

# 催化学报

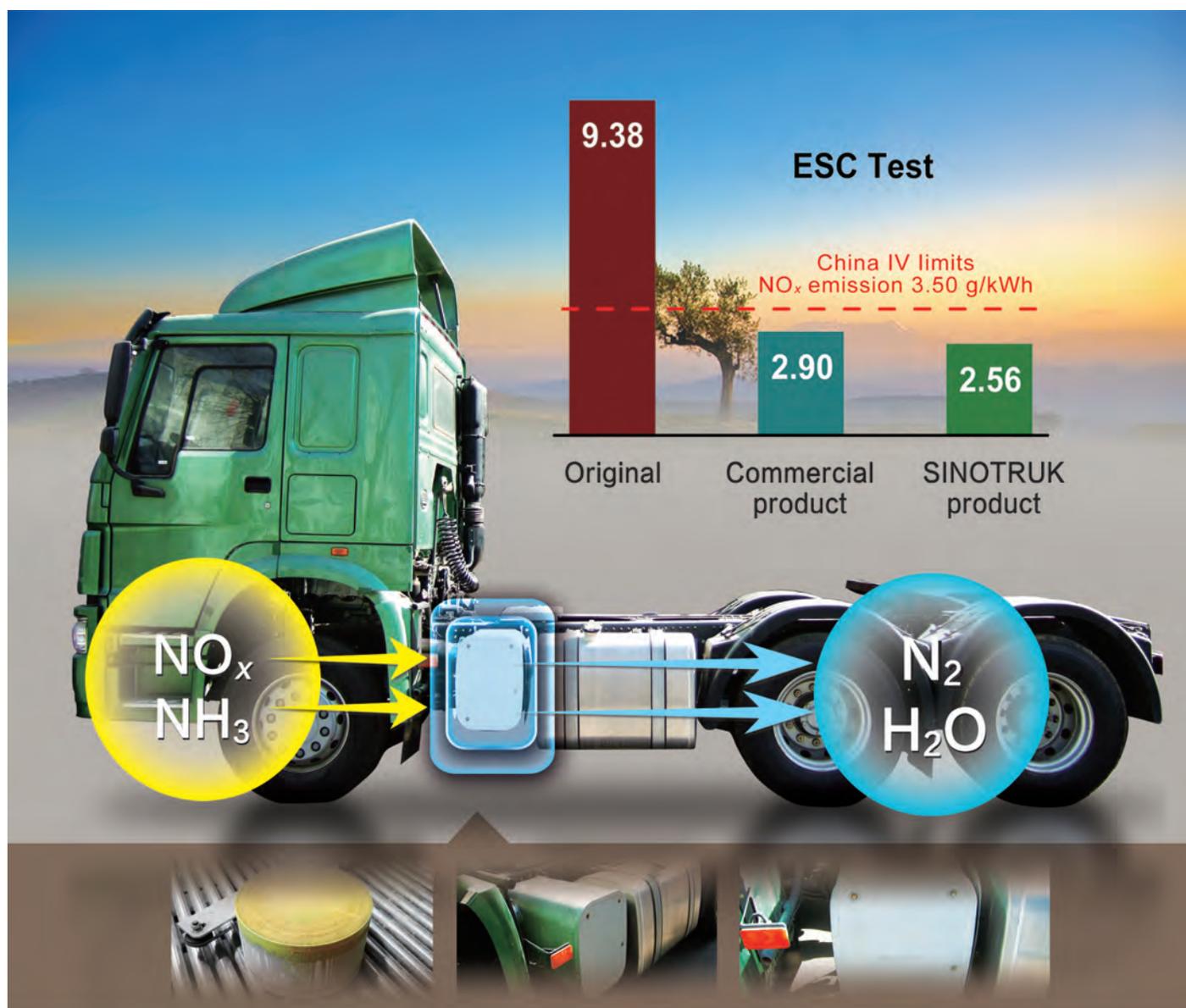
# Chinese Journal of Catalysis

主编 林励吾

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Transaction of the Catalysis Society of China

## In This Issue



**封面:** 贺泓及研究团队基于实验室对 V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> 催化剂配方及涂覆成型技术的大量研究, 在中国重汽集团建成了一条 NH<sub>3</sub>-SCR 催化剂生产线, 产品满足国产重型柴油车国 IV 排放标准要求. 见本期第 1438-1445 页.

**Cover:** Prof. He and his coworkers in their Article on pages 1438-1445 reported the laboratory study of catalyst formulation and washcoating technology for the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> system, and also the establishment of an NH<sub>3</sub>-SCR (selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>) catalyst production line of which the product can make the heavy duty diesel vehicles meet the China IV emission standard.

## About the Journal

*Chinese Journal of Catalysis* is an international journal published monthly by Chinese Chemical Society, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and Elsevier. The journal publishes original, rigorous, and scholarly contributions in the fields of heterogeneous and homogeneous catalysis in English or in both English and Chinese. The scope of the journal includes:

- ◆ New trends in catalysis for applications in energy production, environmental protection, and production of new materials, petroleum chemicals, and fine chemicals;
- ◆ Scientific foundation for the preparation and activation of catalysts of commercial interest or their representative models;
- ◆ Spectroscopic methods for structural characterization, especially methods for in situ characterization;
- ◆ New theoretical methods of potential practical interest and impact in the science and applications of catalysis and catalytic reaction;
- ◆ Relationship between homogeneous and heterogeneous catalysis;
- ◆ Theoretical studies on the structure and reactivity of catalysts.
- ◆ The journal also accepts contributions dealing with photo-catalysis, bio-catalysis, and surface science and chemical kinetics issues related to catalysis.

### Types of Contributions

- **Reviews** deal with topics of current interest in the areas covered by this journal. Reviews are surveys, with entire, systematic, and important information, of recent progress in important topics of catalysis. Rather than an assemblage of detailed information or a complete literature survey, a critically selected treatment of the material is desired. Unsolved problems and possible developments should also be discussed. Authors should have published articles in the field. Reviews should have more than 80 references.
- **Communications** rapidly report studies with significant innovation and major academic value. They are limited to four Journal pages. After publication, their full-text papers can also be submitted to this or other journals.
- **Articles** are original full-text reports on innovative, systematic and completed research on catalysis.
- **Highlights** describe and comment on very important new results in the original research of a third person with a view to highlight their significance. The results should be presented clearly and concisely without the comprehensive details required for an original article.
- **Viewpoints** describe the results of original research in general in some area, with a view to highlighting the progress, analyzing the major problems, and commenting the possible research target and direction in the future.
- **Academic Arguments** can discuss, express a different opinion or query the idea, concept, data, data processing method, characterization method, computational method, or the conclusion of published articles. The objective of an academic argument should be to enliven the academic atmosphere.

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# 催化学报

(CUIHUA XUEBAO)

## CHINESE JOURNAL OF CATALYSIS

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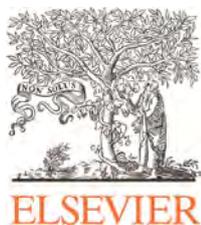
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**1437** 《催化学报》2013 年 SCI 影响因子为 1.552

**1590** 作者索引

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## Chinese Journal of Catalysis

## Graphical Contents

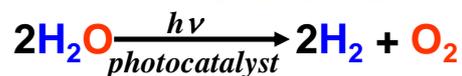
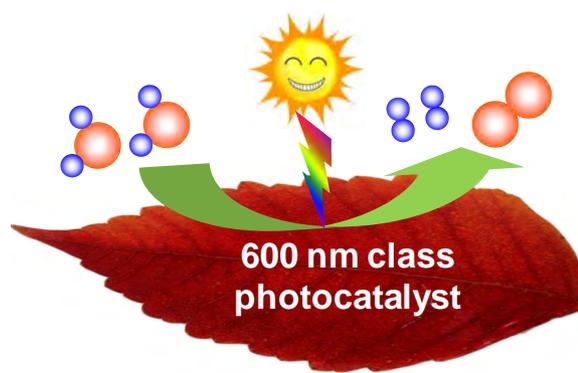
## Highlight

Chin. J. Catal., 2014, 35: 1431–1432 doi: 10.1016/S1872-2067(14)60183-2

## Recent progress on photocatalysts with wide visible light range absorption for heterogeneous water splitting

Shanshan Chen, Fuxiang Zhang\*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences



Recent progress on wide visible light range photocatalysts for heterogeneous water splitting was summarized, and the next challenge of developing an efficient 600 nm class photocatalytic water splitting system was highlighted.

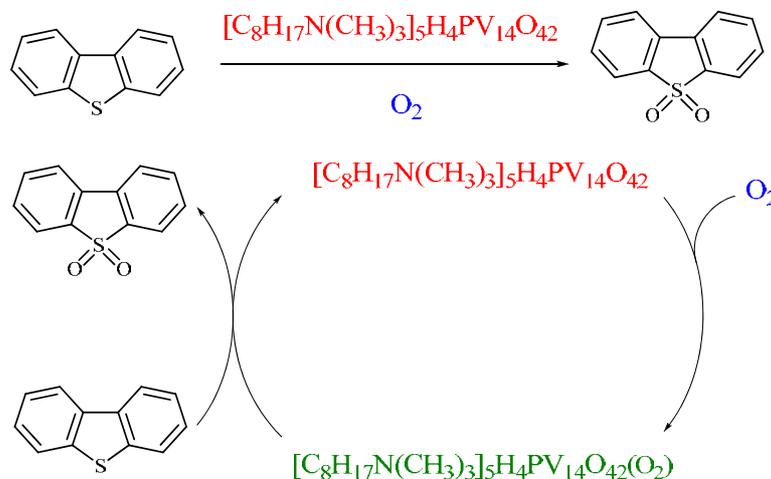
## Communication

Chin. J. Catal., 2014, 35: 1433–1437 doi: 10.1016/S1872-2067(14)60194-7

## Oxidation of dibenzothiophene using oxygen and a vanadophosphate catalyst for ultra-deep desulfurization of diesels

Nanfang Tang, Xiaoping Zhao, Zongxuan Jiang\*, Can Li\*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences; Shaanxi Yanchang Petroleum (Group) Co., Ltd.



