

Catalytic Activity of 0.4 % Rhodium Supported Microporous $\text{AlPO}_4\text{-5}$ Catalyst for $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ Reactions

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Temperature-programmed reactions of mixtures of NO , CO , C_3H_6 and O_2 were investigated over rhodium supported on microporous $\text{AlPO}_4\text{-5}$ catalyst. Same reactions were studied after treating the catalyst in a stream of H_2 to evaluate the catalytic performance after reduction treatment. Microporous $\text{AlPO}_4\text{-5}$ was synthesized hydrothermally using triethylamine as structure directing agent and then been used as a support for rhodium metal. A lower amount of rhodium (0.4 wt %) supported on microporous $\text{AlPO}_4\text{-5}$ catalyst exhibited satisfactory light-off at temperature ($T_{50\%} = 300^\circ\text{C}$) with a steep rise in conversion efficiency after aging the catalyst at 900°C for 25 h in a stream of 10 % $\text{H}_2\text{O}/\text{air}$. Outstanding result was observed after reduction treatment of the catalyst, where light-off shifted to a lower temperature 200°C maintaining steep rise in conversion efficiency. Rhodium nanoparticles were well dispersed on the high surface area microporous $\text{AlPO}_4\text{-5}$ material, which is believed to be the key factor for exhibiting excellent catalytic activity both in the oxidizing as well as reducing environment. This newly developed rhodium supported microporous $\text{AlPO}_4\text{-5}$ catalyst with minimum rhodium loading having excellent catalytic performance after reduction treatment, has the potential to serve as a new generation three-way catalyst.

Keywords: Microporous, $\text{AlPO}_4\text{-5}$, Rhodium nanoparticle, Three-way catalyst, Reduction treatment.

INTRODUCTION

Exhaust gases from internal combustion engines of vehicles and industrial combustion process contain noxious oxides of nitrogen (NO_x), which is well-known for its detrimental contribution to our environment [1,2]. As a consequences of environmental hazards, strict restrictions have been imposed time to time to control its emission from both stationary and mobile sources [3-6]. Catalytic abatement of (NO_x) attracted lots of attention as direct decomposition of this pollutant is kinetically not suitable due to its high activation energy barrier [7]. Therefore, catalytic reduction of NO_x is one of the feasible options to reduce this pollutant into innocuous gas. Three-way catalyst (TWC) was introduced in automobiles in the late 1970s to control CO , NO_x and hydrocarbon together and was successful until introducing lean-burn technology, which improves fuel economy [8,9]. In lean-burn mode of operation auto-vehicles has to run both in oxidizing as well as reducing environment and three-way catalyst got deteriorates particularly for controlling NO_x [10,11]. Also demand for precious metals, which are essential ingredients of three-way catalyst rises and lessening of their amount is very essential to save these precious metals [12]. There are two

options to solve this problem. One is the alternative to precious metal and another one is development of support material for the precious metal. Much efforts have been directed by the researchers in the first option but little success has been achieved. Because there is no viable substitute of precious metals for exhibiting unparallel activity to control noxious automotive pollutants. To address this issue, we focused on the second option and developed varieties of new support materials for Pt and Rh metal for dissipating NO_x by using these supported catalysts [13-16].

For NO_x abatement, previously we reported Rh supported dense AlPO_4 catalyst for the catalytic removal of NO_x [17]. We got promising catalytic activity along with thermal stability using this support having low surface area. Then we started our new journey with a view to synthesize new phosphate materials [13]. In the context of development of support material by lessening precious metals, we got promising result by using high surface area mesoporous support for Pt catalyst [16]. Keeping this into our mind we started searching new type of porous phosphate materials for the Rh metal. Among the porous phosphate materials with pore sizes near molecular dimensions such as aluminophosphate (AlPO), has physical/chemical properties similar to zeolites and more important applications have been

used as adsorbents for separation and purification, catalyst supports in the chemical process due to their high specific surface area, thermal stability and selectivity of reactant/product [18-20]. We are now reporting the new outcome of our work using 0.4 % rhodium supported microporous $\text{AlPO}_4\text{-5}$ for $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reactions.

