greater mobility of Pd, with respect to Ir, over alumina. Ir would prevent the sintering or agglomeration of Pd during the preparation. A size–Pd concentration correlation has also been observed for Au–Pd/C catalysts prepared by incipient wetness impregnation with chlorinated precursors followed by calcination [47].

We suggest that our results originate from the combination of two facts. First, there is a strong interaction between Ir and Pd acac species. This is demonstrated by (i) TG–DTA–MS experiments (Fig. S1), which show a significant difference between the bimetallic and monometallic cases; (ii) EDS analyses (Fig. 3) directly proving the bimetallic character of the nanoparticles; and (iii) TEM observations (Fig. 2a–f) showing a gradual upshift and spreading



Fig. 3. Nanoparticle composition (determined by EDS) vs. nanoparticle size (TEM) for Ir55–Pd45/ASA. 2–5 nm- and 10–100 nm-sized EDS probes were used for individual particles (open symbols) and groups of particles (filled symbols), respectively. Typically, 20 particles were simultaneously analyzed when using a 25-nm-diameter probe. Two samples, reduced at 350 °C (squares) or 550 °C (circles), were analyzed. The red lines are a linear fit of the data and the corresponding standard deviation limits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Activity in tetralin hydroconversion expressed as rate and turnover frequency (a), and selectivity to ring-opening/contraction products (b) vs. Pd concentration for the Ir–Pd/ASA series. The concentration of H_2S in the feed was 100 ppm. The conversion was kept constant and equal to *ca*. 50%.

of the size distribution when the Pd concentration increases. The interaction between Ir and Pd species during the preparation is confirmed by the abrupt variations of the particle size *vs.* sample composition curve at the extreme compositions (Fig. 2f). Note that a previous work by Renouprez et al. has evidenced the possibility to form mixed Cu–Pd bis-acetylacetonate crystals, showing the significant interaction between the acac precursors before ligand removal [24].

Second, Ir and Pd species interact differently with the ASA support. Indeed, while the heating of $Ir(acac)_3/ASA$ in H_2 yields 1.5 ± 0.3 nm Ir particles, that of Pd(acac)_2/ASA gives rise to 4.5 ± 1.3 nm Pd particles. This suggests a faster diffusion of Pd species on the support, as already proposed by López-De Jesús et al. In regard to the similarities of our results with those for Ir–Pd/ γ -Al₂O₃ synthesized from chlorinated precursors by these authors [32], the difference of interaction with the ASA surface, which is aluminarich [41]. In summary, appears to arise from the metal atoms themselves, that is, Ir interacts more strongly than Pd with the support.

From the above two arguments, our results can be qualitatively explained by considering the nanoparticles growth process through "Ostwald ripening" during the thermal ramp used for the catalysts preparation. It consists of the thermally activated detachment of metal atoms from small clusters and their surface diffusion on the support toward bigger particles [48]. In other words, the small particles, which have the higher evaporation rates, get smaller or even disappear at the benefit of the large particles, which get larger. For nanoalloys containing species with different mobilities, this phenomenon is expected to cause sizedependent particle composition. This has been recently observed for Au-Pd nanoparticles exposed to hydrogen (large particles are Pd-enriched) [49], and Pt-Co particles annealed under ultrahigh vacuum (large particles are Co-enriched) [50]. Our Ir-Pd system is believed to be formally equivalent to the Au-Pd and Pt-Co ones, with a faster detachment or surface diffusion of Pd atoms as compared to Ir atoms during annealing in H₂. In particular, the surface energy of Pd (2.1 | m⁻²) is much lower than that of Ir (3.0 | m⁻²) [51], suggesting a lower activation energy for Pd detachment. Moreover, as mentioned above, Pd atoms diffuse faster than Ir atoms on the support.

The above-mentioned studies of Au–Pd and Pt–Co used physical deposition on amorphous carbon as synthesis method. However, the previously cited studies on Au–Pd [47] and Ir–Pd [32] used chemical preparation methods, as well as the present work. This shows that the previous concept is extendable to practical bimetal-lic catalysts. Obviously, the situation is more complex for chemical impregnation than for physical deposition. Indeed, in the former case, the nucleation and growth of the nanoparticles is simultaneous to the precursors decomposition during the thermal ramp.

