

Nano-structured Catalytic Materials for Unsteady-state Reactions

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Catalytic materials for unsteady-state reactions attract considerable attention in the area of environmental protection and energy production. One typical example is oxygen storage materials (OSMs), which are important in automotive emission-control catalysts. They can store or release oxygen to achieve the ideal air-to-fuel ratio needed for complete fuel combustion. The combustion processes also creates noxious pollutants and OSMs are able to convert these pollutants to less harmful compounds by oxidation and reduction. We have developed new materials, lanthanide oxysulfates, $\text{Ln}_2\text{O}_2\text{SO}_4$, having a larger oxygen storage than traditional one ($\text{CeO}_2\text{-ZrO}_2$). The present work in this research direction deals with the synthesis of the nano-structured materials to achieve a higher performance.

$\text{Ln}_2\text{O}_2\text{SO}_4$ utilizes for the first time the nonmetallic element (S) as a redox site instead of metallic elements. The

reduction by H_2 , CO, and/or hydrocarbons and subsequent reoxidation by O_2 between $\text{Ln}_2\text{O}_2\text{SO}_4(\text{S}^{6+})$ and $\text{Ln}_2\text{O}_2\text{S}(\text{S}^{2-})$ achieved the oxygen storage capacity of $2 (\text{mol of O}_2) \cdot \text{mol}^{-1}$ (Fig.1), which is eight times larger than that of the conventional $\text{CeO}_2\text{-ZrO}_2$ material.

We have synthesized $\text{Pr}_2\text{O}_2\text{SO}_4$ by a template-assisted route resulting in a layered mixed organic/inorganic mesophase (Fig.2), which forms a mesoporous oxide upon calcination. The obtained material can release oxygen at a substantially lower temperature than a reference material prepared directly from $\text{Pr}_2(\text{SO}_4)_3$. Oxysulfate materials possessing both a higher surface area and uniform mesoporosity would therefore be indeed very interesting in our future research.

The potential for $\text{Pr}_2\text{O}_2\text{SO}_4$ as an unsteady-state catalyst has been investigated by evaluating the effect of large oxygen storage on catalytic conversions of CO, C_3H_6 , and NO in an alternative lean/rich cycling mode, which was conducted in a dual-supply flow system. The full capacity oxygen storage of $2 (\text{mol of O}_2) \cdot \text{mol}^{-1}$ and anaerobic oxidation of $4 (\text{mol of CO}) \cdot \text{mol}^{-1}$ could be cycled. The CO/ O_2 cycled feed stream reactions achieved the CO conversion higher than 85 % at 700°C , which is almost comparable to that of a steady-state CO- O_2 reaction. The catalytic activity was not affected by the presence of a typical catalyst poison, SO_2 , which rather improved the stability of $\text{Pr}_2\text{O}_2\text{SO}_4/\text{Pr}_2\text{O}_2\text{S}$.

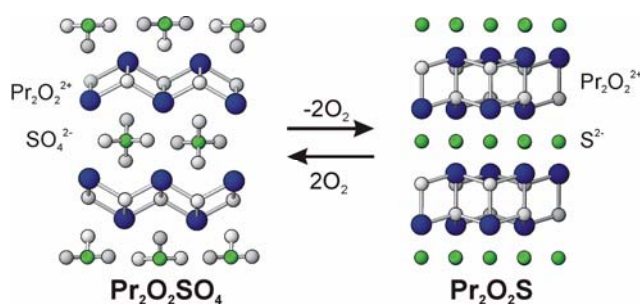


Fig.1 Oxygen storage/release by oxysulfate/oxysulfide.

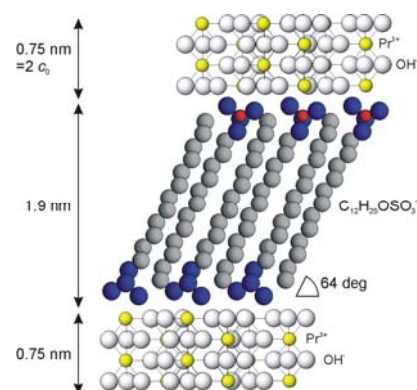


Fig.2 Structure of Pr-DS mesophase.
 $\text{DS}=\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$

M.Machida et al, *Chem.Commun.* **2004**, 662; *Chem. Mater.* **2005**, 17, 1487; *J. Catal.* **2006**, 238, 58; *J. Mater. Chem.* **2006**, 16, 3084; *Chem. Mater.* **2007**, 19, 954; *J. Catal.* **2007**, 248, 46; *J. Ceram. Soc. Jpn.* **2007**, 115, 597.