Development of Pd-incorporated perovskite catalyst for various organic reactions

Leo Saputra, Takashi Kojima, Takayoshi Hara, Nobuyuki Ichikuni, Shogo Shimazu*
Graduate School of Science and Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan
**Corresponding author: shimazu@faculty.chiba-u.jp*

Abstract: Incorporation of Pd into a highly stable perovskite-titanate (Pd-KSTO) has been successfully performed via a simple hydrothermal method (100 °C) without any posterior calcination step. Particle size and porosity of the Pd-KSTO could be precisely tuned by changing the molar ratio of water/NH_3 in the preparation of amorphous titania sources (ATS). The Pd-KSTO catalyst showed remarkable activity and selectivity for alcohol oxidation and Suzuki cross-coupling reactions at low temperature (70 °C). The mesoporous Pd-KSTO showed superior catalytic performance to the others. The Pd-KSTO catalyst also could be recycled without any significant loss of its activity.

Keywords: *Pd-incorporated perovskite, hydrothermal, alcohol oxidation, Suzuki cross-coupling*

1. Introduction

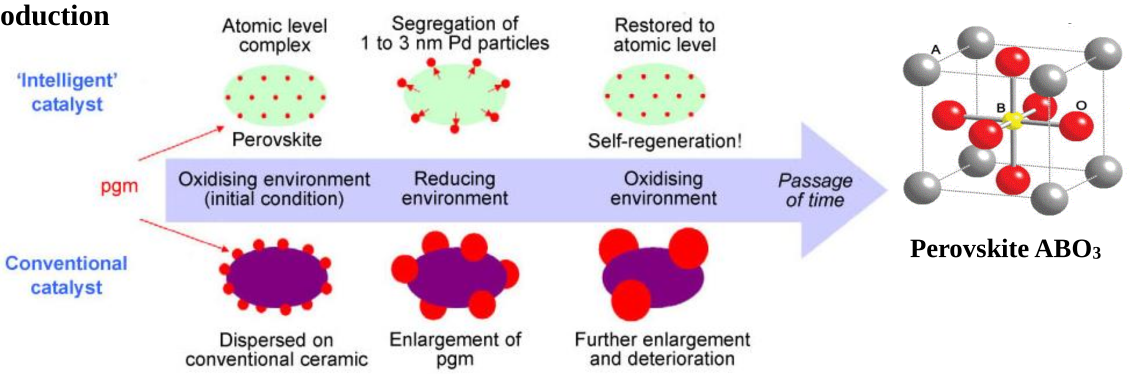


Fig. 1. Self-regenerative Pd-contained perovskite as an "intelligent" catalyst.[1]

Perovskite oxides with ABO_3 composition (A= rare/alkaline earth, B= transition metals) are promising materials for many catalytic applications, both as active species and as supports. Because perovskite oxides are low-cost materials with high stability, they are more practical for industrial applications. Since Pd nanoparticle on the perovskite surface could be reversibly re-incorporated into the perovskite lattice, Pd-KSTO is referred as "intelligent catalyst" which keeps high dispersion and prevents leaching or aggregation unlike conventional catalyst (Fig. 1). In a previous work, we have prepared Pd-KSTO catalyst by using a molten-salts method, however, a very high temperature (>600 ºC) was required for perovskite formation.[2] Therefore we prepared Pd-KSTO by hydrothermal method (100 ºC).

2. Experimental

ATS was prepared as a following manner. 5 mmol of $Ti(OBu)_4$ was dissolved in BuOH/MeCN (1:1 v/v) (Solution A). A quantity of aqueous NH_3 28% and water were also dissolved in BuOH/MeCN (Solution B). The molar ratio of water/NH_3 was varied at 5.0, 12.5, and 25.0. The two solutions were mixed and heated at 80 ºC for 30 min. The white precipitate (ATS) was rinsed with ethanol and water, and then dried at 75 ºC for overnight. Perovskite-titanate denoted as Pd-KSTO(x) (x= water/NH_3) was prepared as a following method. Typically, ATS (2 mmol), $Sr(OH)_2{\cdot}8H_2O$ (2 mmol), and Pd solution (0.028 mmol) were poured into a Teflon-line autoclave. Then, 20 mL of KOH 0.1 M and 80 mL of water were also poured into the autoclave. The mixture was put into an oven for hydrothermal reaction at 100 ºC for 24 h. The obtained brown powder was rinsed with water and dried at 75 ºC for overnight. The perovskite catalyst was then applied for aerobic alcohol oxidation and Suzuki cross-coupling reactions.

3. Results and discussion

All of the ATS could be used for perovskite formation as shown in Fig. 2. The phase was confirmed to $SrTiO_3$ perovskite with composition of $Pd_1K_{0.5}Sr_{78.5}Ti_{85.6}$ (ICP-OES). There is no other phases observed, confirming high purity of the resulting perovskite. Additionally, we also used commercial titania (anatase and rutile), but the perovskite was not formed proving the necessity of an amorphous titania source.

