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1	Deactivation causes of supported palladium catalysts for
2	the oxidative carbonylation of phenol
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30 31	HIGHLIGHTS	
32		
33	• Leaching and reduction of Pd species are main causes of catalyst dead	ctivation.
34	• The palladium leaching is attributed to the presence of O ₂ , not CO.	
35	• High temperature promotes Pd agglomeration, leading to the reduction	n of active sites.
36	• The decreases of average manganese valence leads to the weakening	of redox ability.
37	• Lattice oxygen take part in the regeneration of reduced Pd (0) in the c	catalytic redox cycle.
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60 Abstract

Palladium catalysts supported on manganese oxides octahedral molecular sieves (OMS-2), Pb doped OMS-2 (Pb-OMS-2) and perovskite-type La_{0.5}Pb_{0.5}MnO₃ were prepared for investigating the deactivation causes of catalysts during the oxidative carbonylation of phenol. The catalytic experiments on three different sets of catalysts demonstrated that they were inactive after continuous reaction for 22h. XRD patterns and HRTEM images demonstrated that carbonaceous pollution and palladium leaching occurred during the reaction process. The solvent and oxygen have significant impact on the palladium leaching by ICP-AES analysis. In addition, hot filtration tests and SH-HZSM-5 adsorption studies indicated that the leached palladium species are not active species. The results of XPS patterns and H₂-TPR profiles showed that aggregation and reduction of Pd species was another deactivation cause. It was discovered that lattice oxygen species decreased and palladium aggregated, which hindered the re-oxidation of Pd(0) to Pd(II). In summary, carbonaceous pollution, Pd leaching, aggregation and consumption of oxygen species hindered the redox recycling of palladium, which resulted in the deactivation of supported palladium catalysts for the oxidative carbonylation of phenol.

Keywords: Diphenyl carbonate; Oxidative carbonylation; Deactivation causes; Pd leaching; Oxygen species

89 **1. Introduction**

90 Palladium-catalyzed oxidative carbonylation reaction has become a novel and powerful tool for diphenyl 91 carbonate (DPC) synthesis [1, 2]. The process of oxidative carbonylation has several advantages over the 92 traditional phosgene process as the latter comprises the use of toxic and corrosive reagents. The process of 93 oxidative carbonylation is environmentally-friendly and utilizes easily available raw materials with 94 molecular oxygen as the oxidant. Many efforts were made to develop a high-performance catalyst for the 95 oxidative carbonylation reaction which could be easily separated and repeatedly used. It is generally 96 accepted that palladium is active species and its catalytic performance is better than the other metal 97 catalysts[3-4]. At the previous stage, homogenous palladium catalysts were referred and PdCl₂, Pd(OAC)₂, 98 or $Pd(acac)_2$ were common homogeneous catalysts. Because the ligands are beneficial to cis-reaction 99 between phenol and CO, the Pd-carbene complex with bis(heterocyclic carbene) ligands and Pd-2,2'-100 bipyridyl complex with 2,2'-bipyridyl ligands were prepared and became another kind of high efficient 101 homogeneous catalysts. Homogeneous catalysts have not been commercialized because of one major 102 disadvantage compared with heterogeneous catalysts: the difficulty encountered when trying to separate 103 the catalyst from reaction product or solvent. In recent years, heterogeneous palladium catalysts turn into 104 mainstream according to the reported literature. A number of heterogeneous palladium catalysts anchored 105 on supports including activated carbon, polystyrene, silicon dioxide, layered double hydroxides, organic-106 inorganic hybrid materials and mixed metal oxides were investigated [5].

107 A number of homogeneous or heterogeneous palladium catalysts were reported to be effective, but 108 catalyst deactivation has not been addressed in detail until now [5-11]. Among the several catalyst 109 deactivation causes described in the literature, five main causes of deactivation are poisoning, fouling, 110 thermal degradation initiated by high temperature, mechanical damage, and corrosion/leaching by the 111 reaction mixture. In palladium-catalyzed oxidative carbonylation of phenol, the deactivation of palladium 112 catalysts is generally attributed to the reduction and aggregation of the active center Pd(II) to Pd(0). The 113 formation of metallic Pd nanoparticles in significant amount occurred with homogeneous palladium 114 systems [10, 12], which indicated that Pd (II) transformed into Pd(0) in the reaction and led to catalyst 115 deactivation. Song [13] observes the peak representing metallic Pd in XRD patterns of carbon-supported 116 palladium catalyst and speculated that metallic Pd catalyst was readily sintered in an enriched reducing 117 CO atmosphere. He even considered that zero-valent palladium particles were an active species. Leaching 118 is another deactivation cause to be considered [14]. The leached compounds rather than the solid phase