EXPERIMENTAL

Catalyst preparation and characterization: Microporous $\text{AlPO}_4\text{-5}$ was synthesized by hydrothermal crystallization under autogeneous pressure without agitation. The starting materials were pseudoboehmite as a source of Al, orthophosphoric acid (85%) and triethylamine (99.5%) as a structure directing agent. Synthesis were carried out in 100 cm^3 stainless steel reactor lined with Teflon tube and molar composition of the reaction mixture was $\text{AlO}(\text{OH})\text{:H}_3\text{PO}_4\text{:0.5TEA:20H}_2\text{O}$. First 6.8 g of $\text{AlO}(\text{OH})$ was dissolved in 36 mL of distilled water and sonified for few seconds, then stirred it for another 30 min. Then 7.1 mL of 85 wt % H_3PO_4 acid was added to this suspension dropwise slowly. The mixture was stirred 1.5 h at room temperature. After that 6.9 mL triethylamine was added to this mixture and stirred another 5 h. Finally this mixture was transferred to Teflon tube within the stainless steel autoclave and was heated in a oven by autogenous pressure at 200 °C for 18 h without stirring. Then precipitate was collected by centrifugation and washed thrice and dried overnight in vacuum. The white product of $\text{AlPO}_4\text{-5}$ was calcined at 550 °C in air for 5 h to eliminate the template. Rh-loaded on $\text{AlPO}_4\text{-5}$ (0.4 wt % as Rh metal) was prepared by impregnation of an aqueous solution of $\text{Rh}(\text{NO}_3)_3$, followed by drying in air (100 °C, 10 h), then air calcination (600 °C, 3h). All chemicals used in this study were high purity (99 %) reagent grade and purchased from Wako Chemicals Ind. Ltd. Japan. Crystal phases were determined by powder X-ray diffraction (XRD) using monochromated $\text{CuK}\alpha$ radiation (30 kV, 20 mA, Rigaku Multiflex, Japan). Specific surface area was calculated by BET method from N_2 adsorption isotherm measured at 77 K (Belsorp, Bel Japan, Inc.). TEM observation was performed in a FEI TECNAI F20 electron microscope operating at 200 kV.

Catalytic measurement: The steady state catalytic $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reactions were carried out in a conventional flow reactor equipped with a water cooled infrared image furnace at atmospheric pressure. Prior to catalytic test, Rh-loaded catalysts were hydrothermally pretreated in a stream of 10 % H_2O /air at 900 °C for 25 h. Unless otherwise stated, this will be considered as an aged catalyst for 25 h. A granulated catalyst (10-20 mesh, 0.05 g) was fixed by quartz wool in a pyrex glass tube (4 mm i.d.). Temperature dependence of catalytic activity was evaluated by heating the catalyst bed from room temperature to 600 °C at constant rate of 10 °C/min with supplying a simulated exhaust gas mixture containing NO (0.050 %), CO (0.510 %) C_3H_6 (0.039 %), O_2 (0.400 %) and He (balance) supplied at 100 $\text{cm}^3\text{ min}^{-1}$ ($\text{W/F} = 5.0 \times 10^{-4}\text{ g min cm}^{-3}$, $\text{SV} = 2 \times 10^4 \sim 6 \times 10^4\text{ h}^{-1}$). The gas composition corresponds to stoichiometric air-to-fuel ratio ($\text{A/F} = 14.6$). The effluent gas was analyzed using a Pfeiffer GSD30101 mass spectrometer and a Horiba VA3000 NDIR gas analyzer.

