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Structural evolution of bimetallic Pd-Ru catalysts in oxidative and reductive applications



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ABSTRACT

Two types of bimetallic Pd-Ru catalysts with a 2:1 Ru:Pd molar ratio were prepared using a poly-(vinylpyrrolidone) stabilizer: one alloy structure with mixed-surface atoms and one core-shell structure with a Pd core and Ru shell, which were confirmed by a surface-probe reaction at mild conditions. In indan hydrogenolysis at 350 °C, inversion of the core-shell structure began with Pd atoms appearing on the surface of the particles. Both catalysts displayed distinctively different catalytic behavior and indicated the importance of structure control for this particular application within a studied time frame. For methane combustion over the 200–550 °C temperature range, both structures demonstrated identical activity, which was due to their structural evolution to one nanoparticle type with Pd-enriched shells, as evidenced by extended X-ray absorption fine structure.

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1. Introduction

Introducing a second metal component to supported catalysts is widely recognized as an efficient way to increase catalyst activity, selectivity, and stability. Numerous large-scale industrial productions benefit from synergism phenomena in bimetallic catalysis [1–5]. Two metals may form intrinsic alloys with or without preferential shell or core segregation of one of the metals, or individual monometallic nanoparticles. Such structures, however, often are not maintained during catalysis [6], leading to unstable catalyst performance and even deactivation. The changes are driven by thermodynamics (the metal with lower surface energy segregates to the surface of bimetallic nanoparticles) and/or chemically activated selective metal diffusion ("adsorbent-induced segregation") due to different metal affinities to the reaction mixture components [7,8]. Thermodynamic considerations predict that nanoparticles with the same metal ratios but initially different structures at high enough temperatures transform into one most- thermodynamically-stable configuration [9]. At different metal ratios, nanoparticles may be stabilized in different core-shell or alloyed structures even at temperatures above 1600 K [10].

(N. Semagina).

In thermodynamically driven changes, achieving prolonged catalyst stability is still feasible (especially in low-temperature regions) because the structural evolution is often kinetically limited. The adsorbent-induced segregation [7,8], on the contrary, may happen on the same time scale as the catalytic reaction and requires lower temperatures and shorter times to modify the parent bimetallic nanoparticles. For example, a ternary CuPdY alloy did not segregate in a vacuum, but in the presence of oxygen, Y oxides were formed on the surface, driven by preferential oxygen-induced Y segregation [11]. Similarly, parent alloy Pt-Co nanoparticles evolved into Pt(shell)/Pt-Co(core) particles upon annealing in CO [7].

Studies of the particle structural evolution during pre-treatment or catalysis are complicated not only by the limited availability of operando and in situ catalyst characterization techniques but also by the nature of the catalysts themselves. The traditional preparation methods that support impregnation with metal precursor solutions followed by calcination do not allow the production of well-defined uniform nanoparticles, so their structural evolution studies are complicated by the wide polydispersity of the original nanoparticles. At present, the steadily increasing number of colloidal chemistry techniques to prepare structure- and size-controlled metal nanoparticles [12–15] enable experimental studies of the bimetallic nanoparticle rearrangement, including structure inversion during synthesis or after thermal activation and/or catalysis [16–18]. The structural changes depend on the

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Scheme 1. Structure-controlled synthesis of alloy and core-shell bimetallic nanoparticles.

atmosphere (for example, oxidizing or reducing) and may or may not take place depending on the involved metals [15].

The objective of this work is to demonstrate the structural changes of well-defined bimetallic nanoparticles in reductive and oxidative catalytic reactions. We start with two different Pd-Ru nanostructures synthesized with a protective stabilizer either via simultaneous reduction of the metal precursors ("alloy" Ru2Pd1) or via Ru atom deposition on the core of preformed Pd nanoparticles ("core-shell" Pd(c)Ru(s) sample), as depicted in Scheme 1. The overall metal ratio is the same in both structures so that their structural evolution is not affected by their composition [10]. We further use these nanoparticles as catalysts for the hydrogenolysis of indan at 350 °C and combustion of methane in air at up to 550 °C. In the former case, the structural evolution is minimal, and the alloy and Pd(core)-Ru(shell) nanoparticles' performance is distinctively different. In methane combustion, both structures transform into the very same nanoparticle structure with a Pd-enriched shell and show similar catalytic performance. This comparative study demonstrates the advantages and limitations of the structurecontrolled bimetallic nanoparticle synthesis for different catalytic applications.

2. Experimental

2.1. Materials

Ruthenium (III) nitrosyl nitrate (Ru(NO)(NO₃)₃, Ru 31.3% min, Alfa Aesar), palladium(II) chloride solution (PdCl₂, 5% w/v, Acros), poly-(vinylpyrrolidone) (PVP) (MW: 40,000, Sigma–Aldrich), reagent alcohol (ethanol, 95 vol.%, Fisher Scientific), ethylene glycol (EG, 99.8%, Sigma–Aldrich), gamma aluminum oxide (γ -Al₂O₃, 150 mesh 58 Å pore size, Sigma–Aldrich), and acetone (99.7%, Fisher Scientific) were used as received. MilliQ water was used throughout the work.