maybe the actual active species. Takagi [15] reports that soluble Pd existed in Pd/C-PbO catalytic system. Pd leaching was also observed in the system containing acetate salts, but the activity of PdCl₂-OIH(organic–inorganic hybrid) catalysts remained virtually unchanged when the catalyst was recycled and reused [16]. Unlike PdCl₂-OIH catalysts, on account of Pd leaching and destruction of the tubular structure, the activity of the Pd-O/CeO₂-nanotube catalyst decreased substantially when the catalyst was recycled and reused [17].

Our research group has always placed emphasis on the enhanced activity of Pb-doped supported palladium catalysts in oxidative carbonylation of phenol [18]. Nevertheless, the importance of catalyst stability is often underestimated. Therefore, a better understanding of deactivation causes is essential for improving and optimizing the performance of palladium catalysts, and several measures were taken to evaluate the deactivation behavior of catalyst. Herein, deactivation causes for supported palladium catalysts were studied, and some fundamental conclusions were obtained.

131 **2.** Experimental

132 2.1. Catalyst preparation

133 Three sets of oxide supports were obtained as suggested in literature. Manganese oxide octahedral 134 molecular sieves(abbreviated as K-OMS-2) supports were synthesized by the reflux method. Lead doped 135 OMS-2 supports(labeled as Pb-OMS-2) were prepared by an impregnation method. The K-OMS-2 was impregnated with a suitable volume of Pb(NO₃)₂ solution and then dried at 70°C under vacuum. 136 137 Perovskite-type La_{0.5}Pb_{0.5}MnO₃ supports were obtained by a sol-gel method, using metal nitrates and 138 citric acid as starting materials in stoichiometric amounts. Reagents of KMnO₄ (99.0%), MnSO₄ • H₂O 139 (99.0%), $La(NO_3)_3 \cdot nH_2O(La_2O_3 \ge 44\%)$, $Pb(NO_3)_2$ (99.0%), $Mn(NO_3)_2$ solution(60%), citric acid 140 (98.0%), nitric acid (AR, 60%) were used as starting materials purchased from Sinopharm Chemical 141 Reagent Co., Ltd.

142 K-OMS-2 was prepared by a reflux method according to the literature [19]. To a 500 ml of round-143 bottomed flask with a condenser, potassium permanganate solution (0.4 M, 225 ml) was added to a 144 mixture of manganese sulfate hydrate solution (1.75 M, 67.5 ml) and concentrated nitric acid (6.8 ml). The 145 dark brown slurry was refluxed for 24 h, then filtered and washed with deionized water for several times. 146 The K-OMS-2 was dried at 120° C overnight before use.

147To prepare Pb-OMS-2, 7.000 g K-OMS-2 prepared by the reflux method was impregnated with 70.0148ml of Pb(NO₃)₂ aqueous solutions with different concentrations. And then the mixture was stirred for 24 h,

followed by evaporation. Pb-OMS-2 were obtained by calcination in a muffle furnace at 450° C for 6 h[18].

151 The Perovskite-type La_{0.5}Pb_{0.5}MnO₃ supports were obtained by a sol-gel method, using metal nitrates 152 and citric acid as starting materials with nominal atomic ratios. Then, the aqueous solutions of metal 153 nitrates with nominal atomic ratios La: Pb: Mn=0.5:0.5:1 were mixed together in deionized water. Citric 154 acid(CA) was proportionally added to the metal solution to have the same amounts of equivalents. Then, 155 the solution was concentrated by evaporation at approximately 50° C with stirring for 1 h to convert them 156 to stable (La, Mn)/CA complexes. The solution, while being stirred, heated at approximately 75°C to remove excess water. During the evaporation, reddish-brown gases corresponding to N_XO_Y removed from 157 158 the solution and a viscous and bubbly mass was produced upon cooling. Then, the dry gel was obtained by 159 letting the sol into an oven and heated slowly to 120°C. The gel pieces were ground to form a fine 160 powder. Finally, La_{0.5}Pb_{0.5}MnO₃ nanoparticles were gained by thermal treatment of the precursor at 650° C 161 for 9 h in air. [20].