RESULTS AND DISCUSSION

Structure and thermostability: Phase identification and purity were demonstrated by X-ray powder diffraction. Fig. 1 shows XRD patterns of as-synthesized $\text{AlPO}_4\text{-5}$, calcined $\text{AlPO}_4\text{-5}$ and 0.4 % Rh loaded $\text{AlPO}_4\text{-5}$. The XRD patterns of these samples correspond well with that for reported $\text{AlPO}_4\text{-5}$ structure and do not show any impurity [21-26]. Upon calcination, a little increase in intensities of XRD patterns were observed due to little increased particle size. XRD patterns of Rh impregnated sample (Fig. 1c) remained unchanged. The measured XRD data of $\text{AlPO}_4\text{-5}$ with $a = 13.771\text{ \AA}$, $b = 13.771\text{ \AA}$, $c = 8.397\text{ \AA}$, is very closely matched with JCPDS-ICDD Card No.: 44-0044 that belongs to space group $P6/mcc$ having hexagonal symmetry. Hexagonal symmetry of $\text{AlPO}_4\text{-5}$ crystal has also been reported by other researchers [18]. Upon calcinations at 550 °C crystalline phase of $\text{AlPO}_4\text{-5}$ remained same as for as-synthesized one and BET surface area was found $350\text{ m}^2\text{ g}^{-1}$. For our current catalytic application, we utilized this pure crystalline $\text{AlPO}_4\text{-5}$ single phase as an active support of Rh metal. Small amount of Rh (0.4 %) was not enough to detect by XRD measurement. For this reason, next we took TEM micrograph to visualize Rh nanoparticles and from this image particle size of Rh is roughly estimated. TEM micrograph of 0.4 % Rh/ $\text{AlPO}_4\text{-5}$ catalyst (aged at 900 °C for 25 h in 10 % H_2O /air) is presented in Fig. 2. It can be seen that Rh nanoparticle which are few nm in size well dispersed on the outer surface of support. More importantly dispersions of Rh nanoparticles are very well and no agglomeration has been found there at such high temperature. This is one of the most desired things for the researchers because agglomeration destroys catalytic activity of catalyst.

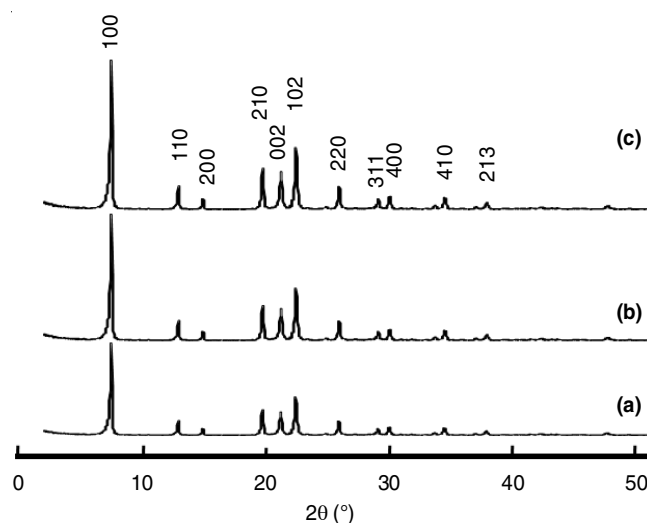


Fig. 1. XRD patterns of (a) as synthesized $\text{AlPO}_4\text{-5}$ (b) Calcined $\text{AlPO}_4\text{-5}$ at 550 pC and (c) 0.4 % Rh supported $\text{AlPO}_4\text{-5}$

Temperature programmed $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reaction: The steady state catalytic $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reactions were carried out in a conventional flow reactor. Catalytic tests in this current study was carried out after aging the catalyst at 900 °C for 25 h in a stream of 10 % H_2O in air. Fig. 3 shows the temperature dependences of conversion efficiencies of NO, CO, C_3H_6 in a simulated exhaust with a stoichiometric air-to-fuel ratio. After aging at 900 °C for 25 h in a stream of 10 % H_2O in air 0.4 %