2.2. Catalyst preparation

All catalysts were prepared by synthesizing PVP-stabilized 2–3 nm nanoparticles in colloidal solutions, followed by deposition

on γ -Al₂O₃ support with 5.8 nm pores. Monometallic Ru nanoparticles were prepared using the ethylene glycol reduction method [19] with some modifications [20]. At room temperature, 0.2 mmol Ru(NO)(NO₃)₃ and PVP (2 mmol, PVP-to-Ru molar ratio = 10/1) were dissolved in 200 mL EG in a 500 mL single-neck roundbottom flask. The reaction temperature was increased from room temperature to the reflux point of EG (198 °C), and maintained at 198 °C for 3 h under stirring. Monometallic Pd nanoparticles were synthesized by the one-step alcohol reduction method [21] with some modifications [20]. A mixture containing 0.2 mmol PdCl₂, PVP (4 mmol, PVP-to-Pd molar ratio = 20/1) and 170 mL of ethanol/water (41 vol.% ethanol) was stirred and refluxed in a 500 mL single-neck round-bottom flask for 3 h under air.

Bimetallic Ru-Pd nanoparticles with different surfaces were prepared according to our previously published synthesis techniques as shown in Scheme 1 [20]. For the Ru2Pd1 alloy, the monometallic Pd synthetic procedure was followed using 0.133 mmol of Ru and 0.067 mol Pd precursors. The Pd (core)-Ru (shell) nanoparticles were synthesized by Teranishi and Miyake's stepwise growthreaction method in ethanol/water [21] with some modifications [20]. The Pd core colloids were prepared using the synthesized Pd seed colloidal solution (0.05 mmol Pd, 42.5 mL) and 0.1 mmol Ru(NO)(NO₃)₃ were dissolved in 170 mL ethanol/water (41 vol.% ethanol) at room temperature, without more fresh PVP addition. The mixture was then stirred and refluxed for 3 h to allow the formation of the Ru shell.

The catalyst support, γ -Al₂O₃, was dried in static air at 500 °C for 3 h. The PVP-stabilized monometallic Ru nanoparticles prepared in EG were precipitated with acetone (acetone-to-colloidal solution volumetric ratio = 4/1), and deposited on γ -Al₂O₃ by incipient wetness impregnation. The ethanol/water colloidal solutions of PVP-stabilized monometallic Pd and bimetallic Ru-Pd nanoparticles were concentrated by vacuum evaporation of solvents, followed by incipient wetness impregnation on the γ -Al₂O₃ support. Finally, all catalysts were dried in static air at 60 °C overnight. The target total metal(s) loading was 0.3 wt.%.

The actual loadings in the supported catalysts were determined by neutron activation analysis as 0.250 wt.% Ru/ γ -Al₂O₃; 0.240 wt.%

 Pd/γ - Al_2O_3 ; 0.154 wt.% Ru, 0.065 wt.% Pd in Ru2Pd1/ γ - Al_2O_3 ; and 0.200 wt.% Ru, 0.072 wt.% Pd in Pd(c)Ru(s) catalysts. The Ru-to-Pd molar ratios in the final catalysts are 2.4 and 2.8 for the Ru2Pd1 and Pd(c)Ru(s) samples.

2.3. Catalyst characterization

The PVP-stabilized nanoparticles and/or pretreated catalysts were characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HRTEM) at 200 kV on a JEOL 2100 transmission electron microscope (Cell Imaging Facility, University of Alberta). The mean diameter and standard deviation of nanoparticles were calculated by counting more than 200 particles from TEM images using Image] software. X-ray powder diffraction (XRD) patterns were recorded on a -Bruker AXS diffractometer (Department of Chemical and Material Engineering, University of Alberta) with a Cu-K α radiation source ($\lambda = 1.54059$ Å) at 40 kV and 44 mA. Continuous X-ray scans were carried out from 2θ of 10° to 110° with a step width of 0.05° and a scan speed of 2°/min. XRD peak identification and data processing were performed using MDI Jade 9.0 software combined with the ICDD database. The colloidal solutions were concentrated by rotary evaporation of solvents under vacuum, followed by drying in an oven at 60 °C under air for a day. Nanoparticle powders (without further deposition on alumina support) were collected for XRD analyses.

The actual loadings of Ru and Pd on γ -Al₂O₃ before and after pretreatment were determined by neutron activation analysis (NAA) at Becquerel Laboratories (Maxxam Company, Ontario). Samples were irradiated for 20 min in the Cd shielded, epithermal site of the reactor core. Palladium and ruthenium were counted for 15 min after 24 h decay on an Aptec CS13-A31C gamma detector.

CO chemisorption analyses were performed by dosing 3% CO/He gas mixture at room temperature with an AutoChem 2950HP instrument equipped with a quartz U-tube reactor and a thermal conductivity detector (TCD). The volumetric flow rates of CO/He loop gas and the He carrier gas were 25 mL/min. Prior to CO chemisorption experiments, the catalysts were calcined at $550 \,^{\circ}$ C in air for 16 h in a furnace. The precalcined catalysts were reduced in a flow of $10\% \text{ H}_2/\text{Ar}$ ($25 \,\text{mL/min}$) at $550 \,^{\circ}$ C for 1 h. After the calcination-reduction pretreatment, the samples were purged with argon for 30 min at $550 \,^{\circ}$ C and cooled to ambient temperature under inert atmosphere. The results were corrected by subtracting the CO uptakes of alumina support.

Diffuse reflectance infrared spectra of the adsorbed CO (CO-DRIFTS) were obtained using NEXUS 670 FT-IR fitted with a Smart Diffuse Reflectance accessory. DRIFT spectra were recorded against a KBr standard (256 scans, 4 cm^{-1} resolution). Data processing was performed with OMNIC software. The detailed experimental procedures including catalyst pretreatment can be found in our previous work [20]. Monometallic Pd and Ru and bimetallic Pd(c)Ru(s) samples were calcined at 200 °C for 1 h in air, and followed by reduction in a flow of 10% H₂/Ar at 375 °C for 30 min to simulate conditions of pretreatment before the catalytic indan ring opening. Prior to CO treatment, the sample was purged with Ar at 375 °C, and cooled down to room temperature in Ar. Then 3% CO/He was passed through the sample for 30 min, followed by degassing in an Ar environment to remove the physically adsorbed CO.

