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Spent automotive three-way catalysts towards C-C bond forming reactions

Ewa Mieczyńska, Andrzej Gniewek, Anna M. Trzeciak*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland

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ABSTRACT

Spent automotive three-way catalysts, containing Rh, Pd and Pt nanoparticles supported on oxide-based ceramic materials, catalyze the Heck cross-coupling of iodobenzene with butyl acrylate and unsaturated alcohols at 140 °C. Under Suzuki reaction conditions, biphenyl was formed with high yield when the same catalysts were applied. Successful hydroformylation of 1-hexene was performed in the presence of PPh₃. The catalytic activity of spent automotive three-way catalysts was compared with that of airborne matter collected in the city of Wrocław.

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1. Introduction

The amount of platinum group metals (PGMs) in atmosphere and in soil has increased in recent years, mainly as a result of the worldwide application of catalytic converters in motor vehicles [1-10]. Catalytic converters are widely used today to decrease the level of pollutants such as CO, NO_x, and unburned hydrocarbons (HCs) emitted with exhaust gases from combustion engines [11,12]. The active components of automotive catalytic converters consist of PGMs, such as Pd, Pt, and Rh, supported on ceramic material coated with Al₂O₃ and other metal oxides (CeO₂, ZrO₂). Palladium and platinum are active in the oxidation of CO and HCs to CO₂ and H₂O, whereas rhodium catalyzes the reduction of NO_x to N₂. Besides a very beneficial effect of automotive catalytic converters on the environment, especially the atmosphere, some negative aspects of their application should also be considered. Thus, PGMs in the form of nanoparticles may be released from the catalytic converter during car operation and accumulated in dust and subsequently in water and soil [13-15]. Moreover, spent catalytic three-way converters can be classified as hazardous waste materials, which is why the development of efficient and cheap methods of PGM recovery is very important [16–19]. In this context, it is also very important to recognize the catalytic activity of waste PGMs present in road dust and to estimate the catalytic activity of spent automotive catalysts which may find application in other catalytic reactions. For example, it has been demonstrated that scrap catalytic converters efficiently catalyze the hydrogenation of various alkenes [20] and show activity in VOC combustion [21]. Thus, it could also be possible to use spent catalytic converters not only as a source of PGMs but also as active catalysts for organic reactions.

The aim of the studies presented in this paper was to estimate the catalytic ability of (a) airborne particulate matter and (b) spent automotive three-way catalysts that have been used for a period of 6 years or more for the purification of exhaust gases. We applied these materials without any special pretreatment as catalysts for C—C bond forming reactions to test their catalytic potential. Aryl halides were used as substrates in the model C—C bond forming reactions. It is important to point out that the presence of aryl halides as wastes in water or soil should be seriously considered today. Consequently, knowledge about the catalytic activity of waste PGMs towards aryl halides might be useful in anticipation of possible transformations of aryl halides in the environment.

Usually, C—C cross-coupling reactions are catalyzed by palladium compounds, both organometallic complexes and Pd(0) nanoparticles [22–31]. In most cases these catalysts are not only specially prepared but also stored in an inert atmosphere before use. In this context, it was interesting to check whether PGMcontaining wastes could compete in catalytic activity with carefully designed species.

Chemical deactivation or poisoning of the spent three-way catalysts is an important factor to consider. The properties of such double-use catalysts, which were first employed as a part of gasoline-powered vehicle emission control systems, and then engaged as the catalysts of C—C coupling reactions, might be much

^{*} Corresponding author. Tel.: +48 713757253; fax: +48 713282348. *E-mail address:* anna.trzeciak@chem.uni.wroc.pl (A.M. Trzeciak).

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Scheme 1.

influenced by contaminants that could have been introduced during their operation in car exhaust systems. Sources of three-way catalysts poisons include: fuel, lubrication oils and wear of engine, and exhaust tailpipe parts. Pb, S and Si originate from fuel additives, P, Ca, Zn and Mg from lubricants, while Fe, Cu, Ni, Cr and Cd are derived from the engine and exhaust pipe construction materials [32,33].

2. Experimental

2.1. Characterization of PM₁₀ filters

Samples of airborne particulate matter were collected on quartz or glass filters designed for the analysis of particles up to $10 \,\mu m$ (PM₁₀) in diameter. The sampling time was 24 h. The filters were used in the city of Wrocław in 2005 and 2006 and then stored in air at ambient temperature.