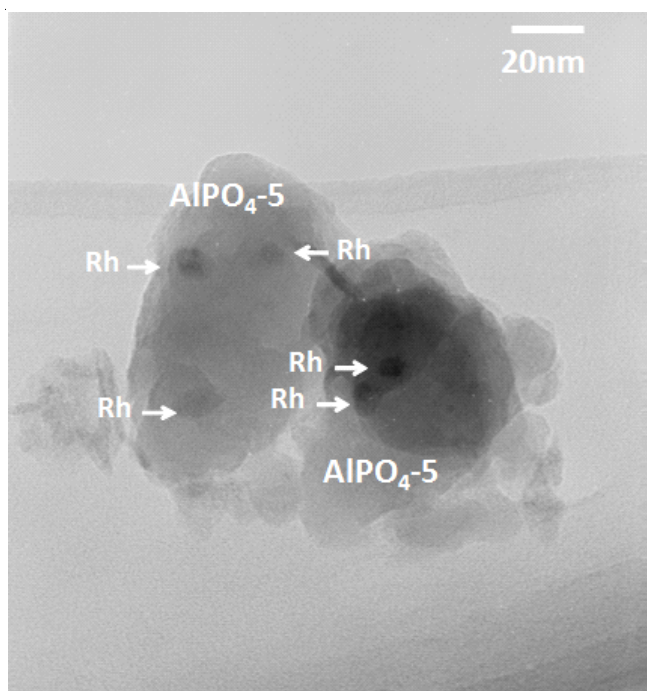


Fig. 2. TEM images of 0.4 % Rh supported on $\text{AlPO}_4\text{-5}$ after aging at 900 °C for 25 h in 10 % $\text{H}_2\text{O/air}$

$\text{Rh/AlPO}_4\text{-5}$ catalyst initiated catalytic reaction at 300 °C (Fig. 3b) achieving light-off $T_{50\%}$ at 312 °C (light-off here is arbitrarily taken at $T_{50\%}$ where 50 % gas conversion reached at this temperature. The steep rise of conversion efficiency of NO, CO, C_3H_6 within a narrow temperature range is an important feature of this catalyst similar to our previous findings of Rh/AlPO_4 [17]. Before aging, fresh 0.4 % $\text{Rh/AlPO}_4\text{-5}$ catalyst initiated the reaction at lower temperature 280 °C and achieved light-off $T_{50\%}$ at 285 °C (Fig 3a). Thermal aging caused the light-off shifting towards higher temperature but steep rise of conversion efficiencies within a narrow temperature range remained unchanged.

Then we treated our 0.4 % $\text{Rh/AlPO}_4\text{-5}$ catalyst in a stream of 1 % H_2/He at 500 °C at rate of 10 °C/min. The steady state catalytic $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reactions were again carried out in a conventional flow reactor using the same simulated exhaust composition with a stoichiometric air-to-fuel ratio. Exciting results of this experiment is demonstrated in Fig. 4. Reduced 0.4 % $\text{Rh/AlPO}_4\text{-5}$ catalyst initiated the reaction at lower temperature 210 °C and achieved the light-off $T_{50\%}$ at 215 °C. Reduction treatment caused the light-off shifting towards lower temperature maintaining steep rise of conversion efficiencies within a narrow temperature.

0.4 % $\text{Rh/AlPO}_4\text{-5}$ catalyst exhibited better catalytic performance in reducing atmosphere than in oxidizing atmosphere. This is due to the metallic Rh particle which remains in reduced state than in RhOx state in harsh oxidizing atmosphere. This signifies the good reducibility feature of this catalyst from oxidized state to reduced state. It is to be noted that sustainability of auto catalyst at higher temperature as high as 900 °C along with low light-off to start up chemical reaction in oxidizing atmosphere is desirable and is quite challenging in the context of reality. Taking these harsh realities into account, our catalytic tests in this current study was therefore carried out after aging the catalyst at 900 °C for 25 h in a stream of 10 % H_2O in air.