The hydrogenation of 2-methyl-3-buten-2-ol (MBE) to 2methylbutan-2-ol (MBA) that is catalyzed by Pd only was selected to elucidate whether Pd atoms are present in the outermost layer of bimetallic Ru-Pd nanoparticles, as described previously [20]. A semibatch stainless reactor was filled with 0.04 M MBE in 200 mL ethanol and 0.5 g of as-prepared catalyst. The MBE hydrogenation reaction was carried out at 40 °C, 0.45 MPa absolute pressure and 1200 rpm stirring speed. During the reaction, the hydrogen pressure drop in the gas burette was recorded. The initial reaction rate was calculated from the slope of the hydrogen consumption graph after complete dissolution of hydrogen in ethanol.

Extended X-ray absorption fine structure spectroscopy (EXAFS) was performed at Canadian Light Source (Saskatchewan). X-ray absorption spectra at the Pd K-edge and the Ru K-edge were recorded at the HXMA beamline 061D-1 (energy range, 5–30 keV; resolution, $1 \times 10^{-4} \Delta E/E$ at the Canadian Light Source (CLS, 2.9 GeV storage ring, ~250 mA current). All samples were pressed into pellets and measured in transmission mode at room temperature. Samples for EXAFS analyses were prepared with an expected metal(s) loading of 2 wt.%. The Ru-Pd catalysts for EXAFS study were pre-calcined at 550 °C for 16 h under air followed by H₂ reduction at 400 °C, which is confirmed to be enough to reduce oxidized Ru-Pd nanoparticles to metallic forms by our previous TPR analysis [20]. After the reduction the catalysts were kept at ambient temperature under air atmosphere for one week followed by pre-reduction in hydrogen at 350 °C in situ before the EXAFS analyses. A doublecrystal Si(220) monochromator was employed for energy selection. Higher harmonics were eliminated by detuning the double-crystal Si(220) by using a Pt-coated 100 mm long KB mirror.

The IFEFFIT software package was used for EXAFS data processing [22]. More details about obtaining EXAFS function can be found in previous publications [23,24]. The EXAFS fitting was performed in R-space using theoretical phase shifts and amplitudes generated by FEFF. Lattice parameters and first shell coordination numbers of 12 for bulk fcc Pd and (or hcp Ru) were used to generate the amplitude reduction factor for Pd (or Ru) by fitting Pd foil (or Ru foil). The amplitude reduction factors found from Pd and Ru foils were 0.828 and 0.773, respectively. Ru-Pd bimetallic systems were fitted using bulk Pd lattice parameters, as XRD and SAED confirmed the fcc structures of the bimetallic nanoparticles. Additionally, the lattice spacings for the Ru-Pd bimetallic catalysts calculated from (1 1 1) diffractions are very close to that of monometallic Pd nanoparticles, which will be discussed later.

2.4. Catalysis in reductive atmosphere: indan ring opening in hydrogen, 350 $^\circ\mathrm{C}$

The developed monometallic and bimetallic Ru-Pd catalysts were studied in a low-pressure indan ring opening, as described in our previous study [20]. The PVP-stabilized catalysts were calcined at 200 °C in static air, followed by in situ reduction at 375 °C in a flow of hydrogen (80 mL/min). The catalytic indan ring opening was carried out at an internal temperature of 350 °C and 1 atm pressure. Indan ($(4.7 \pm 0.6) \times 10^{-6}$ mol/min flow rate) was fed into the catalytic system by bubbling 120 mL/min hydrogen through indan at a constant temperature of 10 °C. The gas outlet from the reactor was analyzed online using a Varian 430 gas chromatograph equipped with FID. As reported previously [20], the ring opening products are 2-ethyltoluene, *n*-propylbenzene, *o*-xylene, ethylbenzene, toluene, benzene, and lights (mainly C₁ and C₂), in which only 2-ethyltoluene and *n*-propylbenzene are the desired ring opening products with a naphthenic ring being cleaved once.

2.5. Catalysis in oxidative atmosphere: methane combustion in air, up to 550 $^\circ\text{C}$

Methane combustion was investigated over the developed Ru-Pd nanocatalysts according to the previous study published by Abbasi et al. [25]. A 20 inch long tubular reactor with an inner diameter of 3/8 inch was packed with calcined catalysts (550 °C, 16 h in static air) corresponding to 1.2 mg active Pd (and/or 3.1 ± 0.4 mg Ru). Layers of quartz wool were placed at both ends of the catalyst bed to hold the catalyst in place. The reactor was then placed inside a furnace equipped with a temperature controller. The inter-