0.42 g PdCl₂ was dissolved in 50.0 ml aqueous solution when the pH value was adjusted to 1.0 with
concentrated hydrochloric acid. K-OMS-2, Pb-OMS-2 and La_{0.5}Pb_{0.5}MnO₃ supports were dipped into the
PdCl₂ solution, respectively. 5.0% NaOH solution as a precipitant was dropped slowly till the pH value
was kept at 9.5. After stirred for 2 h, the solid was separated by filtration, then dried at 80° C overnight and
calcined at 300° C for 3 h. The powdery catalysts prepared were labeled as Pd/K-OMS-2, Pd/Pb-OMS2and Pd/La_{0.5}Pb_{0.5}MnO₃, respectively.

168 2.2. Characterization

169 The phase identification and crystalline structure analysis were determined by X-ray diffraction 170 (XRD) on a Panalytical X'Pert PRO X-Ray diffractometer with high-intensity Cu K α radiation (λ =1.54060 171 Å).

The chemical shift, valence of element and Pd content on surface were studied by X-ray
photoelectron spectra (XPS) in a Perkin-Elmer PHI 1600 ESCA system with Mg Kα X-ray radiation
(1253.6 eV, 250 W).

The bulk chemical composition of the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer ELAN DRC-e. Solid samples were dissolved in the mixture of HCl and HNO₃, and then diluted with ultrapure water.

178 H₂-TPR experiments were performed on a Micromeritics AutoChem II 2920. Each sample (50mg of

fresh catalyst) was pretreated at 300° C for 0.5 h and subsequently cooled to ambient temperature under an Ar flow (30 mL/min). Then, a 10% H₂-95% Ar flow (30 mL/min) was passed over the catalyst bed by heating at a rate of 10° C /min up to 900° C. Finally, the catalyst was cooled under an Ar flow (30 mL/min). The consumption of H₂ was monitored by a thermal conductivity detector (TCD).

High resolution transmission electron microscopy (HRTEM) images of the samples were obtained
using a FEI Tecnai G20 electron microscope operated at an accelerating voltage of 200 kV with an energy
dispersive X-ray analysis (EDXA) system.

186 2.3. Activity test

187 The oxidative carbonylation reaction was performed in a 250mL stainless steel autoclave equipped 188 with a magnetic stirrer. A typical reaction condition was as follows: phenol 47g (0.5mol), 189 (TBAB) 1g (3mmol) and Pd (in the catalyst) 0.9mmol were introduced into 190 the autoclave. Then the autoclave was sealed and heated up to 65° C. Subsequently, the gas mixture of CO 191 and O_2 (CO/ $O_2 = 12/1$ molar ratio) was charged. The conditions employed in this procedure fell within the 192 flammability range of CO in O2. After the reaction sustained at the pressure of 4.8MPa, the autoclave was 193 cooled and the products were taken out every 2 hours. The reaction products were quantified by a 194 capillary gas chromatography with a FID detector and a SE-54 capillary column.

195 **3. Results and discussion**

196 3.1 Catalytic performance of supported palladium catalysts

197 Figure 1 describes the DPC yields of different supported palladium catalysts and also shows that the 198 DPC yields increase in the order of Pd/OMS-2<Pd/La_{0.5}Pb_{0.5}MnO₃<Pd/Pb-OMS-2. Further the DPC 199 yields for all the catalysts increased slightly when the oxidative carbonylation reaction extended up to 22h. 200 The majority of catalysts was inefficient and could be deemed of deactivated. Moreover, the Pd/OMS-2 201 catalyst is found to be deactivated much faster than the other two supported catalysts. The DPC yields of 202 Pd/OMS-2 catalyst almost remained constant after 10h reaction, while the DPC yields of Pd/Pb-OMS-2 203 catalyst continued to increase from 39.8% to 51.2% when reacted from 10h to 24h. To find out the causes 204 of fast deactivation of supported palladium catalysts, a comprehensive experimental study was planned 205 and utilizing various characterization techniques the causes were explored.