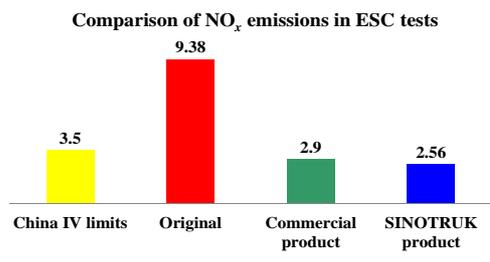
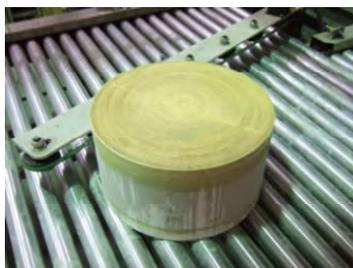
Oxygen was by interaction with a vanadophosphate, and it oxidized dibenzothiophene to sulfone.

## Articles

*Chin. J. Catal.*, 2014, 35: 1438–1445 doi: 10.1016/S1872-2067(14)60048-6

### Selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> for heavy-duty diesel vehicles

Fudong Liu, Wenpo Shan, Dawei Pan, Tengying Li, Hong He\*  
*Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences;  
 China National Heavy Duty Truck Group Jinan Rubber and Plastic Co., Ltd.*



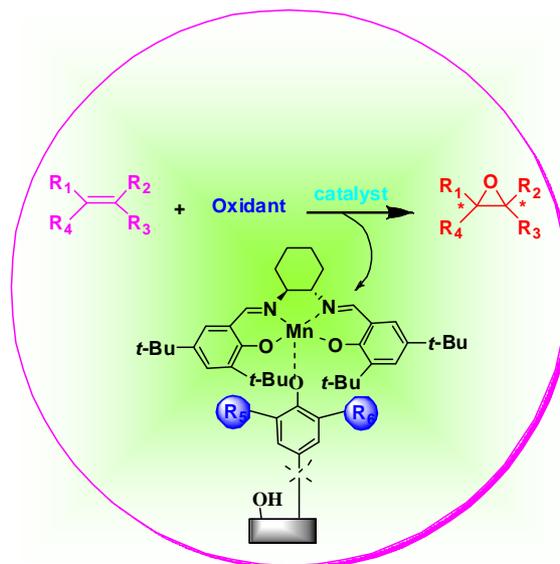
NH<sub>3</sub>-SCR catalysts manufactured by SINOTRUK efficiently reduced NO<sub>x</sub> emission from diesel engines to meet the China IV standard.

*Chin. J. Catal.*, 2014, 35: 1446–1455 doi: 10.1016/S1872-2067(14)60064-4

### Chiral Mn<sup>III</sup>(Salen) supported on tunable phenoxy group modified zirconium poly (styrene-phenylvinylphosphonate)-phosphate as an efficient catalyst for epoxidation of unfunctionalized olefins

Xiaochuan Zou\*, Kaiyun Shi, Cun Wang  
*Chongqing Education College; Southwest University*

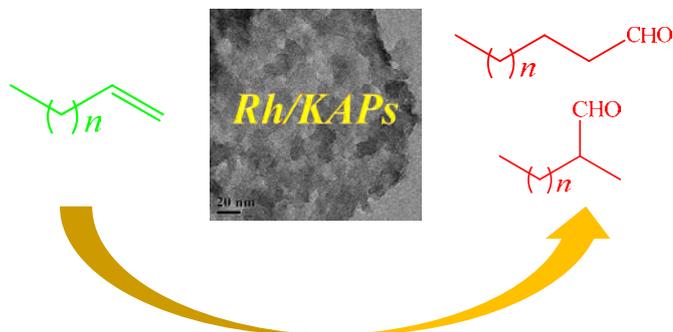
We have reported for the first time that the use of tuneable rigid phenoxy linkers bearing *ortho* substituents imposing different steric hindrance effects has a critical effect on the catalytic activity of the supported systems towards the epoxidation of olefins, especially heterogeneous epoxidation systems.



*Chin. J. Catal.*, 2014, 35: 1456–1464 doi: 10.1016/S1872-2067(14)60068-1

### Rh catalysts supported on knitting aryl network polymers for the hydroformylation of higher olefins

Miao Jiang, Yunjie Ding\*, Li Yan, Xianguen Song, Ronghe Lin  
*Dalian Institute of Chemical Physics, Chinese Academy of Sciences;  
 University of Chinese Academy of Sciences*



Rh catalysts supported on knitting aryl network polymers (KAPs) showed high activity for the hydroformylation of higher olefins.

*Chin. J. Catal.*, 2014, 35: 1465–1474 doi: 10.1016/S1872-2067(14)60070-X

### Ozone catalytic oxidation of benzene over AgMn/HZSM-5 catalysts at room temperature: Effects of Mn loading and water content

Yang Liu, Xiaosong Li, Jinglin Liu, Chuan Shi, Aimin Zhu\*  
Dalian University of Technology



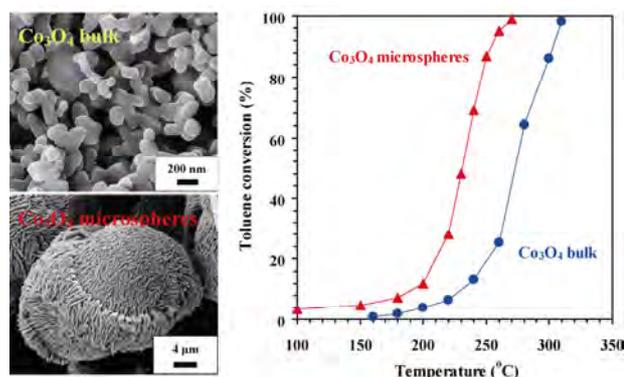
AgMn/HZSM-5 catalyst with Mn loading of 2.4 wt% has the best activity and stability.  $O_3$  decomposition is crucial for AgMn/HZSM-5 (Mn loading  $\leq 2.4$  wt%), whereas benzene activation is important for AgMn/HZSM-5 (Mn loading  $> 2.4$  wt%). Water vapor greatly enhances the OZCO reactivity and stability.

*Chin. J. Catal.*, 2014, 35: 1475–1481 doi: 10.1016/S1872-2067(14)60072-3

### Nanoplate-aggregate $Co_3O_4$ microspheres for toluene combustion

Fang Wang, Hongxing Dai\*, Jiguang Deng, Shaohua Xie, Huanggen Yang, Wen Han  
Beijing University of Technology

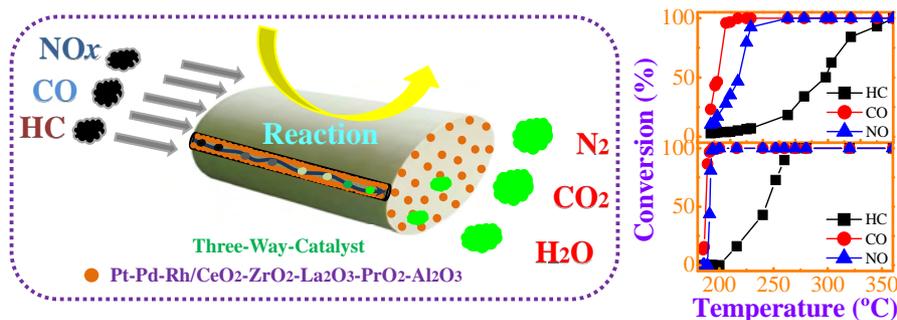
Nanoplate-aggregate microspherical  $Co_3O_4$  prepared by the ethylenediamine-assisted hydrothermal route exhibits good catalytic performance for toluene oxidation because of its high surface area and concentration of adsorbed oxygen and good low-temperature reducibility.



*Chin. J. Catal.*, 2014, 35: 1482–1491 doi: 10.1016/S1872-2067(14)60092-9

### A new monolithic Pt-Pd-Rh motorcycle exhaust catalyst to meet future emission standards

Suning Wang, Yajuan Cui, Li Lan, Zhonghua Shi, Ming Zhao, Maochu Gong, Ruimei Fang, Sijie Chen, Yaoqiang Chen\*  
Sichuan University



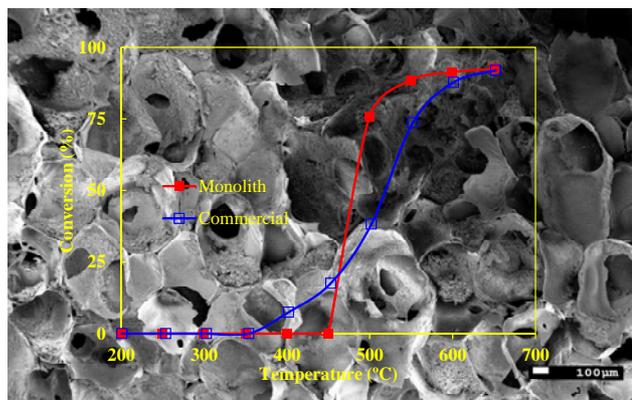
A new composite oxide,  $CeO_2-ZrO_2-La_2O_3-PrO_2-Al_2O_3$ , was successfully synthesized by co-precipitation, and the supported monolith Pd-Rh, Pt-Rh, and Pt-Pd-Rh catalysts were obtained through an impregnation route. The Pt-Pd-Rh catalyst delivers outstanding performance and is suitable as a motorcycle exhaust gas catalyst that can meet future emission standards.