For analyzes of Pd content, the filters were cut into small pieces and a sample of ca. 0.3 g was weighed and transferred to a flask. Next, 10 mL H₂O, 4 mL HNO₃, and 3 mL H₂O₂ were added and left for 24 h. After that time, the sample was heated for 1 h at 70 °C and again left for 24 h. The resulting mixture was filtered and the obtained filtrate diluted with water to 25 mL. The palladium content determined by ICP was found to be in the range from 0.08 ppm to 8 ppm in five samples analyzed.

2.2. Characterization of spent automotive catalysts

A sample of ca. 0.001 g of the spent catalyst was treated with 3 mL of HCl and 1 mL of HNO₃. The resulting mixture was heated for 10 min at 60 °C and left for 48 h. After that time, water was added to obtain a total volume of 10 mL, and ICP analysis was performed to determine the PGM content.

2.3. TEM measurements

First, the catalyst was ground to a form of powder. Next, it was added to several milliliters of methanol and such suspension was treated for 5 min with ultrasounds. Finally, a droplet of the suspension was placed on a carbon-coated microscope grid and dried for 40 min. TEM measurements were carried out using a FEI Tecnai G² 20 X-TWIN electron microscope operating at 200 kV.

The kind of noble metal forming nanoparticles observed in the TEM micrographs was recognized in each case by means of EDX analysis. Rh was identified using the X-ray K α line at 20.167 keV and L α at 2.696 keV, Pd using the K α line at 21.123 keV and L α at 2.838 keV, Pt using the L α line at 2.838 keV and M α at 2.051 keV.

2.4. Suzuki-Miyaura reaction

The Suzuki–Miyaura reaction was carried out in a Schlenk tube with magnetic stirring. *Reagents*: phenylboronic acid (0.183 g, 1.5 mmol), iodobenzene (0.114 mL, 1 mmol), Cs₂CO₃ (0.652 g, 2 mmol), ethylene glycol (10 mL) or 2-propanol/water (1:1; 10 mL), and 1 or 2 g of the spent automotive catalyst were introduced

directly to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber stopper and introduced into an oil bath preheated to 80 °C. The reaction was carried out at 80 °C for period of time between 6 and 24 h and then the reactor was cooled down. The organic products were separated by extraction with hexane (3 portions of 10 mL). The combined extracts (25 cm^3) were GC-FID analyzed (Hewlett Packard 5890) with 0.075 mL of dodecane as an internal standard. The products were identified by GC–MS (Hewlett Packard 5971 A).

The same procedure was applied for the filters containing airborne matter (4.46 g).

2.5. Heck reaction

The Heck reaction was carried out in a Schlenk tube with magnetic stirring. Reagents: butyl acrylate (0.27 mL, 1.91 mmol), iodobenzene (0.49 mL, 4.38 mmol), NaHCO₃ (0.4 g, 4.76 mmol), DMF (10 mL), and 1 g of the spent automotive catalyst were introduced directly to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber stopper and introduced into an oil bath preheated to 140 °C. The reaction was carried out at 140 °C for period of time between 4 and 24 h and then the reactor was cooled down. In order to separate the organic products, 10 mL of diethyl ether was added to the reaction mixture, which was then stirred for 30 min. Subsequently, 10 mL of water was added and stirring continued for 10 min. After that time an upper phase was separated, 10 mL of diethyl ether was added to the residue, and stirring continued for 10 min. The extraction was repeated and all ether fractions were collected and GC-FID analyzed (Hewlett Packard 5890). The products were identified by GC-MS (Hewlett Packard 5971A).

The catalytic experiments with the filters containing airborne matter (0.47 g) were performed according to the same procedure, using the following amounts of reactants: butyl acrylate (0.13 mL, 0.9 mmol), iodobenzene (0.25 mL, 2.23 mmol), NaHCO₃ (0.2 g, 2.38 mmol), DMF (7 mL). The reaction was carried out at 140 °C for 48 h.

2.6. Hydroformylation reaction

Catalytic reactions were carried out in a 55 cm³ steel autoclave, which was charged with a 1 g sample of the spent automotive catalyst, PPh₃ (9.22 × 10^{-3} g–2.15 × 10^{-2} g), toluene (7–12 mL), and 1-hexene (1.5 mL, 12 mmol) under N₂ atmosphere. Next, the autoclave was filled with an equimolar mixture of H₂ and CO to a pressure of 10 atm and heated at 80 °C for 24 h. During that time, the reaction mixture was stirred magnetically. After that, the autoclave was cooled down, opened and the organic products were separated from the catalyst by decantation and analyzed using a GC-FID (Hewlett Packard 5890).