206 3.2 Structure stability of supported palladium catalysts

207 XRD patterns of fresh and used supported palladium catalysts are represented in Figure 2. Based on 208 the literature and our past research[18-20], the XRD patterns of Pd/OMS-2 catalyst, Pd/Pb-OMS-2

209 catalyst and Pd/La_{0.5}Pb_{0.5}MnO₃ catalyst correspond well to the cryptomelane-type phase of K_{2-} 210 _xMn₈O₁₆(JCPDS 44-1386), the hollandite-type phase of Pb_{2-x}Mn₈O₁₆ (JCPDS 42-1349)and the perovskite-211 type phase of La_{0.5}Pb_{0.5}MnO₃(JCPDS 22-1123) respectively. Figure 2(a) and 2(b) shows that no peak shift 212 is observed for the Pd/OMS-2 catalyst, but its peak intensity at $2\theta = 28.7^{\circ}$, 37.5° weakens. As illustrated in Figure 2(c)-2(f), the crystal structures of the Pd/Pb-OMS-2 catalyst and the Pd/La_{0.5}Pb_{0.5}MnO₃ catalyst 213 214 remain original structure before and after the reaction. Noticeably, no additional peaks related to active 215 palladium species appear in any of the catalysts, indicating that the palladium species is well-dispersed on 216 the surface of supports.

217 The structure stability of the supported palladium catalysts was analyzed using TEM images. Figure 3(a) relates to the fresh Pd/OMS-2 catalyst and demonstrates that highly dispersed palladium species with 218 219 particle (size of about 3nm) is loaded onto the OMS-2 nanorod supports. Figure 3(b) relates to the used 220 Pd/OMS-2 nanorod catalysts and demonstrates that catalysts are covered with membrane-like compounds 221 which contain a large amount of carbon element as determined by EDXA analysis. This is consistent with 222 the weakening of its diffraction peaks in the XRD patterns caused by the embedding of carbon on the 223 surface. It is important that the active palladium species seems to have disappeared on the surface of 224 OMS-2 nanorod supports. The palladium species also drops off of the surface of Pd/Pb-OMS-2 nanorod 225 catalysts similar to the Pd/OMS-2 nanorod catalysts (Figure 3(c) and 3(d)). Further Figure 3(e) and 3(f) 226 shows that Pd/La_{0.5}Pb_{0.5}MnO₃ catalysts look rather spongy due to a fast release of a large amount of gas in 227 the decomposition of the reacting precursors. Unfortunately, the palladium species could not be 228 distinguished in both fresh and used Pd/La_{0.5}Pb_{0.5}MnO₃ catalysts. The above TEM images reveal that part 229 of the palladium species broke away from the catalyst carrier and this precisely indicates that leaching can 230 occur in oxidative carbonylation reaction. Thus, leaching is an important deactivation cause of supported 231 palladium catalysts. In order to explore whether palladium leaching results in the deactivation, we 232 conducted a verification test.

233 3.3 Palladium leaching

The palladium content of the fresh and used supported catalysts was measured by ICP-AES analysis and the results are listed in Table 1. The data clearly indicate palladium leaching occurs during an oxidative carbonylation reaction. Pd loss ratio is 6.2%, 9.1% and 35.0% for Pd/OMS-2, Pd/Pb-OMS-2 and Pd/La_{0.5}Pb_{0.5}MnO₃ catalysts, respectively. Because there is a serious palladium leaching, Pd/Pb-OMS-2 catalyst was selected as only target and their parameters that influence the palladium leaching were then

239 explored and are summarized in Table 2. It is clear from the data that the solvent and oxygen atmosphere 240 have a significant impact on the palladium leaching (Table 2, entries $7 \sim 9$) [21]. The palladium content in 241 solution reached 3.51% for DCM and 8.90% for DMF (Table 2, entries 8~9). At O₂ atmosphere (Table 2, 242 entries 7), 8.73% of the total palladium amount removed from the catalyst and were found in solution 243 compared to only 0.13% under CO and O₂ mixed atmosphere (Table 2, entries 1). While the amount of Pd 244 leaching at CO+O₂ atmosphere is much the same as that at air atmosphere (Table 2, entry 6). Thus, the 245 palladium leaching is attributed to the presence of O₂, not CO. Reaction temperature has little bearing on 246 palladium leaching, and the palladium contents in solution dangle just below 1% at different temperatures 247 (Table 2, entries $1 \sim 5$). We verified that the leached palladium was not a catalytically active species by the 248 hot filtration test. Hot filtration tests were conducted after running the normal 4h reaction and then the 249 solid catalysts were filtered under hot conditions [22]. The composition of the filtrate was monitored in the 250 same reaction environment to determine the DPC yield in the absence of the supported palladium catalyst. 251 As shown in Table 1, all catalysts in this study showed no activity after the hot filtration test. The reaction 252 never proceeded in the filtrate without the supported palladium catalyst and a slight decline of DPC yields 253 suggests that the DPC is being hydrolyzed instead of generation. Further, SH-HZSM-5 was added into the 254 reactor and the corresponding DPC yield was 11.6%, compared to 12.1% without SH-HZSM-5 under the 255 same condition [23, 24]. The results indicate that the leached palladium species is not active.