*Chin. J. Catal.*, 2014, 35: 1492–1496 doi: 10.1016/S1872-2067(14)60085-1

### Synthesis of novel hierarchical ZSM-5 monoliths and their application in trichloroethylene removal

João Pires\*, Ana C. Fernandes, Divakar Duraiswami  
*Universidade de Lisboa, Portugal;*  
*PSG College of Technology, India*

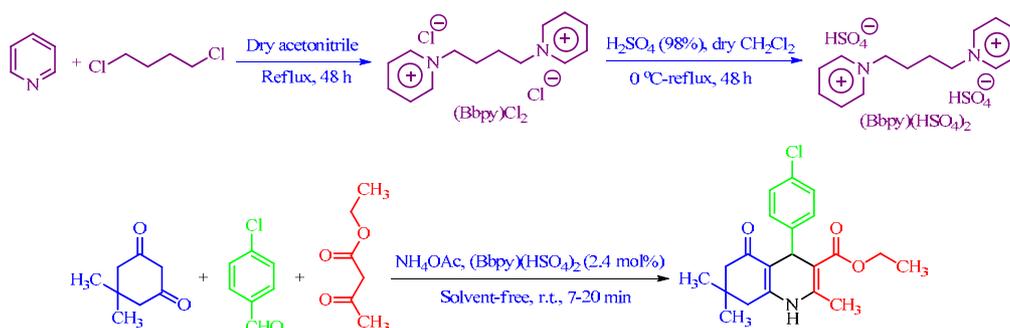
An open-cell polyurethane foam template is combined with a zeolite synthesis process to produce ZSM-5 zeolite monoliths that are catalytically active towards the oxidation of trichloroethylene.



*Chin. J. Catal.*, 2014, 35: 1497–1503 doi: 10.1016/S1872-2067(14)60087-5

### One-pot multicomponent synthesis of unsymmetrical polyhydroquinoline derivatives with 1,1'-butylenebispyridinium hydrogen sulfate as an efficient, halogen-free and reusable Brønsted ionic liquid catalyst

Nader Ghaffari Khaligh\*  
*Research House of Professor Reza, Education Guilan, Iran*

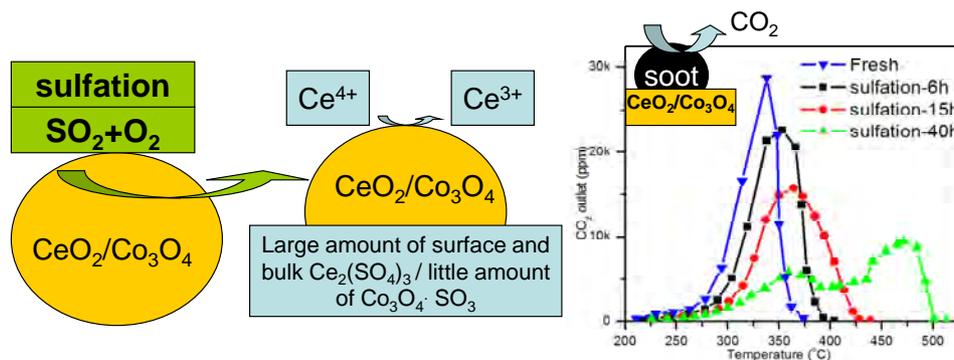


Ethyl-4-aryl/heteryl-hexahydro-trimehtyl-5-oxoquinoline-3-carboxylates were synthesized by the one-pot condensation of dimedone, aryl/heteryl aldehydes, ethyl acetoacetate, and ammonium acetate with 1,1'-butylenebispyridinium hydrogen sulfate (Bbpy)(HSO<sub>4</sub>)<sub>2</sub> as an efficient, halogen-free, and reusable Brønsted ionic liquid catalyst under solvent-free conditions. High yield, clean reaction, simple methodology, short reaction time, and recyclability of the ionic liquid are the advantages of the method.

*Chin. J. Catal.*, 2014, 35: 1504–1510 doi: 10.1016/S1872-2067(14)60088-7

### Effect of sulfur poisoning on Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> composite oxide catalyst for soot combustion

Xiaoyan Shi, Yunbo Yu, Li Xue, Hong He\*  
*Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences; Shandong University of Technology*



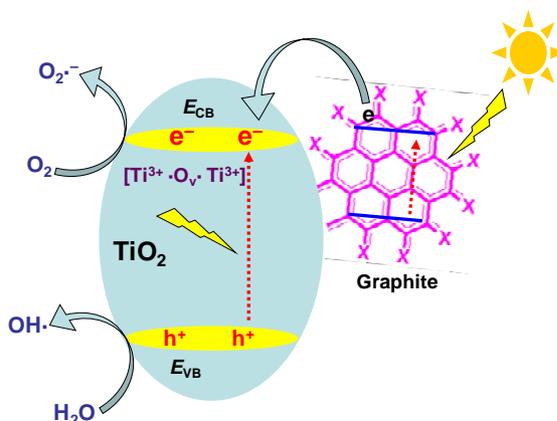
Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> composite oxides showed better SO<sub>2</sub> tolerance and higher activity than CeO<sub>2</sub> but was more easily poisoned by SO<sub>2</sub> than Co<sub>3</sub>O<sub>4</sub> during soot combustion in NO/O<sub>2</sub>.

*Chin. J. Catal.*, 2014, 35: 1511–1519 doi: 10.1016/S1872-2067(14)60093-0

### Ti<sup>3+</sup> and carbon co-doped TiO<sub>2</sub> with improved visible light photocatalytic activity

Yunchang Liu, Mingyang Xing\*, Jinlong Zhang\*  
East China University of Science and Technology

The synergistic effect between Ti<sup>3+</sup> self-doping and graphite surface coverage is responsible for the improvement of the visible light photocatalytic activity of Ti<sup>3+</sup> and carbon co-doped TiO<sub>2</sub> catalyst.

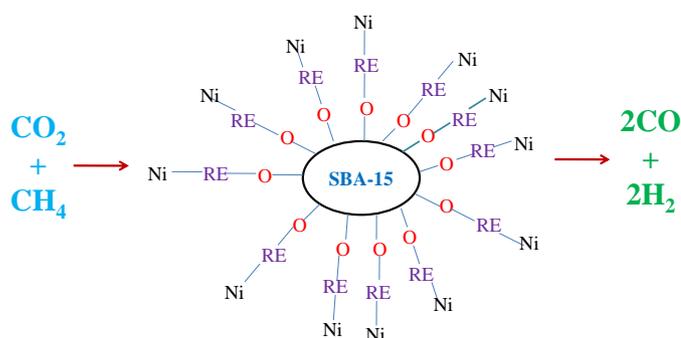


*Chin. J. Catal.*, 2014, 35: 1520–1528 doi: 10.1016/S1872-2067(14)60095-4

### Effects of Nd, Ce, and La modification on catalytic performance of Ni/SBA-15 catalyst in CO<sub>2</sub> reforming of CH<sub>4</sub>

Huimin Liu, Yuming Li, Hao Wu, Weiwei Yang, Dehua He\*  
Tsinghua University

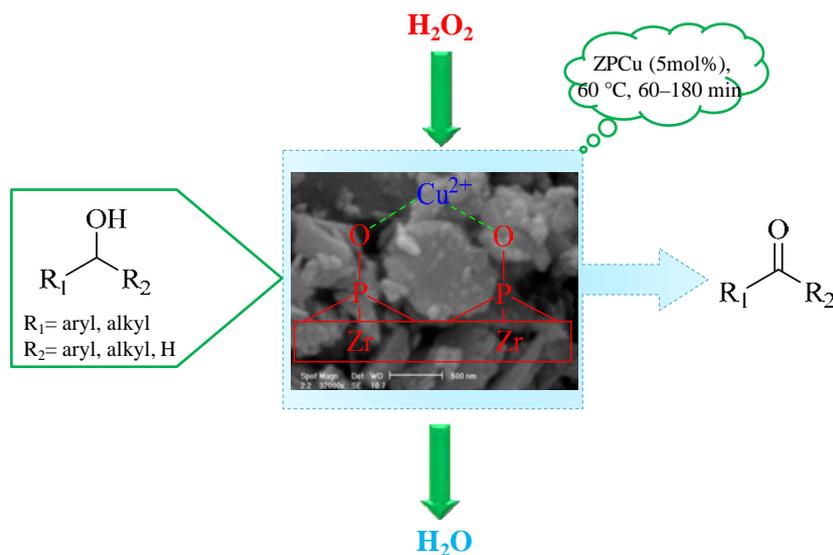
Rare-earth (RE) metals acted as promoters by connecting NiO and SBA-15 through Ni-RE-O species, which facilitated NiO reduction and improved the performance of modified Ni/SBA-15 catalysts in CO<sub>2</sub> reforming of CH<sub>4</sub>.