nal reaction temperatures were measured by two thermocouples at each end of the catalyst bed. The flow rates of the feed gases (10% CH_4/N_2 and air) were regulated by mass flow controllers (Matheson and MKS). Methane (10% balanced in nitrogen, 8.5 mL/min) and air (extra-dry, 200 mL/min) were pre-mixed and fed into the catalytic system. The concentration of CH₄ in the gas mixture was 4100 ppm. Methane oxidation reactions in this study were performed as described in our previous work [26], except the catalysts were tested at dry conditions. Methane oxidation was carried out at a constant pressure of 30 psi. Ignition and extinction curves were obtained by increasing and decreasing the reaction temperature stepwise (50 °C for each step; 60 °C/min ramping rate), respectively. The ignition curves were initiated at 200 °C and ended at 550 °C, which refer to the lowest and highest combustion temperatures in the present work, respectively. The extinction curves were performed in the opposite direction to investigate the catalytic performance during cooling. Two ignition-extinction experiments were performed to stabilize the catalysts. This was then followed by a 40-hour thermal aging test in 4100 ppm methane by increasing reaction temperature to 550 °C (60 °C/min ramping rate) and then cooling the reactor to 375 °C. The 550–375 °C temperature cycling was repeated 8 times (\sim 25 h); after this cycling, the catalyst was aged at 375 °C for another 15 h. Finally, the catalytic test in methane combustion was terminated by a third ignition-extinction cycle to check the catalytic activities after 40 h thermal aging. During methane combustion, the temperature at each stage was held for 30 min in ignition-extinction tests and 1 h in thermal aging tests. The gas outlet from the reactor was analyzed online every 15 min using an Agilent HP-7890-A gas chromatograph equipped with series TCD and FID. The reported curves in the results section represent the initial 1st ignition-extinction, cycling and ignitionextinction results after the cycling.

3. Results and discussion

3.1. Characterization of as-synthesized nanoparticles

We intentionally selected two different procedures for the bimetallic catalyst preparation to obtain nanoparticles with different structures, as outlined in Scheme 1. The ruthenium precursor, without the palladium seeds present, could not be reduced in ethanol, so no monometallic Ru nanoparticles could be obtained in the ethanol solution used for syntheses. The presence of palladium nanoparticles facilitated Ru³⁺ reduction by an autocatalytic surface-growth mechanism, as suggested by Liu et al. for similar Pt-Ru systems [27].

Fig. 1 shows HRTEM images and SAED patterns of PVP-stabilized Pd(c)Ru(s) and Ru2Pd1 nanoparticles; the samples were prepared from colloidal solutions without further treatment. Both materials are single crystals with an fcc structure as follows from the comparison of the observed ring-diffraction patterns with the simulated fcc pattern. No monometallic hcp Ru structures were found, as expected from the synthetic procedure. Statistical analysis of the nanoparticle size distribution based on TEM revealed the sizes for monometallic Pd, monometallic Ru, Pd(c)Ru(s) and Ru2Pd1 systems to be 2.0 ± 0.5 nm, 2.0 ± 0.3 nm, 2.3 ± 0.7 nm and 2.6 ± 0.6 nm, respectively, as reported in our previous work [20]. Larger sizes of the bimetallic samples as compared to the monometallic forms suggest the formation of intrinsic bimetallic structures. As-synthesized Ru-Pd catalysts were in metallic form; however, a small degree of Pd and Ru surface oxidation was possible after exposing to air for few weeks (at room temperature), as shown in our previous XPS analysis [28].

The crystal structures of the mono- and bimetallic nanoparticles were further investigated by XRD (Fig. 2). Pd and Ru nanoparticles



Fig. 1. HRTEM images and SAED patterns of as-synthesized Pd(c)Ru(s) (a) and Ru2Pd1 (b) nanoparticles.



Fig. 2. XRD patterns of as-synthesized Ru, Pd, Pd(c)Ru(s) and Ru2Pd1 nanoparticles.

display an fcc and hcp structure, respectively. Both bimetallic samples with the same Ru-to-Pd molar ratio of 2:1 reveal (111), (200), (220) and (311) fcc peaks, which are consistent with the SAED patterns (Fig. 1). This observation is similar to a previous study on the structural change when alloying Pt with Ru [29]: Ru-Pt bimetallic systems revealed fcc structures up to 75 mol% of Ru in the bimetallic particles, as was shown by XRD and HRTEM [29]. The fcc (111) lattice spacings of our bimetallic samples were 2.23 Å for both samples using Bragg's law, higher than that of pure Ru (2.14 Å) and very close to that of pure Pd (2.24 Å). The TEM, XRD and SAED observations are consistent with the proposed intrinsic bimetallic nature of the synthesized nanoparticles.

For the Pd(c)-Ru(s) nanoparticle preparation, the palladium seeds were formed first followed by ruthenium precursor addition to form a Ru shell. Indeed, the size change of the Pd seeds from 2.0 ± 0.5 nm to 2.3 ± 0.7 nm after the Ru deposition indicates the proposed structure is likely (no monometallic Ru nanoparticles were observed, as shown above). The indicated sizes were calculated based on length; the mass/volume average for the monometallic Pd particles is 2.1 nm. 80% by mass of all Pd(core)-Ru(shell) particles are larger than 2.6 nm diameter with an average diameter (by mass) of 3.0 nm. Using crystal statistics for 2.1 nm Pd core and 3.0 nm bimetallic particles [29], the predicted molar ratio in the core–shell sample is 2.2:1 Ru to Pd, that is consistent with the ratio used for synthesis and found by NAA in the final catalysts.

