

# Modification of lanthanide elements on selective hydrogenation of acrylonitrile

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**Abstract:** The modification of rare earth elements to palladium catalysts led to great promotion on both the activity and stability in selective gas hydrogenation of acrylonitrile to propionitrile. The promotion effect of lanthanide-dopant was briefly discussed.

**Key words:** lanthanide; hydrogenation; acrylonitrile.

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## 1 Introduction

Lanthanide doped catalysts have long been investigated on three-way catalysts (TWCS). While their application on hydrogenation of unsaturated function, such as alkyne<sup>[1]</sup>, ketone<sup>[2]</sup>, has been reported recently. In this paper, we investigated the selective gas hydrogenation of acrylonitrile over Pd/Al<sub>2</sub>O<sub>3</sub> modified by various lanthanide elements in fixed bed reactor, which proved that the modification effect of lanthanide to palladium based catalysts on both structure and electronic states improved the catalytic activity and stability. But different lanthanide elements exhibited different modification behavior.

## 2 Experimental

The Pd - LnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples were prepared by consecutive impregnation of  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> (40 - 50 mesh) with an aqueous solution of Ln(NO<sub>3</sub>)<sub>3</sub>. After impregnation for 24h at room temperature, the mixture was dried at 120°C for 3h followed by calcination at 500°C for 3h with heating rates of 10°C/min. Then the mixed support was added to an aqueous solution of PdCl<sub>2</sub>, disposed as the precedent above and reduced by H<sub>2</sub> at 500°C for 2h at last. The concentration of palladium over all the as-prepared catalysts was 0.05w. t% , and the content of lanthanide was from 1w. t% to 10w. t% (calculated by lanthanide atom).

Gas phase hydrogenation of acrylonitrile was carried out in fixed bed microreactor at atmospheric pressure. The weight of catalyst was 20mg mixed with 380mg  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> (40 ~ 50 mesh) to adjust the residence time of raw materials in the fixed bed. Before rising up to the first reaction temperature, the catalyst was contacted with the reaction mixture prepared by bubbling hydrogenation gas through a thermostabilized saturator (39°C) in which acrylonitrile was contained and the flux of hydrogenation was 100ml/min in activity test and

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120mL/min in stability test. The effluents were analyzed on line by gas chromatography which provided with a FID detector and SE30 - PEG20M packed column.

### 3 Results and Discussion

As can be seen in Figure 1, XRD patterns of the reduced Pd - LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> samples (Ln: La, Ce, Sm) revealed that all palladium species remained in the zero state, and the addition of lanthanide elements prevented transformation of  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> to other kinds of lattice, such as  $\alpha$  - Al<sub>2</sub>O<sub>3</sub> and  $\delta$  - Al<sub>2</sub>O<sub>3</sub> which appeared on the pattern of Pd/Al<sub>2</sub>O<sub>3</sub> sample but disappeared on doped lanthanide catalysts. Whilst with the concentration of lanthanide elements increasing more than 3wt.%, large crystals of lanthanide oxides appeared on the XRD patterns. According to TEM pictures of the Pd/Al<sub>2</sub>O<sub>3</sub> doped with La, Ce and Sm, as showed in Figure 2,3,4, Sm was the most potent element to structurally modify the catalyst because only Pd - SmO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> showed a smaller particle size than other Pd - LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, the most of which were at the size around 100nm, though it's reported that the addition of Ce could also decrease the particle size<sup>[3]</sup>. We can also get the information from TEM that the range of particle size became narrower compared with Pd only catalyst, indicating that the addition of rare earth oxides improved the ability to resist calcination<sup>[4]</sup>.

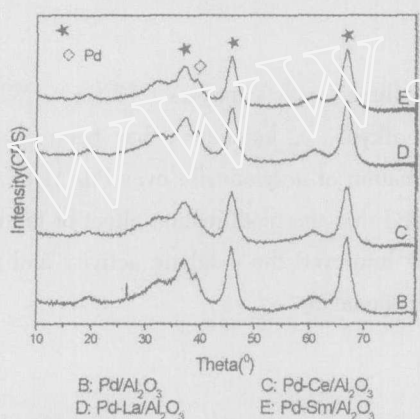


Figure 1 XRD patterns of the Pd - LnO<sub>x</sub> (3 wt. %) / Al<sub>2</sub>O<sub>3</sub>

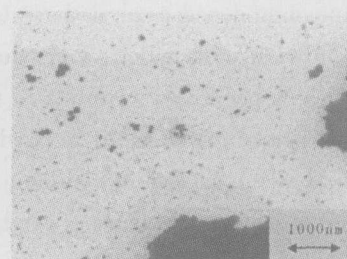


Figure 2 TEM Image of Pd - La / Al<sub>2</sub>O<sub>3</sub>

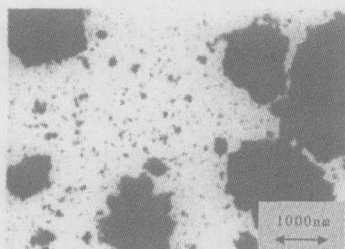


Figure 3 TEM Image of Pd - CeO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub>