*Chin. J. Catal.*, 2014, 35: 1529–1533 doi: 10.1016/S1872-2067(14)60096-6

### Selective oxidation of alcohols over copper zirconium phosphate

Abdol R. Hajipour\*, Hirbod Karimi  
Isfahan University of Technology, Iran; University of Wisconsin, USA

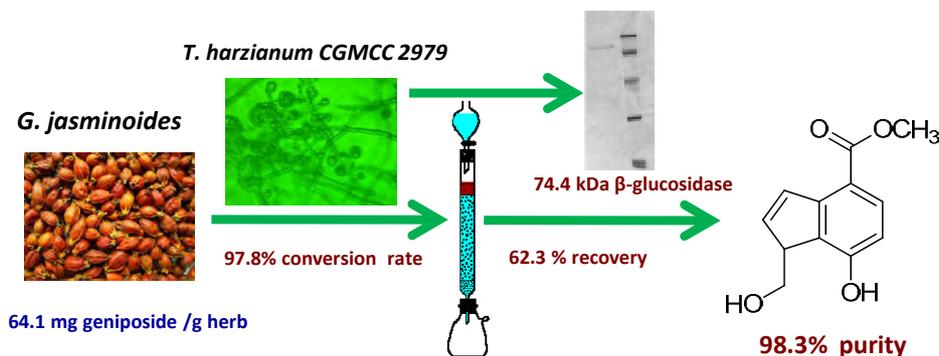


Copper zirconium phosphate was prepared and used as an efficient catalyst for the selective oxidation of various alcohols to the corresponding aldehydes and ketones, in good yields and with excellent selectivities.

*Chin. J. Catal.*, 2014, 35: 1534–1546 doi: 10.1016/S1872-2067(14)60134-0

### Biotransformation of geniposide in *Gardenia jasminoides* to genipin by *Trichoderma harzianum* CGMCC 2979

Yuesheng Dong\*, Leping Liu, Yongming Bao, Aiyu Hao, Ying Qin, Zujia Wen, Zhilong Xiu  
Dalian University of Technology; Dalian Institute for Drug Control

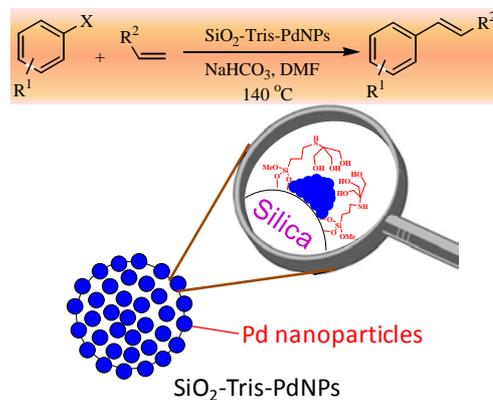


We described a simple and effective method for preparing genipin based on the biotransformation of geniposide in *Gardenia jasminoides* by *Trichoderma harzianum*. The mechanism of biotransformation was also discussed.

*Chin. J. Catal.*, 2014, 35: 1547–1554 doi: 10.1016/S1872-2067(14)60109-1

### Immobilized Pd nanoparticles on Tris-modified SiO<sub>2</sub>: Synthesis, characterization, and catalytic activity in Heck cross-coupling reactions

Abdol R. Hajipour\*, Ghobad Azizi  
Isfahan University of Technology, Iran;  
University of Wisconsin, USA

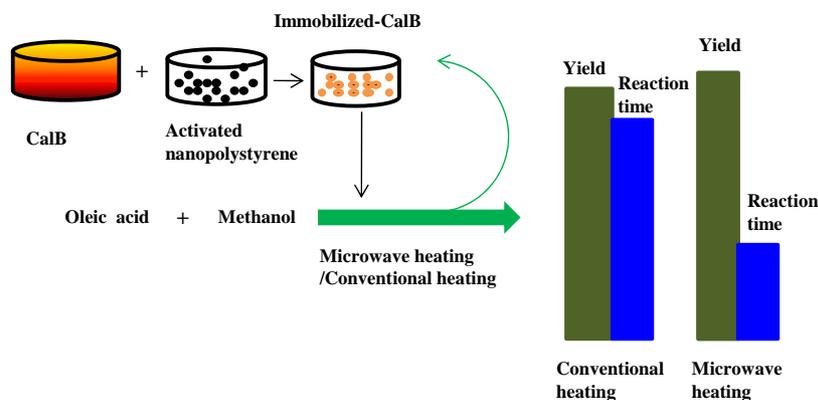


The preparation of palladium nanoparticles supported on tris(hydroxymethyl)-aminomethane-modified silica gel and its catalytic application in Heck coupling are investigated.

*Chin. J. Catal.*, 2014, 35: 1555–1564 doi: 10.1016/S1872-2067(14)60111-X

### Covalent immobilization of *Candida antarctica* lipase B on nanopolystyrene and its application to microwave-assisted esterification

Attaullah Bukhari, Ani Idris\*, Madiha Atta, Teo Chee Loong  
Universiti Teknologi Malaysia, Malaysia

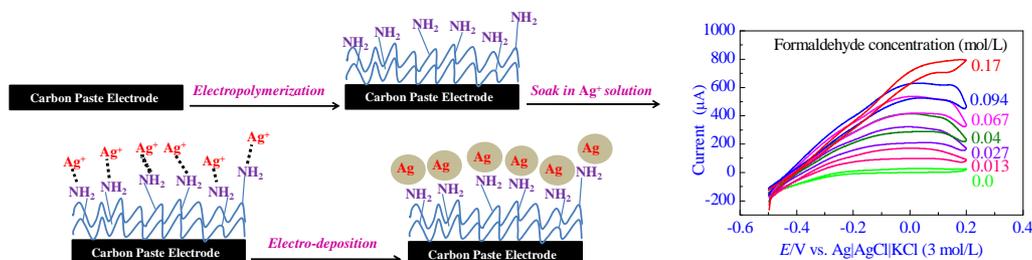


CalB was covalently immobilized on FNAB-activated nanopolystyrene to improve its stability, activity and reusability in applications such as esterification. The esterification time was significantly reduced and the yield was increased when using immobilized CalB and microwave heating.

Chin. J. Catal., 2014, 35: 1565–1570 doi: 10.1016/S1872-2067(14)60115-7

### Silver nanoparticle decorated poly(2-aminodiphenylamine) modified carbon paste electrode as a simple and efficient electrocatalyst for oxidation of formaldehyde

Reza Ojani\*, Saeid Safshekan, Jahan-Bakhsh Raouf  
University of Mazandaran, Iran

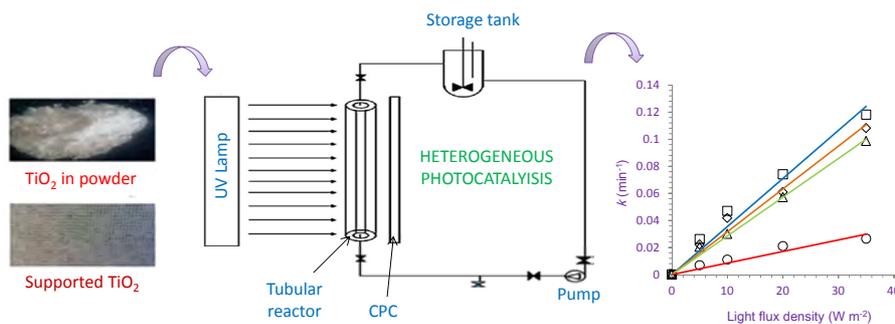


Ag nanoparticles were incorporated on poly-2ADPA modified carbon paste electrode and their electrochemical behavior in alkaline media was investigated. The Ag nanoparticles exhibited promising electrocatalytic activity for formaldehyde oxidation.

Chin. J. Catal., 2014, 35: 1571–1577 doi: 10.1016/S1872-2067(14)60125-X

### Kinetics and efficiency displayed by supported and suspended TiO<sub>2</sub> catalysts applied to the disinfection of *Escherichia coli*

Majdi Kacem\*, Gael Plantard, Nathalie Wery, Vincent Goetz  
National Center for Scientific Research, France; University of Perpignan Via Domitia, France;  
National Institute for Agricultural Research, France

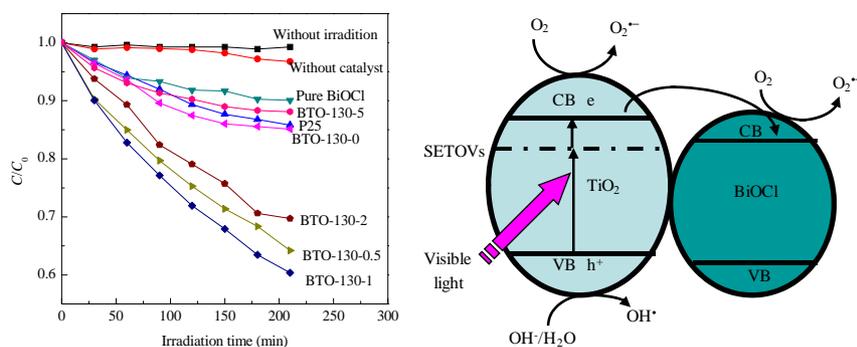


The photocatalytic inactivation of *E. coli* was investigated using different catalysts. The efficiency of a supported titanium dioxide was highlighted with comparison to suspended catalysts considered so far as references in terms of photocatalytic water disinfection.