However, core-shell structure inversion may occur even during catalyst synthesis due to the rearrangement of high-energy corner and edge atoms on ultra-small particles (<2 nm) [16]. To verify whether Pd atoms are present on the surface of the as-synthesized Pd(c)Ru(s) nanoparticles, a selective chemical probe surface reaction was used. The three-phase liquid phase hydrogenation of an allylic alcohol (2-methyl-3-buten-2-ol to 2-methylbutan-2-ol) was performed at 40 °C, 0.45 MPa absolute pressure and 1200 rpm stirring speed. As-prepared monometallic and bimetallic Ru-Pd catalysts were studied in MBE hydrogenation without any further thermal treatment to minimize structural rearrangements so that the as-synthesized structures can be evaluated. Only initial rates were evaluated to avoid in-situ structural evolution. The Pd catalyst initial activity was $2.7 \pm 0.2 \, \text{mol}_{\text{H2}}/(\text{mol}_{\text{Pd}} \text{ s})$ [20], while Ru catalyst had relatively negligible MBE hydrogenation activity. Ru is known





Fig. 3. Catalytic activities and product selectivities over mono- and bimetallic Ru-Pd catalysts in indan hydrogenolysis. Catalysts were pre-calcined at 200 °C followed by reduction in hydrogen at 375 °C for polymer removal.

to be active in many catalytic applications, such as hydrogenolysis, methanation, oxidations, etc., [30]. However, ruthenium, with its lower D-banD occupancy, is relatively inactive in hydrogenations at low temperature and pressure as compared to Pd and Pt, for example, in hydrogenations of 2-methyl-3-butyn-2-ol and 1,4-butynediol [31] or hydrogenation of *o*-chloronitrobenzene in methanol at 303 K and 0.1 MPa [32], which is in line with our observations. The Pd(c)Ru(s) catalyst also did not show any activity confirming that there are no surface Pd atoms in the material and Pd nanoparticles are covered by a Ru shell in the as-synthesized nanoparticles.

3.2. Catalysis in a reductive atmosphere: hydrogenolysis at 350 °C

The as-synthesized particles were deposited on γ -Al₂O₃, and for this particular reductive application, they were pretreated by calcination at 200 °C followed by reduction in hydrogen flow at 375 °C. This particular treatment for surface stabilizer removal resulted in the maximized catalytic activity even in the presence of PVP residuals on the surface, as we reported earlier [20]; higher calcination temperatures caused sintering and/or undesired Pd/Ru rearrangement on the nanoparticle surface. According to our previous TPR analysis, Ru-Pd catalysts showed reduction peak at 80–85 °C [20]. Thus, the in situ hydrogen reduction at 375 °C is enough to provide metallic surfaces for both Ru2Pd1 and Pd(c)Ru(s) catalysts, which are the active sites for indan hydrogenolysis. The catalytic reaction in a reductive (hydrogen) atmosphere was indan ring opening (selective hydrogenolysis) carried out in a packed-bed reactor with gas feed at 350 °C. The reaction serves as a model reaction for fuel upgrading [33]. We already reported these results earlier and details can be found in Ref. [20]. Here we provide a brief summary with a focus on the nanoparticle surface structure only for a sake of comparison with an oxidative application (following Section 3.3, not reported previously).

Monometallic Ru is highly active in indan hydrogenolysis, unlike palladium, but the latter allows selective ring opening to 2-ethyltoluene without successive dealkylation. Ruthenium favors deeper hydrogenolysis to o-xylene (Fig. 3). When the two metals are alloyed together either into an Ru2Pd1 or Pd(c)Ru(s) struc-



Fig. 4. DRIFT spectra of CO adsorbed on Ru, Pd and Pd(c)Ru(s) catalysts after reductive atmosphere treatment. Catalysts were pre-calcined at 200 °C followed by reduction in hydrogen at 375 °C for polymer removal. Reprinted from [20] with permission from Paragon.



Fig. 5. Pd $3d_{5/2}$ XPS of the spent monometallic Pd catalyst (after the reaction from Fig. 6).



Fig. 6. Methane combustion over mono- and bimetallic Ru-Pd catalysts, 4100 ppm methane, 1.1 barg pressure, 1.2 mg Pd and/or 3.1 ± 0.4 mg Ru: (a) thermal aging at 375-550 °C (Ru is not shown because of <10% conversion at 375 °C); (b) ignition–extinction curves after 40 h thermal aging. Error bars represent one standard deviation from average for ignition–extinction curves (no significant hysteresis was observed). Catalysts were calcined at 550 °C for 16 h under static air.

ture, they show intermediate behavior between the two metals (with one exception) but are distinctively different from each other. The exception is that the activity of Pd(c)Ru(s) even surpasses the activity of monometallic Ru, indicating that active ruthenium is more accessible to reactants being dispersed on the Pd core, versus monometallic Ru particles with lower Ru dispersion. The Ru2Pd1 sample shows Ru-like activity but Pd-like selectivity, suggesting the close contact between the two metals in one nanostructure: if Ru is not promoted by Pd on the nanoparticle surface, the Ru2Pd1 will not show suppressed selectivity to *o*-xylene and enhanced selectivity to 2-ethyltoluene as compared to monometallic Ru. The



Fig. 7. TEM images of as-synthesized nanoparticles, calcined catalysts (550 °C, 16 h) and spent catalysts (after the reactions from Fig. 6).