3. Results and discussion

3.1. Airborne matter as catalyst for Heck and Suzuki–Miyaura reactions

The model Heck reactions with the application of the filters containing airborne matter as the catalysts were carried out according

Results of the Heck reaction carried out with different samples of airborne matter.					
Sample no.	Product I [%]	Product II [%]	Sample no.	Product I [%]	
1.	26	-	8.	27	
2.	65	_	9.	28	
3.	22	_	10.	5	
4.	27	-	11.	95	
5.	85	15	12.	98	
6.	70	30	13.	96	
7	8	_	14	94	

Reaction conditions: Phl 0.25 mL (2.23 mmol); CH2=CHC(O)OBu 0.13 mL (0.9 mmol); NaHCO3 0.2 g (2.38 mmol); DMF = 7 mL; 140 °C; 48 h.

Table 2

Content of PGMs in spent automotive three-way catalysts.

Catalyst	Rh [ppm]	Pd [ppm]	Pt [ppm]	Molar ratio [Rh]:[Pd]:[Pt]
I	0.22	1.9	26	1:8.4:62
II	100	3200	65	2.9:90:1
III	7.6	450	2.6	5.5:317:1
IV	100	17	-	6.1:1:0
V	30	1.6	-	19.4:1:0

to Scheme 1 with iodobenzene and butyl acrylate as the substrates. Typical reaction conditions, 140 °C and DMF as the solvent, were applied.

To estimate the reproducibility of the Heck reaction, ten experiments were performed with different filters from 2005 to 2006. In each series of reactions, three were unsuccessful; however, in seven cases the mono-arylated cross-coupling product, butyl cinnamate, was found after 48 h reaction. The yield of butyl cinnamate varied from 8% to 85% for the samples from 2005 and from 5% to 98% for samples collected in 2006 (Table 1). In addition, in four reactions the product of a second arylation, β -phenyl cinnamate, was also formed with yields of up to 30%.

Attempts to use bromobenzene as a substrate for the Heck crosscoupling with methyl acrylate failed and in five experiments the product was not found.

In contrast to the relatively high activity in the Heck coupling, the product of the Suzuki-Miyaura coupling, biphenyl, was formed only in one experiment in the reaction of iodobenzene with phenylboronic acid, with a yield of 38% (Scheme 2).

3.2. Spent automotive three-way catalysts in cross-coupling reactions

3.2.1. Characterization of spent automotive catalysts

In the next step of our studies, five different spent automotive three-way catalysts were tested in the Suzuki-Miyaura and Heck reactions. All the catalysts had been previously used for a period of 6 years or more for the original purpose of purifying exhaust gases in different cars. The content of PGMs, determined by the ICP method, was from 1.6 to 3200 ppm of Pd, from 2.6 to 65 ppm of Pt, and from 0.22 to 100 ppm of Rh (Table 2).

The results of TEM studies of the spent catalytic converters revealed that noble metals (Rh, Pd and Pt) were present in the form of nanoparticles supported on oxide-based ceramic materials. In the catalytic converters investigated, the nanoparticles were well dispersed on the support without forming aggregates. Usually they were characterized by typical crystal outlines (approximately 70%)

Table 3
Results of the Heck reaction carried out with spent automotive catalysts.

Catalyst	[PhX]:[Pd]	PhX	Time [h]	Yield [%]
Ι	176000	PhI	24	15
II	75	PhI	24	100
	139	PhI	24	100
	144	PhI	4	41
	139	PhI	4	100
	142	PhI	4	100
	156	PhBr	24	6
III	980	PhI	24	0
IV	25100	PhI	4	69
V	267 000	PhI	4	100

Product II [%]

5

4

6

Reaction conditions: catalyst 1g: PhI 0.49 mL (4.38 mmol) or PhBr 0.46 mL (4.38 mmol); CH2=CHC(O)OBu 0.27 mL (1.91 mmol); NaHCO3 0.4 g (4.76 mmol); DMF 10 mL: 140 °C.

and only some of them exhibited a rather spherical shape (30%). Particle size distributions of each of the noble metals (Rh, Pd, Pt) in the selected catalyst (II, IV, or V) were narrow (standard deviation σ = 5) with well-defined average crystal diameters (Fig. 1).

3.2.2. Heck reaction

The results illustrating the catalytic activity of the spent automotive catalysts in the Heck reaction are collected in Table 3. The model reaction was carried out according to Scheme 1 with iodobenzene and butyl acrylate as the substrates. Subsequently, other substrates were also used for comparison.

