

Marked effect of In, Pb and Ce addition upon the reduction of NO by CO over SiO₂ supported Pd catalysts

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Introduction

Recently, several studies have been performed to replace Rh in automotive catalysts in view of its high cost and scarce resources. Catalytic properties of Pd have received increasing attention because of its potentiality for the substitution of Rh in the conventional three-way Rh/Pt catalyst. In the present study we have investigated the addition effect of In, Pb and Ce on the NO-CO reaction over SiO₂ supported Pd catalysts. Formation of intermetallic compounds was observed in the cases of Pd-In/SiO₂ and Pd-Pb/SiO₂ catalysts, which caused the three orders of magnitude enhancement of the reaction rate of N₂O formation. From the kinetical as well as infrared spectroscopic analyses, a new reaction pathway was proposed via NO dimer-like intermediates, and the role of additives was the stabilization of these unique intermediates on the slightly oxidized intermetallic compound surfaces.

Materials and Methods

Silica supported Pd, Pd-In, Pd-Pb and Pd-Ce (5 wt% Pd) catalysts were prepared by a conventional co-impregnation. The molar ratio of Pd and the additive was 1:1. The catalyst (0.2 g) was reduced by hydrogen at 733 K to form intermetallic compounds. The NO-CO reaction was carried out in a closed gas circulation system under 1:1 ratio of NO and CO (4 kPa each). The composition of the gas phase during the reaction was followed by TCD gas chromatography. For infrared spectroscopic experiments, the catalyst was pressed into a disk and put in an infrared cell, which was connected to a closed gas circulation system. After the same pretreatment mentioned above, the adsorbed species were observed by IR spectrometer.

Results and Discussion

In the case of Pd/SiO₂, the reaction proceeded at around 500-600 K, and the main product was N₂O with a smaller amount of N₂, which increased considerably after gaseous NO was consumed. When In, Pb or Ce was added to this system, the reaction temperature was lowered more than 200 K and only N₂O and CO₂ were formed even at room temperatures. Although the main product was N₂O below 400K, it shifted to N₂ at high temperatures. Activation energies also decreased considerably over promoted catalysts as summarized in Table 1. XRD analyses revealed the formation of Pd_{0.48}In_{0.52} and Pd₃Pb₂ intermetallic

Table 1. Initial rates of N₂+N₂O formation over various Pd catalysts

Catalyst	Reac. Temp.(K)	Form. Rates (mol/sec · g-cat)		Ea(kJ/mol)
		N ₂ +N ₂ O	CO ₂	
Pd/SiO ₂	523	3.0x10 ⁻⁸	2.6x10 ⁻⁸	106
Pd-In/SiO ₂	308	1.3x10 ⁻⁸	1.2x10 ⁻⁸	32
Pd-Pb/SiO ₂	308	9.5x10 ⁻⁷	5.4x10 ⁻⁷	20
Pd-Ce/SiO ₂	308	8.0x10 ⁻⁹	6.3x10 ⁻⁹	30

compounds in the cases of In and Pb added catalysts. No XRD pattern was observed in the case of Pd-Ce/SiO₂ catalysts.

Fig. 1 represents the XPS spectra of Pd3d, In3d and Pb4f transitions after the reduction at 573 K in an in-situ cell. In the case of Pd/SiO₂, the binding energy of Pd3d_{5/2} was close to zero valent Pd metal (335.0 eV), whereas by adding In, Pb or Ce it shifted 0.4-0.8 eV to higher binding energy side. On the other hand, the binding energy of In3d_{5/2} in Pd-In/SiO₂ was 0.1 eV lower than the zero-valent In (443.7eV) suggesting the formation of Pd-In intermetallic compound. In the case of Pd-Pb/SiO₂, two Pb4f_{7/2} transitions were observed at 137.1 and 139.1 eV. They can be assigned to zero-valent and positively charged Pb species showing the formation of intermetallic compounds as well as PbO₂. In the case of Ce added catalysts, Ce3d_{5/2} transition could be separable into two parts at 885.0 eV and 882.5 eV, which can be assigned to Ce⁴⁺ and Ce³⁺ species respectively. This result suggests the occurrence of SMSI state, where Ce₂O₃ covers most of the Pd surface.

Fig. 2 represents the FT-IR spectra during NO-CO reaction at 373 K. In the case of Pd/SiO₂, both linear and bridged CO(a) and NO(a) were observed at the similar position to the separate adsorption of CO and NO at R.T. In the case of Pd-In/SiO₂, only linearly adsorbed CO(a) was observed on the freshly reduced catalysts indicating the weakening of the adsorption strength by the addition of In. On the contrary during NO-CO reaction, the intensities of CO(a) and NO(a) species at 1965 and 1605 cm⁻¹ increased considerably. These results may suggest the decreasing of ensemble effect of In on the surface of Pd-In intermetallic compound probably because of the partial oxidation of In. Over Pd-Pb/SiO₂, no adsorbed species were observed during NO-CO reaction suggesting inhibition of CO adsorption by excess Pb oxide layers. The situation was somehow different in the case of Pd-Ce/SiO₂, and two strong bands of adsorbed NO were observed at 1746 and 1605 cm⁻¹ similar to the case of Pd-In, although no adsorption peak was observed for CO(a) over Pd metal. Instead, moderate intensity peak was observed at 2158 cm⁻¹, which may be assigned to adsorbed NCO or CN species provably on the reduced cerium oxide under SMSI state.

Detailed kinetical studies as well as IR observation during NO-CO reaction were carried out. It was concluded that, over Pd/SiO₂, the reaction may proceed via redox mechanism through NO dissociation to form the oxidized surface followed by its reduction with CO. On the other hand by adding In or Pb, a new reaction pathway might be opened at the lower temperature region via NO dimer-like intermediates, and the role of additives would be the stabilization of these unique intermediates on the slightly oxidized intermetallic compounds.

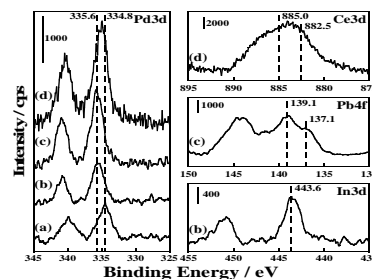


Fig.1 XPS data of (a)Pd/SiO₂,(b)Pd-In/SiO₂, (c)Pd-Pb/SiO₂ and (d)Pd-Ce/SiO₂

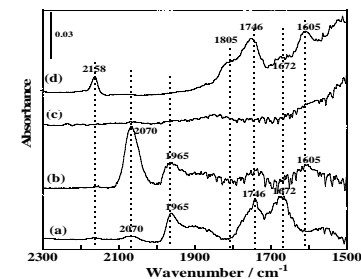


Fig.2 FT-IR spectra during NO-CO reaction over (a)Pd/SiO₂, (b)Pd-In/SiO₂, (c)Pd-Pb/SiO₂,(d)Pd-Ce/SiO₂