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258 3.4 Reduction and aggregation of active palladium species

259 Both homogeneous and heterogeneous palladium catalyst are reported to be active in an oxidative 260 carbonylation of phenol [12]. Palladium species that leached into the solution became inactive which 261 clearly indicates that palladium species may be transforming into reduced state. XPS analysis is required 262 to obtain the information on the reduction degree of palladium species. The XPS spectra in Figure 4 show 263 a peak at 335.5 eV characteristic of Pd(0) and the other peak at 337.2 eV corresponding to Pd(II). The 264 binding energies of the entire used supported palladium catalysts shift toward lower binding energies as 265 compared to the fresh catalysts, indicating the reduction of active Pd(II) species to Pd(0). As shown in 266 Figure 4, the initial valency of palladium could have impact on the DPC yield. The initial valency of Pd 267 species is two in Pd/Pb-OMS-2 catalysts (Figure 4(c)), which shows the best catalytic activity. In contrast, 268 since a large amount of Pd(0) exists in Pd/OMS-2 catalysts (Figure 4(a)), the DPC yield is the lowest and

the deactivation is the fastest among all the catalysts. A pre-reduction experiment was used to further ensure that the reduction of palladium can deactivate the catalyst. The fresh Pd/Pb-OMS-2 catalyst was then reduced with formaldehyde (Figure 1s). Results show that the catalytic activity sharply reduced and the DPC yield was just 0.31%.

273 Take Pd/OMS-2 catalyst as a model to investigate the aggregation of palladium species. Figure 5(a), 274 5(b) and 5(c) manifest that no XRD peaks of Pd(0) or Pd(II) appear in the fresh Pd/OMS-2 catalyst when 275 calcined at 300° C, indicating that calcination time can not affect the aggregation of palladium species. After treating at 400°C, the catalyst showed an XRD peak at 33. 9° (Figure 5(d)), which corresponds 276 well to the 101 plane of Pd(II) (JCPDS 43-1024) and indicates that high calcination temperature prompted 277 278 the reunion of Pd(II) on the surface. As illustrated in Figure 5(e), the aggregation of Pd(II) also occurred in 279 the used catalyst. Besides the peak of Pd(II) species, the spectra shows an additional peak at 40.1° , 280 which corresponds with the character of metal Pd(111)(JCPDS 46-1403). The aggregation of Pd(0) and 281 Pd(II) hindered the re-oxidation of palladium, which is another deactivation cause of the catalyst.

282 3.5 The change of oxygen species

Our research findings have demonstrated that oxygen species played an important role in the redox cycle of palladium species [18], so the change of oxygen species for the fresh and used catalysts were described by H_2 -TPR profiles (Figure 6) and XPS spectra (Figure 7).

286 In the H₂-TPR profiles of Pd/OMS-2 and Pd/Pb-OMS-2 catalysts three reduction peaks could be 287 deconvoluted according to the literature [25]. The α reduction peak can be possibly attributed to the 288 reduction of surface oxygen species. The β and γ reduction peaks stand for the reduction processes of $Mn^{4+} \rightarrow Mn^{3+} \rightarrow Mn^{2+}$. Figure 6 (a) and (c) shows that the reduction peaks of Pd/Pb-OMS-2 catalysts shift 289 290 to the high temperature regions relative to that of Pd/OMS-2. It may be due to the higher Pb-O bond 291 energy than MnO₂ the present of Pb-O bonds in the Mn-O-Pb makes the mobility of the oxygen atoms in 292 the octahedral crystal slow. The addition of the lead weakens the bulk redox ability of the OMS-2. For the 293 La_{0.5}Pb_{0.5}MnO₃ catalysts, each H₂-TPR profiles exhibit two reduction peaks. The first peak is located at 150~250°Cand the other is positioned at 250~380°C The reduction of Mn⁴⁺ to Mn³⁺ occurs in the first 294 process, and the reduction of Mn³⁺ to Mn²⁺ occurs in the second process. Figure 6 shows that the 295 reduction peaks of the entire used catalyst shift to higher temperature regions in comparison to that of the 296 fresh catalyst, implying that the Mn^{4+} reduces and low valence Mn^{3+} and Mn^{2+} increase for the used 297 298 catalysts. The average manganese valence decreases after reaction, which leads to the weakening of redox

ability [18]. A significant shift is observed for the Pd/Pb-OMS-2 catalyst during reaction process, so the
 corresponding redox ability reflects fully in catalytic cycle of active palladium species.