Remarkably good activity was noted for catalyst V, which formed a coupling product with 100% yield already after 4 h despite a high excess of iodobenzene in respect to palladium. Very good results were also obtained with catalyst II, which contained the highest amount of palladium. Interestingly, catalyst II also showed some activity in the coupling of bromobenzene with butyl acrylate. When catalyst IV was used, the best result obtained was 69% of butyl cinnamate after 4 h. From the data presented in Table 3, it can also be concluded that there is no clear correlation between palladium content and conversion. The activity of the spent automotive threeway catalysts in the Heck process depends also on other important factors. For instance, catalyst II showed 41 and 100% in identical experiments (Table 3). Most likely, in spite of the high Pd content, the fragment of the catalyst used in the experiment with a lower yield was partially poisoned. Contaminants introduced during operation of the catalyst in a vehicle exhaust system may cause deactivation of the metal sites or modify electronic properties of palladium [32,33].

With catalyst II, very good results, 97% and 57% of the product, were also obtained for the coupling of iodobenzene with 2-methyl-2-propen-1-ol and with its isomer, but-2-en-1-ol (crotyl alcohol)



Table 1



Fig. 1. Typical forms and most common diameters of transition metal nanoparticles observed in spent catalytic converters.

(Table 4). It was also possible to couple iodobenzene with cinnamyl aldehyde (34% after 4 h) and with ethyl cinnamate (77% after 24 h). Catalyst V was active in reaction of iodobenzene with crotyl alcohol (45% after 24 h). With cinnamyl aldehyde and 2-methylpropen-2-ol, 19% of the cross-coupling product was formed. Again, it is important to point out that the [PhI]:[Pd] ratio for catalyst V was in the range from 200 000 to 300 000.

According to the literature, palladium is considered the most active catalyst for C–C cross-coupling reactions and it is most probably also responsible for the catalytic results observed in these studies [22–31]. However, some activity originating from platinum or rhodium cannot be fully excluded in the Heck reaction or in the Suzuki–Miyaura reaction. Therefore, other metals or components of the spent automotive catalysts might influence the activity of palladium and result in a lack of correlation between palladium content and the observed activity.

The post-reaction mixture obtained after the Heck reaction with catalyst II was analyzed to estimate the amount of PGMs leached from the support. According to ICP, 12 ppm of Pd, 0.3 ppm of Rh and

Table 4

Results of the Heck reaction of iodobenzene with different olefins carried out with spent automotive catalysts.

Catalyst	[PhI]:[Pd]	Olefin	Time [h]	Yield [%]
II	137	PhCH=CHC(O)H	4	34
	142	PhCH=CHCOOEt	24	77
	140	MeCH=CHCH ₂ OH		57
	70	MeCH=CHCH ₂ OH		64
	137	CH ₂ =C(Me)-CH ₂ OH		97
IV	25 900	PhCH=CHCOOEt	24	1
	25 900	PhCH=CHC(O)H		3
	27 000	MeCH=CHCH ₂ OH		17
	13 600	MeCH=CHCH ₂ OH		46
	25 000	CH ₂ =C(Me)-CH ₂ OH		3
V	243 000	PhCH=CHCOOEt	24	5
	243 000	PhCH=CHC(O)H		19
	302 100	MeCH=CHCH ₂ OH		49
	146 000	MeCH=CHCH ₂ OH		45
	300 500	$CH_2 = C(Me) - CH_2OH$		19

Reaction conditions: catalyst 1 g; PhI 0.49 mL (4.38 mmol); olefin 1.91 mmol; NaHCO₃ 0.4 g (4.76 mmol); DMF 10 mL; $140 \,^{\circ}$ C.





Table 5

Results of the Suzuki-Miyaura reaction carried out with spent automotive catalysts.

Catalyst	[PhI]:[Pd]	Solvent	Time [h]	Yield [%]
II	15	Ethylene glycol	24	100
	29	Ethylene glycol	24	100
	32	2-Propanol/water	24	100
	30	2-Propanol/water	24	100
	30	Ethylene glycol	24	100
	32	Ethylene glycol	6	39
	33	2-Propanol/water	6	97
IV	8300	2-Propanol/water	6	35
V	40 600	Ethylene glycol	24	0
	44 500	2-Propanol/water	24	4

Reaction conditions: catalyst 1 or 2g; Phl 0.114 mL (1 mmol) or PhBr 0.106 mL (1 mmol); PhB(OH)₂ 0.183 g (1.5 mmol); Cs₂CO₃ 0.652 g (2 mmol); ethylene glycol 10 mL or 2-propanol/water (1:1) 10 mL; 80 °C.