Pd(c)Ru(s) selectivity is closer to the monometallic Ru selectivity, indicating the shell enrichment with Ru. Fig. 3 also presents the results of earlier reported alloyed Ru10Pd1 catalyst (molar ratio of Ru to Pd=10) only to show how the catalytic properties of Pd(c)Ru(s)(2:1 molar ratio) are close to the Ru-enriched nanoparticles with both Ru and Pd present on the surface. Thus, the catalytic results in indan hydrogenolysis indicate that the two Ru-Pd catalysts with the same molar ratio but initially different structures (alloy Ru2Pd1 and core-shell) still behave differently in the reaction in accordance with their nanoparticle surface enrichment, but the core-shell sample does undergo some structural evolution. If initially, in low-temperature MBE hydrogenation the core-shell sample displays purely Ru behavior, then at high-temperature hydrogenolysis, Pd behavior also manifests, i.e., some Pd migration to the nanoparticle surface occurred. This behavior is expected from thermodynamics: Pd has lower heat of vaporization (380 kJ/mol) as compared to Ru (580 kJ/mol), thus, it tends to segregate to the surface to lower the surface free energy. CO-DRIFTS of the core-shell catalyst (Fig. 4) confirms such structural evolution. Prior to CO-DRIFTS analysis, Ru-Pd catalysts were calcined at 200 °C in air and followed by in situ hydrogen reduction at 375 °C to simulate the pretreatment procedures before indan RO. The low wavenumber adsorption bands corresponding to bridged adsorbed CO mode on Ru (1946 cm⁻¹) and Pd (2026 and 1995 cm⁻¹) are significantly different for the core-shell structure: the bridged adsorption on Ru atoms is suppressed (low intensity of 1951 cm⁻¹ peak) with no bridged adsorption on Pd atoms, but a high-intensity new peak at 1980 cm⁻¹ can be most likely ascribed to the bridged adsorption of CO on adjacent Pd and Ru atoms, which is in line with our hypothesis of the core-shell structure evolution into a surface containing both elements.

To conclude, the catalytic results and CO-DRIFTS indicate structural rearrangement of parent Pd(c)Ru(s) structure via Pd segregation to the surface under indan hydrogenolysis conditions. However, there are still significant differences in behavior of the Ru2Pd1 and Ru(c)Pd(s) sample in the reaction regardless of their identical Pd-to-Ru molar ratio. The occurred structural rearrangements thus did not result in the very same structure; the use of initially applied different synthetic procedures (Scheme 1) is paramount for this particular application: to achieve high single cleavage selectivity to 2-ethyltoluene (Fig. 3), shell enrichment with Ru is undesirable and the alloy structure preparation is preferred.

3.3. Catalysis in an oxidative atmosphere: combustion at 550 °C

Prior to the methane combustion reactions, all catalysts were calcined at 550 °C for 16 h, which is an accepted de-greening procedure for automotive catalysts [25]. Since methane combustion was carried out in oxygen-rich environment, the calcined Ru-Pd catalysts were packed in the reactor without further reduction by hydrogen. Methane oxidation follows Mars-van Krevelen redox mechanism on site pairs consisting of adjacent Pd and PdO species [34,35]. Metallic Pd dissociatively adsorbs CH₄ producing H and CH_x species; while PdO is responsible for oxidation [34,36]. Thus, according to the redox mechanism, the surface state of catalysts should be partially oxidized during methane oxidation. This is confirmed by XPS analysis over a spent Pd catalyst as shown in Fig. 5: the Pd 3d_{5/2} peaks could be assigned to PdO (336.5 eV), PdO_x (337.3 eV) and Pd (335.4 eV), indicating the coexistence of metallic Pd and Pd oxides.

Fig. 6 compares the activities of monometallic and bimetallic catalysts in methane combustion during initial ignition-extinction, low-high temperature cycling (375 and 550 °C), followed by ignition-extinction curve measurements as described in the experimental section. The monometallic Pd catalyst is the most active methane oxidation catalyst [34,37]. The monometallic Ru displays the lowest activity, with less than 10% conversion at 375 °C; initial activity of the bimetallic catalysts in the first ignition-extinction cycle is lower than for the pure Pd (Fig. 6 (a)), but it improves under the reaction conditions and surpasses the Pd activity after 25 h on stream (Fig. 6 (b) and (c)). Indeed, as seen for the cycling experiments (Fig. 6 (b)), 550 °C temperature conditioning leads to progressive deactivation of Pd, while the bimetallic catalysts do not deactivate with cycling and even increase their activity. However, as opposed to the previous case with a reductive atmosphere, both Pd(c)Ru(s) and Ru2Pd1 catalysts display exactly the same behavior for methane combustion during and after structural evolution.

As seen from the TEM images (Fig. 7) of the fresh, calcined (550 °C for 16 h), and spent monometallic Pd (after all the cycling experiments) and Ru2Pd1 catalysts (after all the cycling experiments as in Fig. 6), mono-Pd sintered to a large extent after exposure to 550 °C, which is one of the known reasons for Pd catalyst deactivation during methane combustion [34]. The bimetallic catalyst possesses improved thermal stability, with no visible agglomerates above 30 nm. The CO chemisorption showed the CO/metal(s) molar ratios of 0.19, 0.15 and 0.33 for Pd, Ru and Ru2Pd1 catalysts, respectively. Monometallic and bimetallic Ru-Pd samples for CO chemisorption experiments were also calcined at 550 °C for 16 h to simulate the pretreatment procedure before methane combustion; this is then followed by in situ hydrogen reduction at 550 °C for 1 h, as CO adsorption requires metallic surfaces of Pd and Ru. The higher thermal stability and surface area of the bimetallic catalyst may partly explain the higher observed methane combustion activity versus the monometallic Pd.

One of other feasible hypotheses of the bimetallic catalysts activity improvement over the course of the reaction (Fig. 6) could be volatilization of inactive Ru as oxides, leading to the progressive increase in the Pd atom exposure. To check the hypothesis's validity, the Ru and Ru2Pd1 samples were analyzed by NAA after two different calcination treatments: i) 550 °C, 16 h, and ii) 550 °C, 16 h followed by 600 °C, 72 h. Monometallic Ru content dropped from 0.28 \pm 0.02 wt.% to 0.22 \pm 0.01 wt.% after the 600 $^{\circ}$ C treatment, confirming the oxide volatility. However, when Ru was alloyed with Pd in the Ru2Pd1 sample, the loading remained constant as 0.17 ± 0.01 wt.%. This result is in line with the improved thermal stability of the alloyed Ru-Pd catalysts (Fig. 7), and leads to a rejection of the hypothesis of increasing Pd exposure due to Ru oxides volatilization. Monometallic Ru and bimetallic Ru2Pd1 catalysts treated at 600 °C were used only to the study the possible Ru oxides volatility, so they were not used in the catalytic tests.