301 As shown in Figure 7, the oxygen species derived from fitted O1s spectra was also divided into two 302 groups: surface oxygen (O_{s} , 531.7V) and lattice oxygen (O_{L} , 528.7eV). From the peak area of three sets of 303 catalysts, it can be inferred that the lattice oxygen species reduces when catalysts are used. This is 304 consistent with the change of manganese valence. When the lattice oxygen species reduced, the low 305 valence manganese increased for charge equilibrium. It can be inferred that the oxygen species, especially 306 lattice oxygen, take part in the regeneration of reduced Pd (0) in the catalytic redox cycle. This is because 307 surface oxygen is under-coordinated so that it is less reduced than that in lattice. Thus, the catalytic 308 performance of fresh Pd/Pb-OMS-2 catalyst which more lattice oxygen reduced is superior over the other 309 two catalysts.

310 3.6 Possible deactivation cause of supported palladium catalyst

311 From the results of these tests, possible deactivation causes of supported palladium catalysts can be 312 proposed:

313 Palladium leaching and reduction is the main cause of catalyst deactivation. Active palladium species 314 binds to outer-most oxygen atom to form Pd-O bonds through strong interaction. Presence of higher 315 number of Pd(II) species leads to higher interaction between Pd and O species and this makes the leaching 316 of palladium difficult in case of Pd/Pb-OMS-2 catalysts. However, lower palladium leaching for Pd/OMS-2 catalyst in spite of less Pd(II) species founded in Figure 3 (b), may be due to coating of carbonaceous 317 pollution on the catalyst. Further, the leached palladium is not catalytically active species. Meanwhile, 318 319 Pd(II) reduced to Pd(0) with the concomitant formation of DPC during the reaction. In order to regenerate 320 the catalytic cycle, the formed Pd(0) species needs to be re-oxidized to Pd(II) species. Oxygen species in 321 catalysts is effective to regenerate reduced Pd(0) in catalytic redox cycle.

Apart from causes mentioned above, the carbonaceous pollution can also lead to catalyst deactivation. OMS-2 has excellent hydrophobicity and strong affinity for organic compounds [26]. Surface bonded OH groups on OMS-2 increases the adsorption of phenolic compounds. In oxidative carbonylation reaction, organic reactants are absorbed on the surface of the Pd/OMS-2 catalyst and impeded the contact between reactants and active species.

327 4. Conclusions

328 Supported palladium catalysts were found to be deactivated in less than 22h during oxidative

329	carbonylation of phenol and the deactivation causes have been studied. The structure stability of Pd/OMS-
330	2, Pd/Pb-OMS-2 and Pd/La $_{0.5}$ Pb $_{0.5}$ MnO ₃ catalysts were found to be good in reaction environment. The
331	main deactivation causes are leaching and reduction of the palladium species. During the course of
332	reaction, the palladium was partially leached into the solution and experimental analysis has confirmed
333	that the leached palladium was not catalytically active species. Due to reduction in the amount of lattice
334	oxygen, the redox ability of supports to regenerate Pd(II) was reduced and more Pd(0) formed resulting in
335	the loss of catalytic activity.
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402 Figure Caption

404 Figure 1.



- 410 Figure 2.



Figure 2 XRD patterns of fresh and used supported palladium catalysts (a) fresh Pd/OMS-2; (b) used
 Pd/OMS-2; (c) fresh Pd/Pb-OMS-2; (d) used Pd/Pb-OMS-2; (e) fresh Pd/La_{0.5}Pb_{0.5}MnO₃; (f) used
 Pd/La_{0.5}Pb_{0.5}MnO₃

416 Figure 3.



Figure 3. HRTEM images of fresh and used supported palladium catalysts (a) fresh Pd/OMS-2; (b)
used Pd/OMS-2; (c) fresh Pd/Pb-OMS-2; (d) used Pd/Pb-OMS-2; (e) fresh Pd/La_{0.5}Pb_{0.5}MnO₃; (f) used
Pd/La_{0.5}Pb_{0.5}MnO₃