Table 6

Results of 1-hexene hydroformylation carried out with spent automotive catalysts.

Catalyst	[1-hexene]:[Rh]	[PPh ₃]:[Rh]	n/iso	Conversion [%]	2-hexene [%]	Aldehydes [%]
IV	4000	18	2.1	41	31	11
	4000	9	-	-	-	-
	4000	29				-
V	5100	15	0.9	61	57	4
	5100	12	1.0	79	73	6
	5100	24	1.9	66	8	58

Reaction conditions: catalyst 1 g; 1-hexene 1.5 mL (12 mmol); CO+H₂ 10 atm; PPh₃ 9.22 × 10⁻³ g-2.15 × 10⁻² g (3.52 × 10⁻⁵ - 8.2 × 10⁻⁵ mol); toluene 7–12 mL; 80 °C; 24 h.

0.6 ppm of Pt were found, indicating a very low, but measurable, dissolution of PGMs in the presence of Heck reactants. Redeposition of the leached noble metal species on the support was not observed.

3.2.3. Suzuki–Miyaura reaction

Results obtained in the Suzuki–Miyaura reaction (Scheme 2) carried out in the presence of five spent automotive catalysts are presented in Table 5. In these experiments the amount of a catalyst ranged from 1 to 2g regardless of the PGM content. As a consequence, the [Ph1]:[Pd] ratio varies remarkably for the systems studied. If the amount of palladium is considered, the best results were noted for catalyst IV, which produced biphenyl with 35% yield in 6 h at a high excess of PhI in respect to palladium ([Ph1]:[Pd] = 8300).

Catalyst II, containing the highest amounts of PGMs, formed 39% of the coupling product in 6 h in ethylene glycol and 97% in 2-propanol-water mixture. When the less reactive bromobenzene was used instead of iodobenzene, 43% of biphenyl was formed in 6 h. With catalysts IV, 35% of biphenyl was obtained after 6 h, whereas with catalyst V only 4% of biphenyl was obtained and catalysts I and III were practically inactive in the Suzuki–Miyaura coupling.

3.2.4. Hydroformylation reaction

Two catalysts, IV and V, exhibited activity in catalytic transformation of 1-hexene under hydroformylation reaction conditions (Table 6). This activity most probably originated from the presence of rhodium nanoparticles, similarly as reported by Dupont [34].

In three cases, 2-hexene was the major product, formed with yields of up to 73%. The highest yield of aldehydes (Scheme 3), 58%, was obtained when catalyst V was used with a 24-fold excess of PPh₃ in respect to rhodium. In this reaction, the n/iso ratio was 1.9,

which confirms the positive effect of the phosphine. All the discussed hydroformylation reactions were carried out with addition of PPh₃. It is known that in the first reaction stage the phosphorous ligand labilizes the coordination sphere of rhodium, facilitating formation of [HRh(CO)(PPh₃)₃], the most active hydroformylation reaction catalyst precursor [35]. Moreover when phosphorus-free rhodium systems were applied in hydroformylation, typically n/iso close to 1 was noted [36–38] or sometimes only the isomerization product was formed [35].

Rhodium is known as the most active catalyst for hydroformylation [31,34–40]; therefore, the observed catalytic effect should be related to the presence of rhodium. However, as in the case of palladium, an additional influence of other components present in spent automotive three-way catalysts is possible.

4. Conclusions

It was shown that the spent automotive three-way catalytic converters contain PGMs (Rh, Pt, Pd) in the form of nanoparticles well dispersed on oxide-based ceramic materials. They exhibit catalytic activity when used without any pretreatment in C—C bond forming reactions, such as the Heck or Suzuki–Miyaura cross-coupling. Similarly, airborne matter collected on filters is catalytically active in these reactions. Although the observed catalytic activity cannot be directly correlated with PGM content, the obtained results confirmed a very high catalytic potential of the waste materials. In some cases the molar ratio of converted substrate to catalyst (Turn Over Number; TON) up to 200 000 was noted, which should be considered high even for specially designed organometallic catalysts. Interestingly, the same waste materials showed reactivity towards olefins, forming isomerization or hydroformylation reaction products. The only disadvantage of the studied systems is the poor reproducibility of catalytic results. However, it can probably be improved by a special pretreatment or activation step before the main reaction.

The observed activity of the spent automotive three-way catalysts opens up the possibility of considering their application not only as a source of PGMs but also as active components of catalytic systems applied in organic synthesis.

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