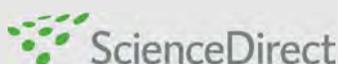
Chin. J. Catal., 2014, 35: 1578–1589 doi: 10.1016/S1872-2067(14)60124-8

### Preparation of Bi-doped TiO<sub>2</sub> nanoparticles and their visible light photocatalytic performance

Haiyan Li, Jinfeng Liu, Junjie Qian, Qiuye Li, Jianjun Yang\*  
Henan University



Bi-doped TiO<sub>2</sub> photocatalysts showed high visible light photocatalytic activity for the degradation of methyl orange and 4-chlorophenol. The high photoactivity was co-determined by single-electron-trapped oxygen vacancies (SETOVs) and the formation of a BiOCl/TiO<sub>2</sub> composite. The formation of SETOVs during the process of NTA hydrothermal treatment accounts for the visible light sensitization, while the formed BiOCl/TiO<sub>2</sub> composite improves the separation of photogenerated electrons and holes and prevents them from recombining.

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## Article

# Effect of sulfur poisoning on $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxide catalyst for soot combustion

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## ABSTRACT

$\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ , and a series of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides prepared by co-precipitation were exposed to  $\text{SO}_2$  under an oxidizing environment at 400 °C. These fresh and  $\text{SO}_2$ -poisoned samples were characterized by in situ diffuse reflectance infrared Fourier transform spectroscopy, X-ray diffraction, temperature-programmed desorption, and X-ray photoelectron spectroscopy. Sulfates were formed on the oxides, with more sulfates on  $\text{CeO}_2$  than on  $\text{Co}_3\text{O}_4$ . On the  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides, both cobalt sulphate and ceria sulfate were formed. Fresh and sulfated samples were tested for soot combustion in a  $\text{NO}/\text{O}_2$  gas flow. The  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides showed better  $\text{SO}_2$  tolerance and higher activity than  $\text{CeO}_2$  but were more easily poisoned by  $\text{SO}_2$  than  $\text{Co}_3\text{O}_4$ .

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## 1. Introduction

A diesel particulate filter is applied for the removal of soot from diesel engine exhaust. The use of an oxidation catalyst coated on the filter is the preferred way to accelerate the combustion of accumulated soot and has been widely studied. Various soot oxidation catalysts have been developed, and many metal oxides can lower the soot oxidation temperature [1–5]. Ceria-supported cobalt oxides prepared by different routes exhibited good performance for soot combustion [6–12]. Harrison et al. [6] deduced that the high catalytic activity of  $\text{Co}/\text{CeO}_2$  in soot combustion was due to the presence of cobalt in the catalyst as  $\text{Co}_3\text{O}_4$  and the redox properties of  $\text{CeO}_2$ . A spillover mechanism at the cobalt oxide-ceria interface was postulated to drive the soot oxidation. Methane oxidation experiments are sometimes performed as a test of soot oxidation

[13].  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides prepared by a co-precipitation method showed a superior activity for methane oxidation and CO oxidation and have good resistance to water vapor poisoning [13,14].

From a practical point of view, studying the effect of  $\text{SO}_2$  on  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides is of importance because  $\text{SO}_2$  is present in the exhaust gases. In the present study, a series of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxide catalysts were prepared by the co-precipitation method. The sulfation of the  $\text{Co}_3\text{O}_4/\text{CeO}_2$  catalysts was investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The soot oxidation activity of the fresh and  $\text{SO}_2$ -poisoned  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides was investigated and compared using temperature-programmed oxidation (TPO).

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## 2. Experimental

### 2.1. Catalyst preparation

$\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides with increasing  $\text{Co}_3\text{O}_4$  loading corresponding to Co/Ce atomic ratios of 0.05–5 (denoted by  $\text{Co}_0.05\text{Ce}$ ,  $\text{Co}_0.2\text{Ce}$ ,  $\text{Co}_1.0\text{Ce}$ ,  $\text{Co}_2.0\text{Ce}$ , and  $\text{Co}_5.0\text{Ce}$ ),  $\text{CeO}_2$ , and  $\text{Co}_3\text{O}_4$  were prepared by a co-precipitation method with a  $\text{K}_2\text{CO}_3$  solution (15 wt%). In a typical preparation,  $\text{K}_2\text{CO}_3$  solution was added dropwise to an aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in appropriate amounts until the pH was 9.10. The mixture solution was stirred for 1 h and was aged at room temperature for 3 h. Then the resulting precipitate was filtered and washed with distilled water until the filtrate pH was neutral. The precipitate was dried overnight at 110 °C and calcined for 2 h at 400 °C in air.

To sulfate the catalysts, 40–60 mesh catalysts were treated with 300 ppm  $\text{SO}_2$  and 10%  $\text{O}_2$  in  $\text{N}_2$  at a flow rate of 400 ml/min at 400 °C for different times. The  $\text{SO}_2$ -poisoned catalysts were denoted according to the treatment time, for instance,  $\text{Co}_1.0\text{Ce-S-10h}$  was the  $\text{Co}_1.0\text{Ce}$  catalyst sulfated at 400 °C for 10 h.

### 2.2. Catalytic activity measurements

The soot used in this work was Printex-U (Degussa), which is a model soot reported elsewhere. The catalyst-soot mixture (9:1 w/w) for the TPO reaction was obtained by careful grinding in an agate mortar for 10 min (tight contact). It is known that the contact between the soot and catalyst influences the oxidation reaction significantly [3,15]. Although the soot/catalyst contact obtained by the current mixing procedure did not reflect the actual contact conditions in a catalytic soot trap, nevertheless it permitted reproducible results under the present experimental conditions [16,17]. A catalyst-soot mixture diluted with 1.00 g quartz pellets was carefully mixed and put into the quartz tube reactor (internal diameter 6 mm). The TPO test was carried out by heating the soot/catalyst mixture from 200 to 600 °C (heating rate 2 °C/min) under a total flow rate of 100 ml/min ( $\text{NO}$  1000 ppm,  $\text{O}_2$  5%, Ar as balance).  $\text{CO}_2$  analysis was performed by GC/TCD (Porapak Q, Agilent) at intervals of

5 min.

### 2.3. Catalyst characterization

The samples were characterized by XRD using a computerized Rigaku D/max-RB diffractometer (Japan,  $\text{Cu } K\alpha$  radiation). Data were recorded in the  $2\theta$  range of 10°–90° with an angle step size of 0.02° and a scanning speed of 4°/min.

XPS analysis was performed with an EASY ESCA instrument. The spectra were excited by an Al  $K\alpha$  source (1486.6 eV), and the analyzer was operated in the constant analyzer energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. Charging of the samples was corrected for by referencing all the energy to the C 1s peak energy (set at 285.0 eV).

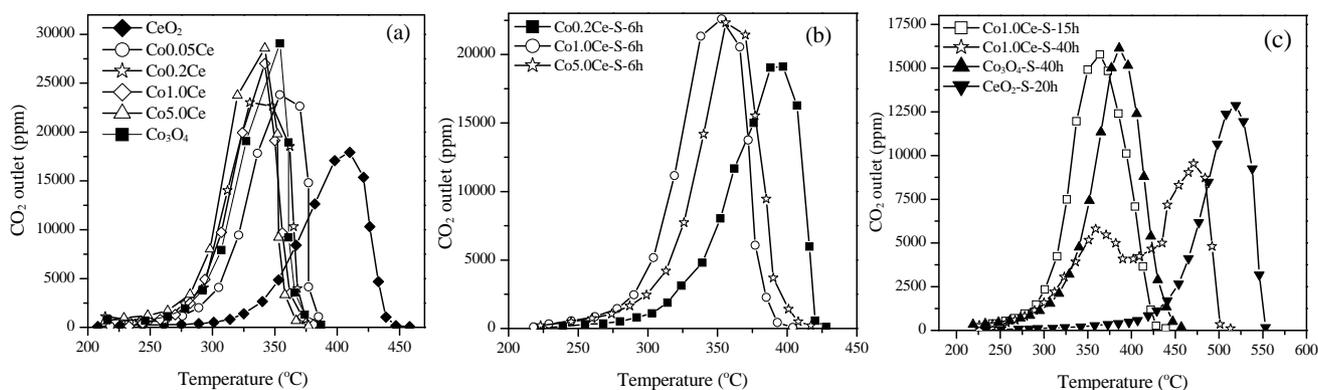
TPD was performed in a system equipped with a quadrupole mass spectrometer (Hiden HPR20). In the  $\text{SO}_2$ -TPD, the  $\text{SO}_2$ -poisoned sample was placed in a quartz tube reactor (internal diameter 4 mm). Pure He was used as the carrier, and the total flow of carrier was held at 30 ml/min with the temperature increase rate of 30 °C/min. All the samples used in the TPD experiments were the same weight of 300 mg and the same size of 40–60 mesh.

DRIFTS spectra were recorded in situ with a Nexus 670 FT-IR spectrometer (Thermo Nicolet) equipped with a diffuse reflection chamber and a high sensitivity MCT/A detector cooled by liquid nitrogen. The catalysts for the DRIFTS study was finely ground and placed in a ceramic crucible. All spectra were measured with a resolution of 4  $\text{cm}^{-1}$  and with an accumulation of 100 scans. Sulfate accumulation on test catalysts was investigated by DRIFTS in a flow of  $\text{SO}_2$  300 ppm,  $\text{O}_2$  20%, and  $\text{N}_2$  as balance for 60 min at 400 °C.