The size-composition correlation has important consequences on the surface composition of the metal nanoparticles. Using the actual metal loadings (Table 1) and particle size distributions (Fig. 2), and assuming that the particles are spherical (diameter d_i), we have estimated the numbers of surface metal sites for the Ir, Pd, and Ir55–Pd45 catalysts (Fig. 5a). For the latter, we have approximated the linear correlation of Fig. 3 by $(d_i - 1)/4$ (d_i in nm). In addition, we have assumed that the surface composition of the particles is identical to that of the bulk, which is evidently an ideal case since surface segregation may occur. Thus, the overall metal dispersions have been calculated according to:

$$\frac{N_{S}}{N}(\text{Ir or Pd}) = 6 \frac{n_{S}}{n_{V}} \frac{\sum_{i}^{N_{i}} n_{i} d_{i}^{2}}{\sum_{i}^{N_{i}} n_{i} d_{i}^{3}} = \frac{6}{\langle d \rangle_{surf}} \frac{n_{S}}{n_{V}}$$
(1)



Fig. 5. Number of surface metal atoms (a) and surface metal composition (b) as a function of the total metal composition of Ir(100-x)-Pd(x) catalysts. The filled and open symbols correspond to the cases of size-dependent particle composition and homogeneous particle composition, respectively (see text). The lines are guides to eye.

$$\frac{N_{S}^{Pd}}{N^{Pd}}(Ir_{55} - Pd_{45}) = 6\frac{n_{S}}{n_{V}} \frac{\sum_{i} n_{i}(d_{i} - 1)d_{i}^{2}}{\sum_{i} n_{i}(d_{i} - 1)d_{i}^{3}}$$
(2)

where n_s is the surface atomic density ($n_s = 15.7$ at. nm⁻² for Ir(111); $n_s = 15.3$ at. nm⁻² for Pd(111)) and n_V is the bulk atomic density ($n_V = 70.7$ at. nm⁻³ for Ir; $n_V = 67.9$ at. nm⁻³ for Pd).

Fig. 5 allows us to compare this situation with the case of sizeindependent particle composition. It appears that with the above correlation, the surface composition is $Ir_{62}Pd_{37}$, instead of $Ir_{55}Pd_{45}$ for homogeneous composition. The decrease of the Pd concentration may have significant effects on the catalysts properties, as we discuss below.

4.2. Dependence of the catalytic selectivity on the metal composition

Although the reaction mechanism is discussed in details in a separate paper [46], a simplified mechanistic reaction scheme will facilitate the interpretation of the results. Scheme 1 is proposed on the basis of our previous works on Ir/ASA [16,19,46], as well as on the present work on Ir–Pd/ASA. It shows that, on the metal, adsorbed tetralin can be hydrogenated to octalin alkenic intermediates, which in turn may be hydrogenated to decalins. These metallic steps are in competition with acidic ones, consisting in the protonation by Brönsted acid sites of octalins having diffused to the support. Subsequently, the corresponding carbocations may undergo a number of transformations including skeletal isomerization, β -scission, hydride transfer, and deprotonation, leading to the ROCPs [7,45,52]. Thus, Scheme 1 reveals a competition between octalins hydrogenation on the metal and protonation on the support. This competition is a key factor in controlling the decalins/ROCPs selectivity ratio. Indeed, in the case of Ir/ASA, by increasing the particle size or decreasing the metal loading, we have shown that the selectivity to ROCPs increased with the acid/metal site number ratio [16,46].

In the case of Ir–Pd/ASA catalysts, a satisfactory interpretation of the results requires to account for the structural parameters established in Section 3.1,that is, the increase in the particle size with the Pd content, both at the global (whole catalyst) and local (nanoparticle) scales. The increase of the selectivity with Pd concentration in the Ir-rich composition domain (Fig. 4b) is ascribed to a decrease in the number of metallic sites, as in the Ir/ASA case. In this domain, due to the fact that the larger particles contain the larger amounts of Pd, the overall amount of surface Pd remains low (Fig. 5) and the acid/Ir site number ratio criterion prevails.

However, not only the number, but also the nature of the metal sites plays a role, as shown here by the similar selectivities to ROC-Ps found for Ir/ASA (14%) and Pd/ASA (16%), in spite of the different numbers of exposed metal sites. Indeed, taking the mean particles sizes, the (similar) metal loadings, and the molar weights into account, the Ir catalyst exhibits almost twice the number of surface metal sites (Fig. 5a). These results suggest that, although the addition of Pd does not modify the reaction mechanism, it induces a change in the kinetic regime. This is confirmed by the qualitatively similar but quantitatively different products distributions measured by GC \times GC for Ir/ASA and Pd/ASA (Fig. S2).