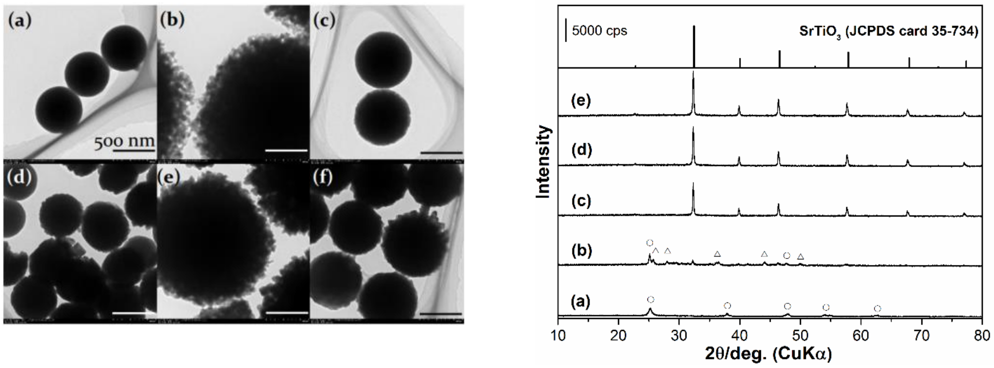
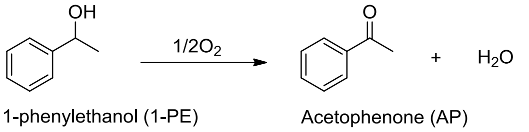


Fig. 2. (Left) TEM images of: (a) ATS(5.0), (b) ATS(12.5), (c) ATS(25.0), (d) Pd-KSTO(5.0), (e) Pd-KSTO(12.5), (f) Pd-KSTO(25.0); (Right) XRD patterns of: (a) KTO(12.5), (b) Pd-KSTO(12.5) by reflux method at 100 ºC, (c) Pd-KSTO(5.0), (d) Pd-KSTO(12.5), (e) Pd-KSTO(25.0). △= $SrCO_3$, ○= Anatase.

The catalytic activity of Pd-KSTO was first tested on the oxidation of 1-phenylethanol (1-PE) to acetophenone (AP) (Table 1). The best performance was shown by Pd-KSTO(12.5) with AP yield of 63% (entry 2). The activity could be enhanced (yield >99%) by addition of molecular sieves (not shown). The gas consumption test and a lower performance at higher reaction temperature (>70 °C) proved the necessity of O_2. The corresponding impregnated catalyst (Pd/KSTO) showed lower stability than the incorporated one (Fig. 3). High catalytic activity and selectivity of the Pd-KSTO was also observed for Suzuki cross-coupling of various boronic acid and aryl halide (yield >99%) in 5 min of reaction.

Table 1. Catalyst screening for Pd-KSTO



Entry	Pd–KSTO(*x*)[a]	Conv. /%	Yield /%[b]	TON
1	Pd–KSTO(5.0)	31	31	85
2	Pd–KSTO(12.5)	63	63	172
3	Pd–KSTO(25.0)	54	54	147
4[c]	Pd–KSTO(12.5)	36	36	98
5	KSTO(12.5)	0	0	0

Reaction conditions: 1-PE/Pd=273; 1-PE, 25 mg; Pd-KSTO(x), 12.5 mg; *n*-hexane, 2 mL; O_2, 1 atm (balloon); 70 °C; 24 h. [a] $x= [H_2O]/[NH_3]$. [b] The selectivity to AP is almost 100%. [c] The catalyst was prepared at 160 °C.

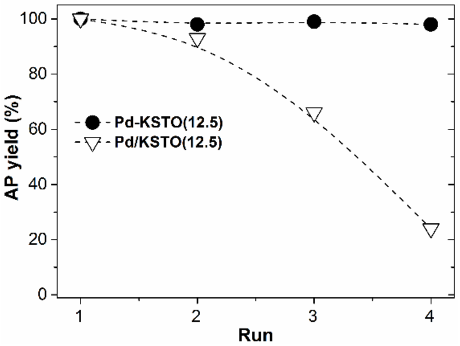


Fig. 3. Recyclability test for Pd/KSTO and Pd-KSTO

4. Conclusion

The Pd-KSTO perovskite with tunable particle size and porosity was prepared using a simple hydrothermal method at low temperature. The Pd-KSTO containing mesoporous showed the highest activity and excellent selectivity for low temperature alcohols oxidation and Suzuki cross-coupling. The Pd-KSTO catalyst also showed a remarkable stability and recyclability.

Acknowledgement

This study was financially supported in part by JSPS KAKENSHI Grant Number 15K06565 and JSPS Bilateral Joint Research Project (2014-2017).

References

1. T. Screen, Platinum Metals Rev. 51 (2007) 87–92.
2. I. B. Adilina, T. Hara, N. Ichikuni, N. Kumada, and S. Shimazu, Bull. Chem. Soc. Jpn. 86 (2013**)** 146–152.