## 3. Results and discussion

### 3.1. Activity test

The TPO results of soot combustion in a  $\text{NO}/\text{O}_2$  mixture over the various  $\text{Co}_3\text{O}_4/\text{CeO}_2$  oxides, pure  $\text{CeO}_2$ , and  $\text{Co}_3\text{O}_4$  are shown in Fig. 1(a). Clearly, the presence of cobalt greatly improved the soot oxidation activity of  $\text{CeO}_2$  even at as low a content as Co/Ce = 0.05. The catalytic activity for soot combustion showed



**Fig. 1.** TPO profiles of soot-catalyst mixtures (soot:catalyst = 1:9 by weight). (a) Fresh catalysts; (b) 6 h  $\text{SO}_2$ -poisoned catalysts; (c) Various  $\text{SO}_2$ -poisoned catalysts. Reactant gas: 1000 ppm  $\text{NO}$  + 5%  $\text{O}_2$  in Ar. Heating rate: 2 °C/min.  $\text{SO}_2$  poison conditions: 300 ppm  $\text{SO}_2$  and 5%  $\text{O}_2$  in  $\text{N}_2$  at 400 °C.

little dependence on the Co/Ce ratio of the  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxide when the Co/Ce atomic ratio was higher than 0.2.  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides with Co/Ce atomic ratios ranging from 0.2 to 5.0 showed a similar activity with a maximum in the temperature range 330–350 °C. In the studies of Dhakad et al. [7] and Liu et al. [8],  $\text{Co}_3\text{O}_4\text{-CeO}_2$  oxides or  $\text{CeO}_2$  supported Co showed significantly improvement for soot combustion compared to  $\text{CeO}_2$  and  $\text{Co}_3\text{O}_4$ . There was a synergistic effect between ceria and cobalt. For studying the effect of  $\text{SO}_2$  on the activity of soot oxidation over  $\text{Co}_3\text{O}_4/\text{CeO}_2$ ,  $\text{Co}_0.2\text{Ce}$ ,  $\text{Co}_1.0\text{Ce}$ , and  $\text{Co}_5.0\text{Ce}$  were treated in a flow of a  $\text{SO}_2 + \text{O}_2$  mixture at 400 °C for 6 h. Then the TPO experiments were carried out. As seen in Fig. 1(b), the treatment by  $\text{SO}_2$  caused some loss of activity for the tested samples. The  $\text{Co}_1.0\text{Ce}$  catalyst displayed the best  $\text{SO}_2$  resistance among the three tested samples. Based on these results, the  $\text{Co}_1.0\text{Ce}$  catalyst was selected for further studies.

Figure 1(c) shows the TPO profiles of the  $\text{Co}_1.0\text{Ce}$  catalysts with different  $\text{SO}_2$  exposure time, the TPO profile for  $\text{CeO}_2$  after sulfation for 20 h and for  $\text{Co}_3\text{O}_4$  after sulfation for 40 h. The activity of the  $\text{Co}_1.0\text{Ce}$  catalyst decreased with increasing sulfur poisoning time. With increasing sulfur poisoning time, soot oxidation by the  $\text{Co}_1.0\text{Ce}$  catalyst started at a slower rate, and it was completed at a higher temperature. The TPO profile of  $\text{Co}_1.0\text{Ce-S-40h}$  consisted of a double peak, which showed better catalytic activity than  $\text{CeO}_2$  sulfated for 20 h.  $\text{Co}_3\text{O}_4$  showed the best sulfur resistance in soot oxidation under tight contact.

### 3.2. Characterization analysis

Figure 2 shows the XRD patterns of the  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Co}_1.0\text{Ce}$  catalysts (fresh, 15 h sulfated, and 40 h sulfated). All the reflections of pure cobalt oxide and pure cerium oxide were assignable to the cobalt spinel structure (JCPDS 80-1541) and fluorite oxide structure (JCPDS 34-0394), respectively. There was no other phase on the  $\text{Ce}_1.0\text{Co}$  catalysts except for these two phases. The broad  $\text{Co}_3\text{O}_4$  peaks observed in the fresh  $\text{Co}_1.0\text{Ce}$  indicated that the  $\text{Co}_3\text{O}_4$  was well dispersed on the  $\text{CeO}_2$ . The XRD patterns of the sulfated  $\text{Ce}_1.0\text{Co}$  catalysts were almost the same as the fresh sample, which indicated that no crystalline sulfate species was formed on the  $\text{Ce}_1.0\text{Co}$  catalysts

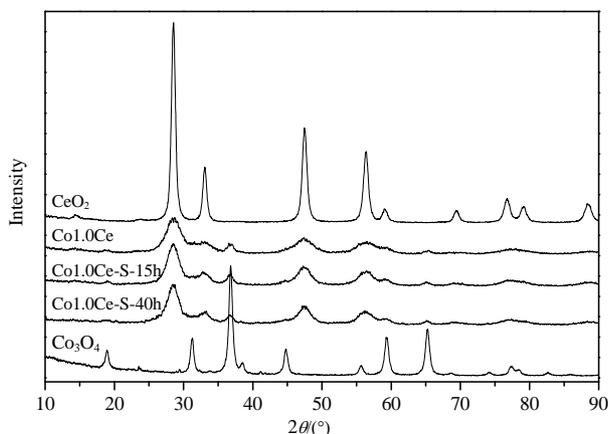


Fig. 2. XRD patterns of  $\text{CeO}_2$ ,  $\text{Co}_1.0\text{Ce}$ ,  $\text{Co}_1.0\text{Ce-S-15h}$ ,  $\text{Co}_1.0\text{Ce-S-40h}$ , and  $\text{Co}_3\text{O}_4$ .

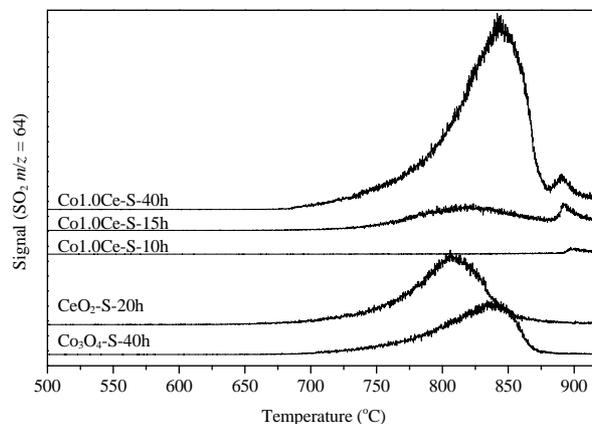


Fig. 3.  $\text{SO}_2$  TPD results using a He carrier gas for the various samples.

from the sulfation.

The  $\text{SO}_2$ -TPD results of the sulfated samples are illustrated in Fig. 3. These showed that the decomposition of the sulfate species to  $\text{SO}_2$  was at 800 °C for  $\text{CeO}_2\text{-S-20h}$  and at 840 °C for  $\text{Co}_3\text{O}_4\text{-S-40h}$ . The TPD curves of  $\text{Ce}_1.0\text{Co-S-15h}$  and  $\text{Ce}_1.0\text{Co-S-40h}$  showed two  $\text{SO}_2$  desorption peaks: a large low-temperature peak at 845 °C and a minor high-temperature peak at 890 °C. In addition, the low-temperature desorption peaks increased significantly with increased  $\text{SO}_2$  treatment time, while the high-temperature peaks were independent of  $\text{SO}_2$  treatment time. More interestingly, the  $\text{Ce}_1.0\text{Co-S-10h}$  sample only showed the high-temperature peak at around 890 °C. It has been reported that sulfation of the  $\text{CeO}_2$  resulted in both surface and bulk sulfates [18,19]. After exposure to 1%  $\text{SO}_2$  in excess  $\text{O}_2$  at 400 °C, the TPD in He of  $\text{Pd/CeO}_2$  gave a  $\text{SO}_2$  peak at 750 °C assigned to  $\text{Ce}^{4+}$  sulfate, and the peak of the decomposition of  $\text{Ce}^{3+}$  sulfate to  $\text{SO}_2$  was at a higher temperature of 850 °C [18]. Only one peak of  $\text{SO}_2$  decomposition on  $\text{CeO}_2$  was observed at 800 °C here. In this study, the exposure of the samples to  $\text{SO}_2$  in excess  $\text{O}_2$  at 400 °C was carried out for a long time (up to 40 h). It has been shown that the stable sulfate formed at 400 °C in the presence of excess  $\text{O}_2$  is  $\text{Ce}_2(\text{SO}_4)_3$  and not  $\text{Ce}(\text{SO}_4)_2$  [18,19]. This suggested that the high intensity peak at 840 °C observed for  $\text{Co}_1.0\text{Ce-S-15h}$  and  $\text{Co}_1.0\text{Ce-S-40h}$  should be associated with  $\text{Ce}^{3+}$  sulfate. The small sulfate decomposition peaks at 890 °C observed in the  $\text{Co}_1.0\text{Ce-S-10h}$ ,  $\text{Co}_1.0\text{Ce-S-15h}$ , and  $\text{Co}_1.0\text{Ce-S-40h}$  were associated with the same sulfate species, and the amount of  $\text{SO}_2$  from the decomposition at 890 °C was the same for  $\text{Co}_1.0\text{Ce-S-15h}$  and  $\text{Co}_1.0\text{Ce-S-40h}$ .