By analogy with acidity, the difference between Ir and Pd can be discussed in terms of metal sites "strength" (*i.e.*, hydrogenation efficiency) in the framework of a bifunctional mechanism. The decrease in the selectivity to ROCPs at the benefit of the hydrogenation products in the Pd-rich composition domain (Fig. 4b and Fig. S3) is governed by strength. Indeed, Pd is expected to be much more active (i.e., "stronger") than Ir for hydrogen activation and the hydrogenation steps, as confirmed by the higher activity of Pd for tetralin conversion (Fig. 4a), keeping in mind that hydrogenation is the main pathway under our conditions. As suggested above, in the Ir-rich domain, the competition between carbocation and decalins formations (Scheme 1) is more and more favorable to the former when the number of Ir sites decreases. Conversely, in the Pd-rich domain, the competition becomes even more favorable to decalins formation when the number of Pd sites increases. The nonlinear shape of the activity vs. composition plot (Fig. 4a) may



Scheme 1. Simplified reaction scheme showing the most important steps for tetralin hydroconversion on metal/ASA bifunctional catalysts.

be due to this change in the reaction regime, which is itself affected by the surface vs. total metal composition profile (Fig. 5).

In summary, at high Ir concentration, the catalysts contain "weak" but numerous metal sites, whereas at high Pd concentration, they contain fewer but much stronger metal sites. As previously mentioned, both situations are unfavorable to the ROCPs selectivity. Conversely, at intermediate composition, the metallic function efficiency for hydrogen activation and hydrogenation reaches a minimum. Overall, this leads to the volcano-shaped selectivity curve of Fig. 4b. The actual situation might obviously be more complex. In particular, we cannot rule out a synergistic electronic effect between Ir and Pd.

5. Summary and conclusion

Ir-Pd/SiO₂-Al₂O₃ catalysts have been prepared by metal-acetylacetonate co-impregnation. The reductive thermal decomposition (mainly to methane) of the metal precursors has been studied by TG-DTA-MS. It is shown that the bimetallic catalysts form at higher temperature and in a different process than their monometallic counterparts. The catalysts characterization by TEM-EDS shows that the size distributions of the metal nanoparticles upshift and widen as the Pd content increases. Consistently, for a given bimetallic sample of intermediate composition, the Pd concentration increases with the particle size. In agreement with the thermal analysis, the size-composition correlation is ascribed to the interaction between Ir and Pd species and the stronger Ir-ASA interaction as compared to the Pd-ASA one. This leads, in the course of the thermal treatment, to an Ostwald ripening process with preferential enrichment of the bigger particles with the less cohesive metal (Pd). As size dependency of the nanoparticles composition is observed for a variety of systems and preparation methods, it can be considered as a general phenomenon that limits the preparation of homogeneous bimetallic catalysts, at least for metals exhibiting significant differences in their cohesion energies.

The catalysts have been tested in tetralin hydroconversion using a high-pressure gas-phase continuous microreactor (4 MPa, 350 °C). While the total activity increases with the Pd content of the catalysts, the selectivity to ring-opening/contraction products (ROCPs) exhibits a volcano shape. By taking into account the structural characteristics of the catalysts and our previous works showing that the selectivity to ROCPs is driven by the catalyst acidity, this behavior is shown to originate from metal-acid bifunctionality. Pd enrichment leads to a decrease in the number of metal sites (larger nanoparticles), but to an increase in their hydrogenation efficiency ("metallic strength"). The maximum selectivity of Ir55-Pd45 catalysts toward ROCPs arises from the best balance between the number and strength of the metal sites. In addition, the size-dependent particle composition leads to an overall surface enrichment in Ir, which affects this balance.

In conclusion, by alloying two hydrogenation metals on a mild acidic support, it has been possible to increase the bifunctional catalyst activity and selectivity in a complex reaction. From the viewpoint of the performances in tetralin hydroconversion, Pd-rich Ir–Pd/ASA catalysts appear as good candidates in terms of activity and ROCPs/naphthalene selectivity ratio. Softening of the metallic function by decreasing the metal loading should improve the selectivity to ROCPs. However, attention must be paid to the nature of the ROCPs, since in practice only (non-branched) ring-opening products exhibit high cetane numbers.

Acknowledgements

We wish to greatly thank Guy Toussaint ($GC \times GC$), Bernadette Jouguet (TG–DTA–MS), Laurence Burel (TEM), and Noëlle Cristin

and Pascale Mascunan (ICP) for their support in sample characterization. We acknowledge the METSA network and Dr. Christine Goyhenex for allowing us to perform experiments with the 2100F microscope in Strasbourg. We also thank the French ANR (CatAlk-Thio project) for supporting the GC \times GC analytical development.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.05.010.

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