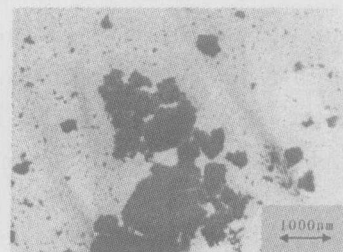


Figure 4 TEM Image of Pd - Sm / Al<sub>2</sub>O<sub>3</sub>

The XPS spectra of the Pd - LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (Ln: La, Ce, Sm) proved further that Pd on all the catalysts remained in the metallic state with the binding energy of 335.6eV or 335.4eV, as listed in Table 1. From the XPS result, palladium species have been reduced to zero valence in agreement with the characterization of XRD, because their binding energies are only a little bigger than those of normal metallic palladium (335.

2eV), and the binding energies of Pd promoted with lanthanide were shifted to higher energies due to the modification of lanthanide elements. But the binding energy of palladium increased no more than 0.4eV, verifying that no aluminate containing palladium was formed because the formation of an aluminate often caused an energy increase of more than 1eV. And what's interesting was the binding energies shift of lanthanide elements on doped lanthanide catalysts. For Pd - CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, the drop of binding energy of Ce<sup>4+</sup> (909.7eV) narrated that there is much possibility for cerium to form an aluminate with Al<sub>2</sub>O<sub>3</sub> to make Ce<sup>4+</sup> rich in electrons and there emerged a characteristic peak of Ce<sup>3+</sup> (890.52eV) illuminated that CeO<sub>2</sub> had been reduced partly. As reported in<sup>[1]</sup>, the standard to distinguish the reduction of CeO<sub>2</sub> is whether there are peaks in the vicinity of 885.2eV and 903.8eV. Though CeO<sub>2</sub> is very difficult to be reduced at conventional atmosphere, it wouldn't be so stable in the existence of Pd. This can be further verified by the XPS pattern of the O1s since the O1s features consist of two different contributions. And according to the integral area of XPS spectrum, 43.39% CeO<sub>2</sub> have been reduced, which might produce new active sites<sup>[7]</sup>. The same behavior can be observed on Pd - LaO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd - SmO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. For Pd - LaO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, however, the peaks appearing on the prepared catalyst can't be all well referred to characteristic peaks of La<sub>2</sub>O<sub>3</sub> or La<sup>0</sup>. What's more, there emerged another peak at the binding energy of 858.0eV that couldn't refer to any kind of species concerning lanthanum and occupied 52.07% of the total lanthanum species, verifying new active sites form on the surface of Pd - LaO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. Samarium can exist on the surface of the catalyst in the state of Sm<sup>3+</sup> or Sm<sup>2+</sup>, determined by the electronic state of Sm 3d, and the discrepancy of their binding energies was more than 7eV. From the pattern of Pd - SmO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, the peak at the site of 1088.0eV can be referred to Sm<sup>3+</sup>, and the binding energy of 1115.6eV affirmed the existence of Sm<sup>0</sup> since there was no characteristic peak of O1s referred to Sm<sup>2+</sup> and the percentage of metallic samarium was 46.82%.

Table 1 Binding energies of various species on as-prepared catalysts

	Pd 3d	Ln 3d	O 1s	Al 2p
Pd - CeO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	335.6	909.7, 890.52, 885.2, 903.8	536.6, 536.0	78.9
Pd - LaO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	335.4 (a shoulder)	834.1, 841.32, 858.0	536.0	78.8
Pd - SmO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	335.6	1088.0, 1115.6	535.8	79.1

Activity test verified that addition of lanthanum, cerium and samarium improved the catalytic activity greatly compared with Pd only catalyst, and Sm improved the activity most greatly. The best concentration of lanthanide elements was 3w.t%. The catalytic behavior of as-prepared catalysts was listed in Figure 5. Hydrogenation result showed that the selectivity of the hydrogenation of acrylonitrile to propionitrile over all the catalysts was nearly 100%. By-product such as allylamine, propylamine may be produced. But under the present reaction condition, no other production but propionitrile was identified, showing a good selectivity to propionitrile. Doped lanthanide catalysts exhibited vital influence on acrylonitrile conversion in the range of 100 - 200°C compared with Pd/Al<sub>2</sub>O<sub>3</sub>, verifying that the addition of lanthanide decreased the activation energy of the reaction. The catalytic activity of Pd - LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was much higher than Pd/Al<sub>2</sub>O<sub>3</sub>. Among the three dopants, Sm exhibited the best promoted effect since the conversion of acrylonitrile over Pd - SmO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was all beyond 99%. The better catalytic activity behavior of Pd - LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> than Pd/Al<sub>2</sub>O<sub>3</sub> may be due to the modification effect of lanthanide elements to Pd by both electronic and structural effect as verified by characterization of XRD, TEM and XPS. And the content of lanthanide played a key role to the activity of the as-prepared catalysts due to the