The interaction of  $\text{SO}_2$  with the chosen  $\text{Co}_1.0\text{Ce}$  catalyst was also studied by XPS. In Fig. 4, the experimental and fitted  $\text{Ce } 3d$  spectra of fresh  $\text{Ce}_1.0\text{Co}$  and  $\text{Co}_1.0\text{Ce-S-40h}$  are shown. The spectra in the  $\text{Ce } 3d$  region were fitted with eight peaks corresponding to four pairs of spin-orbit doublets [19]. The labeling of the peaks followed the convention adopted by Teterin et al. [20]. According to the literature [13,19,20], three pairs of peaks ( $V$ ,  $U$ ;  $V''$ ,  $U''$ ;  $V'''$ ,  $U'''$ ) are the characteristic of the  $\text{Ce}^{4+}$  oxidation state while the couple ( $V'$ ,  $U'$ ) corresponds to  $\text{Ce}^{3+}$  ions. An obvious increase in the intensity of the couple ( $V'$ ,  $U'$ ) peaks was observed in the  $\text{Ce } 3d$  spectra of  $\text{Co}_1.0\text{Ce-S-40h}$ , which suggested that  $\text{Ce}^{3+}$  species on the  $\text{Co}_1.0\text{Ce}$  catalyst increased

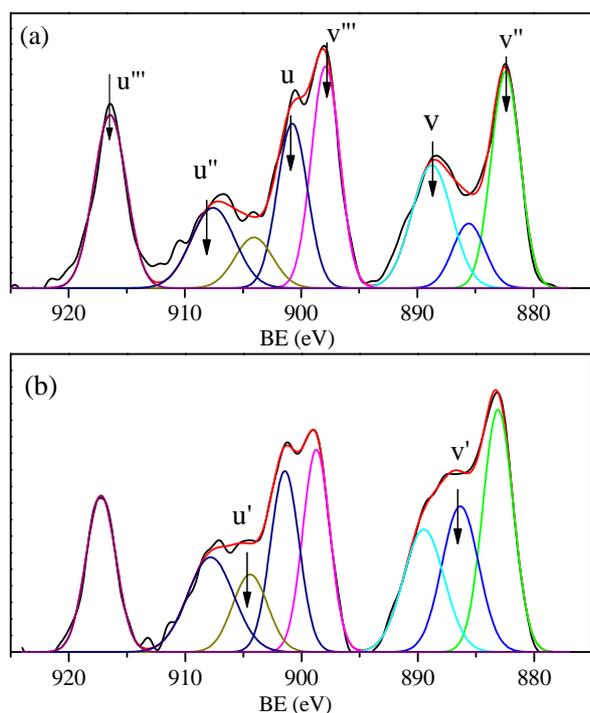


Fig. 4. Experimental and fitted Ce 3d XPS spectra for Co1.0Ce (a) and Co1.0Ce-S-40h (b).

during the reaction with SO<sub>2</sub> in an excess of O<sub>2</sub>. This indicated that during the sulfation of Co1.0Ce at 400 °C, Ce<sup>4+</sup> ions were gradually reduced to Ce<sup>3+</sup>. This result was in accordance with those reported by Smirnov et al. [19]. The atomic ratio Ce<sup>3+</sup>/(Ce<sup>4+</sup>+Ce<sup>3+</sup>) was estimated from the ratio of the intensity of V' and U' components to the total intensity of the entire Ce 3d curve [19]. The calculation showed that the fraction of Ce<sup>3+</sup> ions in the fresh Co1.0Ce and Co1.0Ce-S-40h was 14% and

22%, respectively. This suggested 8% increase in Ce<sup>3+</sup> species of Co1.0Ce related to the 40 h exposure to SO<sub>2</sub> in excess O<sub>2</sub>.

Figure 5 illustrates the experimental XPS spectra of the Co 2p<sub>3/2</sub>, O 1s, and S 2p regions for fresh Co1.0Ce and Co1.0Ce-S-40h. The Co 2p<sub>3/2</sub> peak binding energy (BE) for Co1.0Ce appeared at 781.2 eV, in agreement with the reference data [13,14,21]. There was no change in the BE for Co 2p<sub>3/2</sub> of Co1.0Ce-S-40h, which was observed at 781.1 eV. A high intensity S 2p feature appeared from Co1.0Ce-S-40h at 169.2 eV and can be assigned to cerium sulfate species [19]. The O 1s feature recorded from fresh Ce1.0Co was at 529.6 eV while that from Co1.0Ce-S-40h was sifted to a higher BE (~532 eV) and had increased intensity. The oxygen in the large amount of sulfate species caused the shift and increased intensity of the O 1s BE and peak.

Figure 6 shows the DRIFTS spectra with time of CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and Co1.0Ce after exposure to a flow of SO<sub>2</sub>+O<sub>2</sub> at 400 °C. Several bands in the 1400–900 cm<sup>-1</sup> region appeared after the exposure to the SO<sub>2</sub>+O<sub>2</sub> gas. The broad band at 1130 cm<sup>-1</sup> with the highest intensity was due to the sulfates in the bulk [22,23]. The small bands at 1334 cm<sup>-1</sup> can be assigned to surface sulfate. The species responsible for the peak at 1001 cm<sup>-1</sup> (970 cm<sup>-1</sup> in the spectrum from Co<sub>3</sub>O<sub>4</sub>) can be assigned to sulfites [22].

From the comparison of the changes of the DRIFTS spectra of CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and Co1.0Ce with time, it was deduced that both cobalt sulfate and ceria sulfate were formed during the exposure of the catalysts to the SO<sub>2</sub>+O<sub>2</sub> flow. The spectra recorded from CeO<sub>2</sub> with time were essentially identical (Fig. 6(a)). The shift of the band at 1100 cm<sup>-1</sup> to higher vibration was caused by the accumulation of sulfate species. This strong and broad band at 1138 cm<sup>-1</sup> was due to the formation of bulk Ce(SO<sub>4</sub>)<sub>2</sub> [23,24]. The IR bands from Co1.0Ce are shown in Fig. 6(b). Surface and bulk sulfates species, which were attributed to

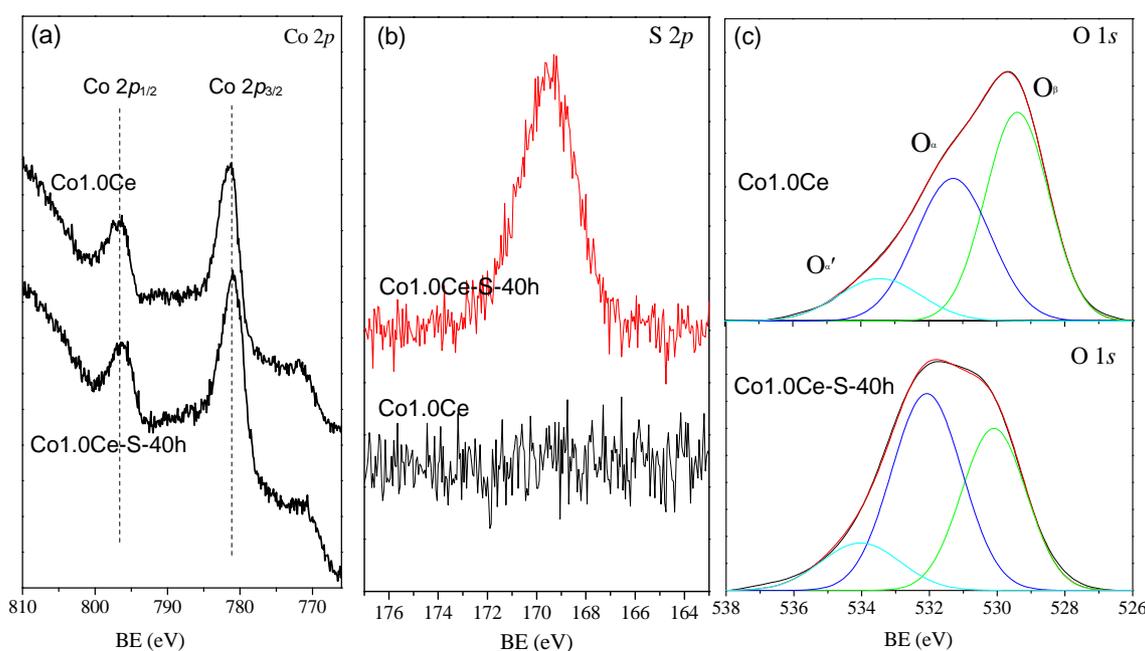


Fig. 5. Experimental and fitted XPS spectra for fresh Co1.0Ce and Co1.0Ce-S-40h. (a) Co 2p; (b) S 2p; (c) O 1s.

