

## Study of cerium-promoted rhodium alumina catalyst as a steam reforming catalyst for treatment of spent solvents

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**Abstract:** This study attempted to develop an appropriate catalyst used for the steam reforming of gasified spent solvents. Rh<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts with various CeO<sub>2</sub> loadings were prepared and heated at different temperatures of 500 and 800 °C, and their surface properties were studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature programmed reduction (TPR) and Brumauer-Emmett-Teller (BET) analyses. Rhodium existed in the form of Rh<sub>2</sub>O<sub>3</sub>, regardless of the sample composition as well as the heating temperature. In the tested range of cerium addition (up to 12 times the rhodium mass), no significant changes in BET surface areas and binding energy corresponding to Rh 3d<sub>5/2</sub> were observed. Instead, the addition of cerium led to a greatly enhanced dispersion of rhodium nanoparticles, and no agglomeration of rhodium was observed for samples heated even at 800 °C. Honeycomb monolith rhodium catalysts promoted with cerium were fabricated and tested for the steam reforming of a gasified spent solvent, mainly consisting of butylene (C<sub>4</sub>H<sub>8</sub>). The test results suggested that a cerium-promoted rhodium catalyst could be used as an appropriate reforming catalyst for treating low-quality non-methane hydrocarbons without the formation of coke at high temperatures of up to 900 °C.

**Keywords:** cerium; rhodium; catalyst; steam reforming; spent resin; rare earths

Steam reforming has been applied as an alternative to conventional incineration for the treatment of hazardous and radioactive wastes<sup>[1]</sup>. Waste steam reforming involves exposing the waste to elevated temperatures. However, unlike incineration, combustion does not occur with steam reforming. Waste steam reforming is a process of non-flame destruction of organic materials. Organic gases and water vapor released from the heated wastes are mixed with super-heated steam to destroy them. The remaining ashes resemble incinerator ash, and are suitable for burial at a disposal facility<sup>[2]</sup>.

This study attempts to develop an appropriate catalyst used in a steam reformer for the treatment of spent solvents. Catalytic reforming of methane into synthetic gas is a well-developed industrial process carried out at high temperatures. However, there have been serious operation problems associated with carbon deposition during steam reforming of low-quality non-methane hydrocarbons [NMHCs] such as biomass or spent solvents<sup>[3]</sup>. Nickel-based conventional reforming catalysts are efficient at reforming methane. However, nickel catalysts are easily poisoned by a coke formation. For this reason, precious metals such as Rh and Pt, and other metals such as Co and Fe, have been studied to improve a conventional nickel-based catalyst<sup>[4]</sup>. Several works have re-

ported that precious metals such as Rh are better for the reforming of hydrocarbons without significant coke formation. A steam reforming reaction is favored by high temperature, but metallurgy limits the application temperature of precious metals, which are relatively unstable at high temperatures when compared to nickel catalysts. Rare earth elements such as cerium have been studied as stabilizers to raise the application temperature of catalysts. The application of rare earth oxides as promoters and stabilizers in combustion catalysts has been extensively described in the literature<sup>[5-7]</sup>. According to these works, cerium oxide appears to be an excellent stabilizer for a precious metal catalyst.

In this study, rhodium catalysts with cerium oxide additive were tested to elucidate the stabilizing effect of cerium oxide at high temperatures of up to 800 °C. Rh<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Rh<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>, and Rh<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with various CeO<sub>2</sub> loadings were prepared to investigate the role of cerium as a stabilizer. Physicochemical properties of the prepared catalyst samples were investigated to establish an optimum composition to fabricate structured steam reforming catalysts. A rhodium-cerium based honeycomb catalyst was fabricated to test its steam reforming performance for gasified spent TBP (tributyl phosphate).

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## 1 Experimental

### 1.1 Preparation and characterization of catalysts

$\gamma$ -alumina (<50 nm in particle size), high-purity rhodium chloride ( $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ ), and cerium carbonate ( $\text{C}_3\text{Ce}_2\text{O}_9 \cdot \text{H}_2\text{O}$ ), supplied by Aldrich, were used for catalyst preparation.  $\text{Rh}_2\text{O}_3/\text{CeO}_2$  catalysts with various Ce loadings (0, 1, 6, and 12 times Rh mass) were prepared from  $\gamma$ -alumina impregnation with mixed aqueous solutions of  $\text{RhCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{C}_3\text{Ce}_2\text{O}_9 \cdot \text{H}_2\text{O}$ . After impregnation, the samples were dried at 110 °C and sintered at two different temperatures of 500 and 800 °C for 4 h. After calcinations, their physicochemical properties were investigated using XRD (Rigaku, D/MAX 2500H), XPS (Thermo Scientific, Multilab 2000), TEM (TEOL, 2100F), TEM/EDX (Oxford, INCA), TPR (Micromeritics, AutoChem II 2920) and BET (Micromeritics, Tristar II 3020) analyses.