Another reason for the bimetallic catalyst activity improvement could be in situ nanoparticle reconstruction and Pd atom diffusion to the surface driven by the minimization of surface free energy. Indeed, the heat of vaporization of Pd (380 kJ/mol) is lower than the one for Ru (580 kJ/mol), so the progressive nanoparticle shell enrichment with Pd is expected during high-temperature applications. Such a hypothesis may also explain the same observed activity of the Pd(c)Ru(s) and Ru2Pd1 bimetallic samples in the methane combustion: regardless of the initial particle structures, they both restructure to the most thermodynamically favourable material. The variation in bimetallic activities with prolonged time on stream could be related to the progressive change in surface oxygen composition as Pd diffuses to the bimetallic surface. Different metals may display different combustion activities not only because of their nature but also due to different metal-to-metal oxide ratios. For example, PdO forms in low temperature range (300-l400 °C), being stable up to 800 °C, whereas, PtO₂ decomposes at a much lower temperature $(400 \circ C)$ [37]. Since PtO₂ is highly unstable, significant amount of metallic Pt may still exist even after calcination at 500 °C in air [37], which explains the poor methane combustion activity of supported Pt catalyst under fuel-lean conditions comparing to Pd metal. According to the Mars-van Krevelen redox mechanism, an optimal surface oxidation state is required for methane activation. In the case of bimetallic Ru-Pd system, Ru binds oxygen too strongly (the heat of formation for RuO₂ is higher than PdO), which can lead to a lower surface density of oxygen vacancies for CH₄ dissociative adsorption. Eventually, the active Pd in bimetallic catalysts became more accessible being dispersed on Ru core, which explains the increasing activities in both bimetallic Ru-Pd catalysts. The Ru2Pd1 and Pd(c)Ru(s) catalysts should have similar surface oxygen compositions during methane combustion, because they both transformed into Ru(c)Pd(s) structure as was shown by EXAFS analysis in the following.



Fig. 8. EXAFS spectra in k-space for monometallic Ru and Pd and bimetallic Pd(c)Ru(s) and Ru2Pd1 nanoparticles in Pd K-edge (a) and Ru K-edge (b). Catalysts were calcined at $550 \degree$ C for 16 h followed by reduction in hydrogen at 400 °C.

EXAFS of the high-temperature-treated Pd(c)Ru(s) and Ru2Pd1 samples was performed to verify their structures. The Ru-Pd catalysts for EXAFS study were treated using the same procedure as in catalyst test that is pre-calcination at 550 °C for 16 h under air; this was followed by H₂ reduction at 400 °C, which is confirmed to be enough to reduce oxidized Ru-Pd nanoparticles to metallic forms by our previous TPR analysis [20]. Prior to EXAFS analysis, samples were stored under ambient conditions for a week and then reduced in hydrogen to avoid complications by the metal-oxygen contributions when estimating coordination numbers. The reductive pre-treatment did not lead to the changes in methane oxidation catalysis: both reduced and oxidized Ru2Pd1 samples showed identical light-off temperature (temperature for 50% methane conversion) of 385 ± 10 °C.

Fig. 8(a) and (b) show the Pd K-edge and Ru K-edge EXAFS spectra in K-space for mono-Ru and Pd and bimetallic nanoparticles. The amplitudes of the signal for Pd(c)Ru(s) and Ru2Pd1 nanoparticles are significantly lower than those of mono-Pd nanoparticles (Fig. 8 (a)), indicating lower coordination numbers around Pd in the bimetallic particles [24]. The EXAFS oscillation patterns of bimetallic nanoparticles at the Ru K-edge are similar in amplitude but differ slightly in periodicity from the pure Ru sample (Fig. 8 (b)); this could be ascribed to alloying between Pd and Ru in the bimetallic structure. Similar changes in the EXAFS oscillation patterns as a result of the formation of Au-Pd bonds have been reported by Liu



Fig. 9. EXAFS single-shell fits in r-space for monometallic Pd and Ru and bimetallic Pd(c)Ru(s) and Ru2Pd1 nanoparticles. Catalysts were calcined at 550 °C for 16 h followed by reduction in hydrogen at 400 °C.

et al. [38]. The negligible change in amplitude of the Ru edge in the bimetallic samples, combined with the decreasing amplitude on the Pd edge, is strong evidence of Ru(c)Pd(s) formation after calcination/reduction; i.e., an inversion of the original structure in the case of Pd(c)Ru(s) particles.