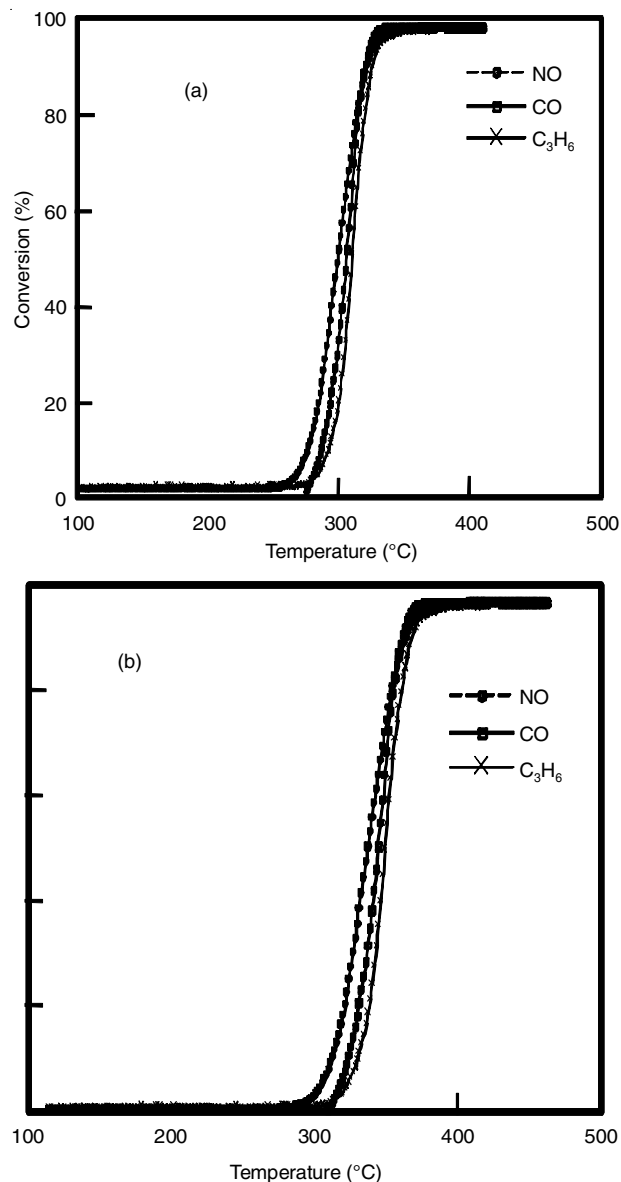


Fig. 3. Light-off curves for $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reaction over 0.4 wt % Rh supported on $\text{AlPO}_4\text{-5}$ (a) Fresh catalyst (before aging) and (b) after aging (aging condition: catalyst was aged at 900 °C for 25 h in 10 % $\text{H}_2\text{O/air}$)

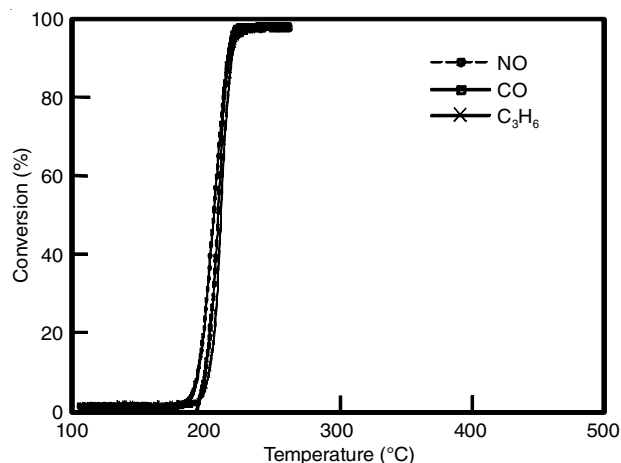


Fig. 4. Light-off curves for $\text{NO-CO-C}_3\text{H}_6\text{-O}_2$ reaction over 0.4 wt % Rh supported on $\text{AlPO}_4\text{-5}$ after reduction treatment in a stream of 1 % H_2/He at a temperature of 500 °C at 10 °C/min rate

Under this harsh oxidizing atmosphere the catalytic performance of this 0.4 % Rh/AlPO₄-5 catalyst is good and reducibility is excellent compare to previously reported supported catalysts [13]. The convenient and cost-effective synthetic route of the support AlPO₄-5 and outstanding catalytic performance of this Rh supported AlPO₄-5 make this a suitable candidate for new three-way catalyst for scavenging auto pollutants from our environment.

Conclusion

High specific surface area microporous AlPO₄-5 without any impurity was synthesized and was used as an active support for 0.4 % Rh. 0.4 % Rh supported on AlPO₄-5 showed excellent catalytic activity for removing NO, CO, C₃H₆ in reducing atmosphere. In oxidizing atmosphere though light-off begins little bit higher temperature, but is satisfactory enough considering the harsh condition applied for aging the catalyst. Thermostability up to 900 °C is also quite sufficient to be used as a three-way catalyst. Further experimental study is keep going on to understand the details behind the interesting metal-support interaction.

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