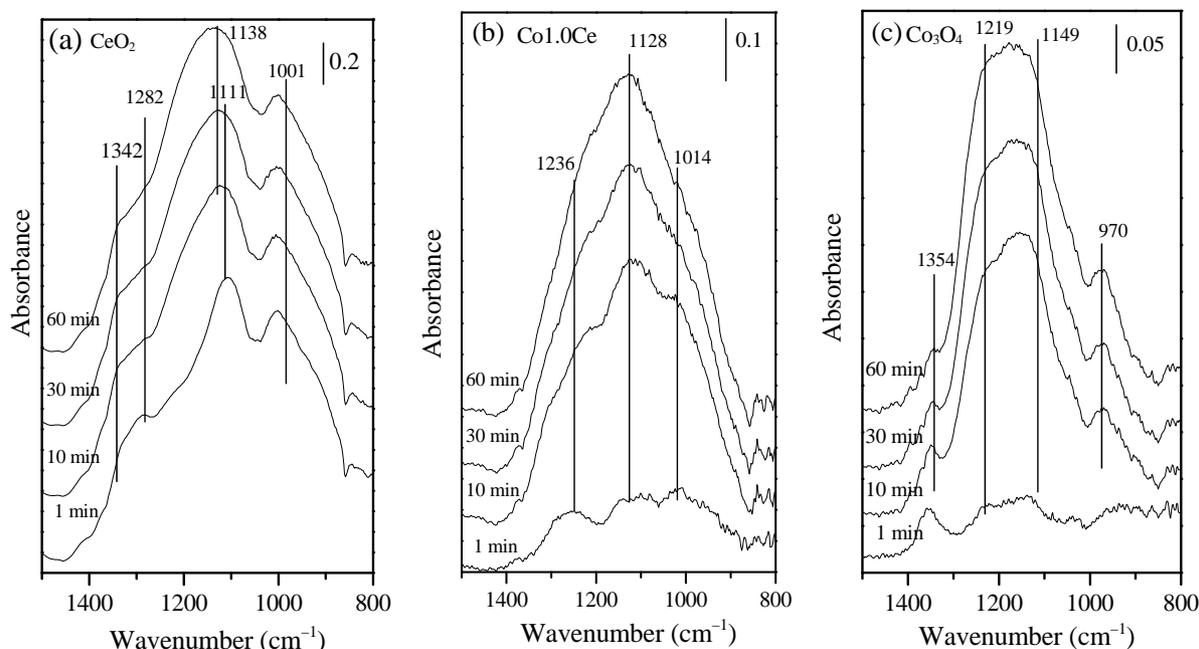


Fig. 6. DRIFTS spectra with time of the different catalysts at 400 °C in a flow of  $\text{SO}_2+\text{O}_2$ . (a)  $\text{CeO}_2$ ; (b)  $\text{Co}_{1.0}\text{Ce}$ ; (c)  $\text{Co}_3\text{O}_4$ .

1400–1340 and 1200–1100  $\text{cm}^{-1}$  range, were formed and increased with increasing sulfur exposure time [21].

### 3.3. Discussion

Soot catalytic oxidation has different mechanisms. The mechanism that dominates depends on the contact between the catalyst and soot. The preparation procedure of the catalyst and soot mixture in this study produced the contact that is essentially “tight contact” [1–3]. In the  $\text{NO}_x$ -assisted soot oxidation reaction over  $\text{CeO}_2$ , ‘active oxygen’ generated from both nitrate and surface oxygen decomposition plays an important role in the acceleration of soot oxidation [4]. A redox mechanism assisted by oxygen spillover on  $\text{CeO}_2$  occurs in the  $\text{Co}/\text{CeO}_2$  catalyzed reaction of soot in a  $\text{NO}/\text{O}_2$  mixture [6]. In the literature [4,6,7,8,25], a redox mechanism on Co sites and a spillover mechanism from Ce sites were proposed for the activity of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides in soot oxidation. The redox properties and the active oxygen generated from surface nitrate decomposition were proposed to be important factors for soot combustion in a  $\text{NO}/\text{O}_2$  mixture. The redox mechanism would be the dominant mechanism for soot oxidation activity in the contact type used in this work. The slight difference in soot combustion activity between the  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides with different Co/Ce ratios (Co/Ce > 0.2) can be understood with this mechanism.

Sulfur exposure significantly decreased the activity of  $\text{CeO}_2$  for soot combustion. The temperature of the TPO maximum for fresh  $\text{CeO}_2$  was 410 °C and for  $\text{CeO}_2\text{-S-20h}$  was 525 °C. Peralta et al. [26] reported that the temperature of the TPO maximum increased from 523 to 558 °C in loose contact after 31 h  $\text{SO}_2$  treatment. This suggested that the effect of sulfur exposure on catalytic activity was more significant for tight contact than for

loose contact, which suggested that the sulfur exposure mainly influenced the redox property of  $\text{CeO}_2$ , which was important for soot combustion in tight contact.

A significant sulfur tolerance was observed with  $\text{Co}_3\text{O}_4/\text{CeO}_2$  compared to  $\text{CeO}_2$ . The TPO maximum for  $\text{Co}_{1.0}\text{Ce}$  was increased from 340 to 370 °C. A continuous decrease in activity of  $\text{Co}_{1.0}\text{Ce}$  was observed with the increase in exposure time. Sulfate accumulation on  $\text{Co}_{1.0}\text{Ce}$  increased with increasing  $\text{SO}_2$  treatment time according to the  $\text{SO}_2$ -TPD profiles (Fig. 4). The FTIR spectra suggested that both cerium sulfate ( $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ ) and cobalt sulfate species were formed on  $\text{Co}_{1.0}\text{Ce}$  after exposure to the  $\text{SO}_2+\text{O}_2$  gas flow at 400 °C. For  $\text{CeO}_2$ , bulk sulfate  $\text{Ce}(\text{SO}_4)_2$  was largely formed by exposure to  $\text{SO}_2+\text{O}_2$  at 400 °C [19,24].  $\text{Ce}_2(\text{SO}_4)_3$  was the only stable sulfate under the current sulfur exposure condition [18]. The formation of sulfate species on ceria was generally accompanied by the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  [19]. The sulfation of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  ( $\text{Co}_{1.0}\text{Ce}$ ) showed similar results to that of  $\text{CeO}_2$ . A significant increase of  $\text{Ce}^{3+}$  in  $\text{Co}_3\text{O}_4/\text{CeO}_2$  was shown by the XPS results. A long exposure time to  $\text{SO}_2 + \text{O}_2$  showed no effect on the electronic state of the cobalt according to the XPS results. Liotta et al. [21] also found that the Co 2p spectrum did not change upon sulfur poisoning when they studied the  $\text{SO}_2$  effect on  $\text{Pd}/\text{Co}_3\text{O}_4$  catalysts for  $\text{CH}_4$  oxidation. This suggested that  $\text{Co}_3\text{O}_4\cdot\text{SO}_3$  was the dominant sulfate formed on  $\text{Co}_3\text{O}_4$  [21]. The double peak in the TPO profile of  $\text{Co}_{1.0}\text{Ce-S-40h}$  can be attributed to the activity of  $\text{Co}_3\text{O}_4$  in the catalyst.

## 4. Conclusions

The exposure of  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides to  $\text{SO}_2$  under oxidizing conditions at 400 °C resulted in the formation of sulfate. The decomposition of cerium sulfate

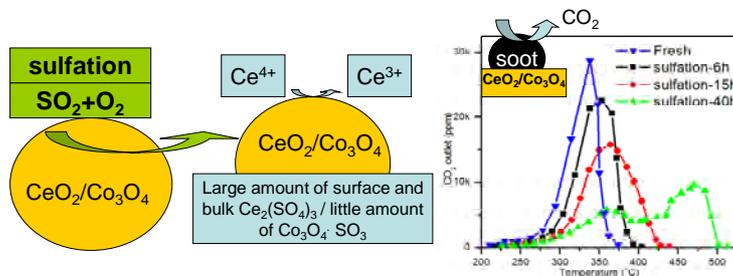
## Graphical Abstract

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Effect of sulfur poisoning on  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxide catalyst for soot combustion

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$\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides showed better  $\text{SO}_2$  tolerance and higher activity than  $\text{CeO}_2$  but was more easily poisoned by  $\text{SO}_2$  than  $\text{Co}_3\text{O}_4$  during soot combustion in  $\text{NO}/\text{O}_2$ .

occurred at a lower temperature than cobalt sulfate. Both cobalt sulfate and ceria sulfate were formed on  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides during  $\text{SO}_2$  exposure.  $\text{Ce}^{4+}$  was gradually reduced to  $\text{Ce}^{3+}$  during the sulfation process. Bulk sulfate was formed on  $\text{CeO}_2$ , and the cobalt sulfate mainly existed as  $\text{Co}_3\text{O}_4 \cdot \text{SO}_3$ .

A series of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides prepared by co-precipitation showed better catalytic activity for soot combustion in tight contact than  $\text{CeO}_2$ . Sulfur poisoning resulted in a decrease in activity of the  $\text{Co}_3\text{O}_4/\text{CeO}_2$  composite oxides,  $\text{CeO}_2$ , and  $\text{Co}_3\text{O}_4$ . The sulfur tolerance of  $\text{Co}_3\text{O}_4/\text{CeO}_2$  was higher than  $\text{CeO}_2$  but lower than  $\text{Co}_3\text{O}_4$ .

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硫中毒对 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物上炭黑催化燃烧的影响

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摘要: 采用共沉淀法制备了 $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ 和一系列 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物催化剂, 在 $400^\circ\text{C}$ 下含 $\text{SO}_2$ 的氧化气氛中对催化剂进行了

硫中毒处理, 通过原位红外光谱、X射线衍射、程序升温脱附和X射线光电子能谱对新鲜和硫中毒的样品进行了表征. 结果表明, 所有测试的硫中毒样品上均形成了硫酸盐,  $\text{CeO}_2$ 上累积的硫酸盐明显比 $\text{Co}_3\text{O}_4$ 上的多,  $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物在硫中毒过程中形成了硫酸钴和硫酸铈. 对新鲜和硫化样品在 $\text{NO}/\text{O}_2$ 气氛下进行了催化炭黑燃烧实验, 发现 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物的活性和抗硫性能优于 $\text{CeO}_2$ , 但抗硫性能低于 $\text{Co}_3\text{O}_4$ .

**关键词:** 炭黑氧化; 氧化钴; 氧化铈; 复合氧化物; 硫中毒

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