Fig. 9 shows high quality EXAFS R-space data with singleshell theoretical fits for monometallic Ru and Pd and bimetallic Pd(c)Ru(s) and Ru2Pd1 nanoparticles. The Pd and Ru experimental EXAFS data of the bimetallic samples were fit by the theoretical phase-shift and amplitudes generated by FEFF [23,24]. The structural parameters of the mono-and bimetallic Ru-Pd nanoparticles generated using IFEFFIT software package are shown in Table 1. The shoulders observed on the Pd edge at low R values are most likely due to the presence of small amounts of surface Pd oxidation [24]. The EXAFS analyses were performed on the samples exposed to air (at room temperature) for about 1 week; Pd surface oxidation was possible; this was also observed by XPS in our previous work [28]. The most useful information on the local structure obtained from EXAFS fits is coordination number, presented in Table 1. The coordination numbers for the bulk fcc and hcp structures are 12. As compared to the reference foils, monometallic Pd and Ru nanoparticles have lower coordination numbers of 9.7 ± 0.7 (N_{Pd-Pd}) and 10.6 ± 1.6 (N_{Ru-Ru}), respectively. These are indications of the existence of large portions of atoms on the surface of the nanoparticles [38]. The higher coordination number seen for Ru after the high temperature treatment agrees with CO chemisorption/TEM evidence that Ru tends to sinter to a greater degree than Pd.

For the bimetallic nanoparticles, N_{Pd-M} and N_{Ru-M} correspond to the total coordination numbers around Pd and Ru, respectively, where M refers both to Ru and Pd. The Pd–Pd and Pd-Ru contributions cannot be well differentiated because of their similar atomic numbers. For core–shell structures, the total coordination number for the core metal should be high, normally close to 12, whereas the total coordination number for the shell metal would be much smaller [38]. For our catalysts, after calcination in air at 550 °C for 16 h, and subsequent reduction, the N_{Pd-M} for Pd(c)Ru(s) and Ru2Pd1 samples were found to be 7.5 ± 0.7

Table 1
EXAFS fitting parameters.

Catalyst	Shell	Ν	$R_{\rm j}({ m \AA})$	$\Delta E^0(eV)$	$s^2 \times 10^3 (\text{\AA}^2)$	R-factor
Pd foil	Pd-Pd	12	2.741 (0.002)	2.3 (0.5)	5.7 (0.4)	0.005
Ru foil	Ru-Ru	12	2.671 (0.002)	2.9 (1.2)	4.2 (0.9)	0.016
Pd	Pd-Pd	9.7 (0.7)	2.735 (0.001)	-5.0(0.5)	6.1 (0.4)	0.009
Ru	Ru-Ru	10.6 (1.6)	2.670 (0.006)	-7.5 (1.2)	4.0 (0.8)	0.023
Pd(c)Ru(s)	Pd-M	7.5 (0.7)	2.713 (0.002)	-9.1 (0.7)	6.5 (0.7)	0.017
	Ru-M	11.3 (1.4)	2.672 (0.002)	3.7 (1.0)	4.6 (0.7)	0.016
Ru2Pd1	Pd-M	8.0 (1.0)	2.699 (0.004)	-9.2 (1.0)	9.0 (1.0)	0.046
	Ru-M	11.5 (1.3)	2.673 (0.002)	3.4 (0.9)	4.9 (0.6)	0.015

and 8.0 ± 1.0 , respectively, while the total coordination numbers around Ru atoms, $N_{Ru\text{-}M}$, were higher (11.3 \pm 1.4 for Pd(c)Ru(s) and 11.5 ± 1.3 for Ru2Pd1). This shows that both structures transformed into a final Ru(c)Pd(s) structure. Only small amounts of Pd oxidation are seen in these samples, and no Ru oxidation, which is further evidence of the migration of Pd atoms to nanoparticle shells. Note that the monometallic catalyst coordination numbers differ significantly from those of the bimetallic samples. TEM evidence shows much more moderate sintering in bimetallic nanoparticles compared to their mono-Pd or Ru counterparts; which confirms that the bimetallic nanoparticles do not segregate into much larger Ru and small Pd monometallic particles. The structural inversion of the parent Pd(c)Ru(s) particle occurred most likely due to the thermodynamics-induced Pd segregation to the surface because of its lower heat of vaporization. The fact that the shell becomes enriched with Pd is in line with the catalytic results: the bimetallic catalysts display dramatically enhanced activity over time as compared to monometallic Pd (Fig. 6), which is consistent with Pd diffusion to the surface over time.

Thus, both samples' methane combustion catalytic results (Fig. 6) and EXAFS evidence show that irrespective of the preparation method (Scheme 1) and differences in parent bimetallic nanostructures (but recall their constant bulk metal ratio), both Pd-Ru systems transform into one structure with Pd-enriched shells. The structural evolution was the most pronounced in the high-temperature oxidative application versus the above-discussed indan hydrogenolysis at 350 °C.

4. Conclusions

Pd-Ru bimetallic nanoparticles with the same bulk metal ratio were synthesized using two different colloidal chemistry techniques. One resulted in particles with mixed surface (alloy), and another with Ru-shell particles. Several catalytic applications were considered:

- A low-temperature liquid-phase hydrogenation of an allylic alcohol showed that the presumably core-shell structure indeed displays the properties of only the shell metal while the alloy sample displayed intermediate properties between the monometallic counterparts.
- In a high-temperature gas-phase hydrogenolysis, the core-shell sample underwent some structural evolution with Pd segregation to the surface, as seen from the catalytic behavior and CO-DRIFTS; however, the two samples still exhibited distinctively different behaviors.
- A high-temperature combustion reaction revealed identical catalytic properties of both samples, and EXAFS confirmed that both parent nanoparticle types evolved into one structure with Pdenriched shells.

The results show that the structure control in bimetallic nanoparticle preparation is crucial for some applications while others do not benefit because of thermodynamically and probably adsorbent-induced structural evolution into one type of structure. The results for methane oxidation showed that nanoparticle structural evolution is kinetically limited even at 550 °C and thus bimetallic catalysts to be evaluated under prolonged times on stream.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.06. 025

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