formation of large crystals on the surface. The conversion always got a maximum when the concentration of lanthanide was 3w.t% no matter what kind of lanthanide element was added. Combined with XPS result, the peak of PdO shifted to higher energy by 0.2 or 0.4eV, indicating the interaction of palladium and lanthanide decreased the electron density of palladium, which may drop the activity of the catalyst. And the binding energy of ceria, lanthana and samaria declined greatly, which may prove the formation of an aluminate of lanthanide elements and  $\text{Al}_2\text{O}_3$ , because the binding energy of Al increased correspondingly. The activity of Pd-LnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was much higher than Pd/Al<sub>2</sub>O<sub>3</sub>, it can be explained by that the formation of the aluminate containing lanthanide made a new active site come into being. S. Fuentes et al<sup>[10]</sup> had ever reported this behavior on Pd/Al<sub>2</sub>O<sub>3</sub> modified by lanthanum. And Pd facilitated the reduction of rare earth oxides, the existence of low valent cation may lead to the formation of new active sites and improvement of the activity too.

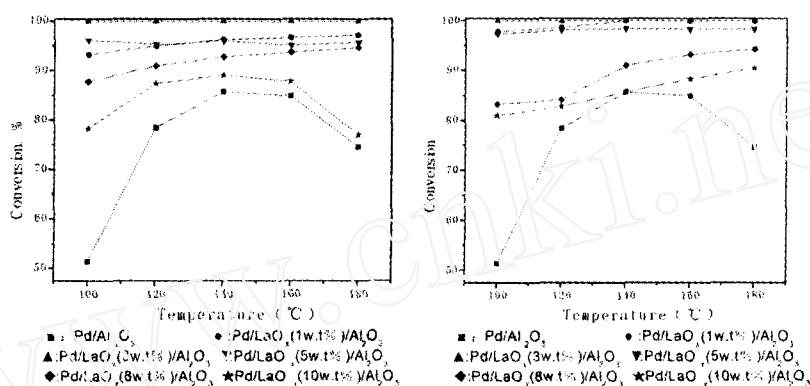


Figure 5 Catalytic behavior of various catalysts

Stability test indicated that some lanthanide elements improved their ability to resist deactivation, but some others, on the contrary, decreased their lifetime. As can be seen in Figure 6, elements such as La, Ce, Nd, Sm, Ga, Ho and Yb improved the ability to resist deactivation, and Yb was the most efficient one to resist deactivation of the catalysts. For hydrogenation of acrylonitrile, the strong adsorption of functions containing carbon was the main reason leading to the catalysts' deactivation<sup>[5]</sup>. While the presence of patches of LnO<sub>x</sub>, such as CeO<sub>x</sub> on Pd could decrease the active surface available for unsaturated functions decomposition and solubility of carbon species, thus increased the desorption of carbon species<sup>[6,7]</sup> to reduce the deactivation. Whilst samarium was the most effective rare earth element to retard the deactivation of the palladium catalysts due to its best structural modification.

But there were still some lanthanide elements, such as Eu, Tb, Dy and Er that shortened catalysts' lifetime. This can be explained by the electronic effect that was close relative to various lanthanide elements' own electronic characters. As was known, Yb and Sm were both stable in the state of +3 or +2 in proper condition; and Gd, La, Ho in +3; Ce and Nd in +2, +3 or +4; while Tb, Dy can only be in +4 or +3 and were unstable in the valence of +2. Since the existence of low valent lanthanide cations was the resource of new catalytic sites<sup>[8,9]</sup>, it could also make

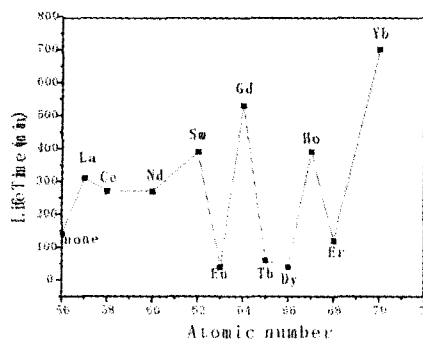


Figure 6 Lifetime of catalysts doped with various lanthanide elements

great influence on the lifetime of the catalysts doped with lanthanide elements and the relationship between them was similar. So the order of their activity was almost the same with their stability to remain in low valence. However, there was still another exception – Eu, which had similar electronic character with Sm, but showed negative behavior in hydrogenation of acrylonitrile.

#### 4 Conclusions

To sum up, low – loaded palladium catalyst showed a good selectivity to gas hydrogenation of acrylonitrile in fixed bed reactor. And the addition of lanthanide elements improved the catalytic behavior of low – loaded palladium catalyst greatly, due to both electronic and structural modification.

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### 镧系元素对丙烯腈选择性加氢的改性效应

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摘要: 稀土元素对钯催化剂的修饰能够极大地促进丙烯腈选择性气相加氢制丙腈的活性和稳定性. 作者主要讨论了掺杂的镧系元素的促进效应.

关键词: 镧系元素; 加氢; 丙烯腈