### 1.2 Catalytic steam reforming experiments

A 5 cm long honeycomb monolith catalyst with a diameter of 4.5 cm was fabricated and used as a steam reforming catalyst. A 400-CPSI (cells per square inch) honeycomb cordierite monolith supplied by Pinxiang A&R Ceramics Co., Ltd. was coated with a 3 wt.% washcoat consisting of  $\gamma$ -alumina (<50 nm in particle size). Impregnation of rhodium and ceria (6 times Rh mass) was achieved by saturating the monolith with mixed aqueous solutions of  $\text{RhCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{C}_3\text{Ce}_2\text{O}_9 \cdot \text{H}_2\text{O}$ , followed by 10 h drying at 110 °C. Catalytic steam reforming experiments were carried out in a flow reactor, as schematically shown in Fig. 1. The experiments were carried out in a 15-cm stainless steel (STS-310S) tubular reactor, in which two prepared 4.5-cm honeycomb steam reforming catalysts were loaded in series. The weight loss of TBP (tributyl phosphate) loaded on a cylindrical crucible in a heated pyrolysis furnace at 300 °C was continuously measured. Investigation into the reforming temperatures varied from 700 to 900 °C with 50 °C intervals. The molar ratios of

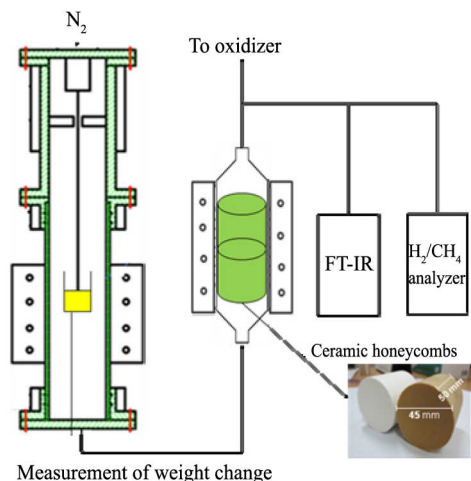


Fig. 1 Schematics of catalytic steam reforming test system

steam to carbon (S/C) were varied to be 2.5 and 5 under each investigating temperature condition. All tests were performed under a GHSV of 20000  $\text{h}^{-1}$ . The concentrations of hydrocarbon species, methane, and hydrogen in the inlet and outlet gas streams were measured using a portable combustion gas analyzer (MK 9000, rbr Messtechnik GmbH) and a FTIR (Nicolet iS10, thermo scientific).

## 2 Results and discussion

### 2.1 Characterization of catalysts

The X-ray diffraction patterns of catalyst samples are shown in Fig. 2. The formation of  $\text{Rh}_2\text{O}_3$  and  $\text{CeO}_2$  was shown in the XRD patterns of samples sintered at both temperatures. The intensity of the characteristic peaks of both  $\text{Rh}_2\text{O}_3$  and  $\text{CeO}_2$  increased with the calcination temperature. The intensity of the  $\text{CeO}_2$  peak increased with the added cerium amount, while that of  $\text{Rh}_2\text{O}_3$  decreased. The disappearance of the characteristic peak of  $\text{Rh}_2\text{O}_3$  for the  $\text{Rh}/12\text{Ce}-\text{Al}_2\text{O}_3$  samples sintered at both temperatures is probably the cause of the surface area diminution of  $\text{Rh}_2\text{O}_3$  by the relatively large surface area of loaded cerium of 12-times the rhodium mass.

BET surface areas of the catalyst samples are shown in Tables 1 and 2. The BET surface area slightly decreased with the added amount of ceria and the sintered tem-

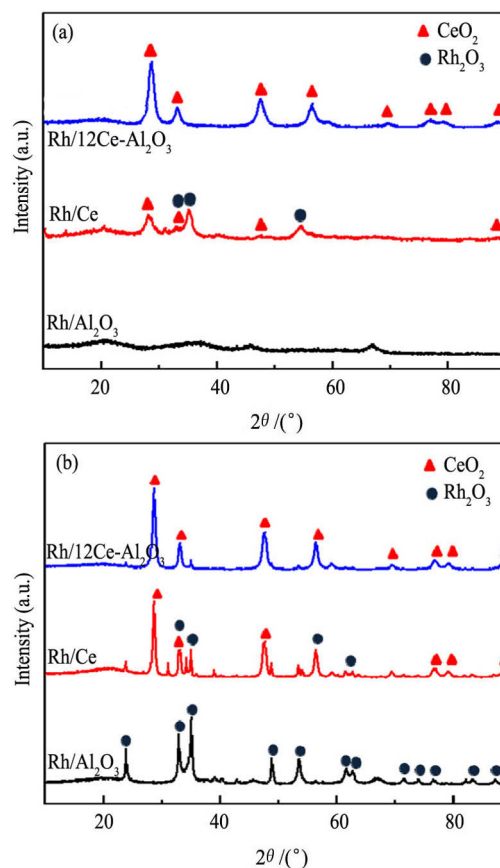


Fig. 2 X-ray diffraction patterns of catalyst samples calcined at 500 °C (a) and 800 °C (b)

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