

## THE EFFECTS OF RARE EARTHS ON ACTIVITY AND SURFACE PROPERTIES OF Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CATALYST FOR WATER GAS SHIFT REACTION

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**ABSTRACT.** A series of Ru-RE/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (RE = Ce, Pr, La, Sm, Tb or Gd) and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnation method. The influence of rare earths on the catalytic performance of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the water gas shift reaction was studied. The catalysts were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD), and CO chemisorption. The results show that the addition of rare earths increases the catalytic activity of Ru based catalyst. Among these cerium is the most remarkably. The addition of cerium increases the active surface area, improves the dispersion of ruthenium, and weakens the interaction between ruthenium and the support. Cerium also affects the adsorption and reduction properties of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

**KEY WORDS:** Rare earths, Ruthenium-based catalyst, Water gas shift reaction

### INTRODUCTION

The water gas shift reaction (WGS) is one of basic processes in the chemical fertilizer industry and the key step in H<sub>2</sub> production by reforming of hydrocarbons for fuel cells. The conventional iron-chromium WGS catalysts do not work well at low steam-to-gas ratios and hence its application is restricted [1, 2]. Meanwhile the copper- and manganese-based catalysts have a good performance on activity at low steam-to-gas ratios [3, 4], but the copper catalysts are easily sintered and the manganese catalysts are not easily produced. Noble metal catalysts, relatively, possess high activity and good thermal stability [5-9]. This paper describes the synthesis and characterization of a series of Ru-based catalysts modified by rare earths (RE).

### EXPERIMENTAL

#### *Preparation of (RE)(NO<sub>3</sub>)<sub>3</sub>.*

Calculated amounts of La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>2</sub>O<sub>3</sub>, Tb<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub> (supplied by the Institute of Rare Earths, Nanchang University, China) were added to concentrated nitric acid. Then H<sub>2</sub>O<sub>2</sub> was added slowly to the hot suspension until the rare earth oxide was fully dissolved.

#### *Preparation of the catalyst*

Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation method.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (2 g, surface area 167 m<sup>2</sup>·g<sup>-1</sup>), calcined in air at 773 K for 2 h, was impregnated by the required amount of a 0.10 M aqueous solution of RuCl<sub>3</sub> for 24 h. The catalyst was dried at 383 K for 2 h, and calcined at 773 K for 4 h afterward.

Ru-RE/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by stepwise impregnation. Firstly,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder was impregnated by the calculated amount of 0.14 M RE(NO<sub>3</sub>)<sub>3</sub> solution, and the samples were

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dried at 383 K and calcined at 773 K for 4 h. Then the RE/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with 0.10 M RuCl<sub>3</sub> solution, dried at 383 K and calcined at 773 K.

RE-Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were impregnated in the reversed order. Other steps are the same as the preparation of Ru-RE/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

In all cases the Ru loading was 1.0 mol %, and the RE loading 1.4 mol %.

### *Measurement of catalytic activity*

Measurement of catalytic activity was carried out in a flow microcatalytic reactor. Catalyst loading was 0.6 g. The samples were heated from room temperature to 673 K at a rate of 5 K·min<sup>-1</sup> and then reduced at 673 K for 2 h in a flow of H<sub>2</sub> (50 mL·min<sup>-1</sup>). After that a gaseous mixture of steam and CO was fed to the catalyst bed. The activities of the catalysts were evaluated under the following condition: reaction temperatures 473-773 K, pressure 1.62 x 10<sup>5</sup> Pa, gas hourly space velocity (GHSV) 2000 h<sup>-1</sup>, ratio of steam to CO 0.75:1. The reaction products were analyzed by on-line gas chromatography equipped with a thermal conductivity detector and a TDX-01 column. The activities of the catalysts were expressed by CO conversion.

### *Characterization*

CO chemisorption is an efficient method for the determination of active surface areas, which is calculated using the following formula.

$$S = \frac{V_0 N A_m}{W_{cat} \times 22.4 \times 10^8} (\text{m}^2 \text{g}^{-1})$$

where  $V_0$  is the total adsorption volume of CO (mL) under standard condition,  $A_m$  the effective cross section of a CO molecule (13 x 10<sup>-16</sup> cm<sup>2</sup>),  $N$  the Avogadro constant, and  $W_{cat}$  the weight of catalyst (g).

X-ray diffraction (XRD) patterns of the samples were recorded with a scanning speed of 4°·min<sup>-1</sup> on a D-Max-3B diffractometer using Cu K $\alpha$  radiation at 40 kV and 40 mA.

Temperature-programmed reduction (TPR) analysis of the catalyst was carried out in a conventional TPR reactor with the catalysts of 0.1 g. The samples were heated from room temperature to 673 K at a rate of 10 K·min<sup>-1</sup> in Ar (40 mL·min<sup>-1</sup>) to remove adsorbed water and solvents. After being cooled down to room temperature under Ar, 10 % hydrogen in nitrogen was introduced and temperature of the reactor was increased from room temperature to 673 K at a rate of 10 K·min<sup>-1</sup>. The water produced by the reduction was trapped by a 5 Å molecular sieve. The rate of hydrogen consumption was measured by a TCD.

For temperature-programmed desorption, the samples of 0.1 g were reduced at 673 K for 2 h in H<sub>2</sub> (50 mL·min<sup>-1</sup>), then heated to 873 K at a rate of 8 K·min<sup>-1</sup> in N<sub>2</sub> (40 mL·min<sup>-1</sup>), and cooled down to the room temperature. Water (1  $\mu$ L, each time) was injected into the reactor until the catalysts adsorption be saturated. Finally the catalysts were heated from room temperature to 873 K at a rate of 8 K·min<sup>-1</sup>.

The number of active atoms and the degree of dispersion were shown as in reference [10].

## RESULTS AND DISCUSSION

*Effects of rare earths on the activity of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst*

Table 1 shows that in all case the presence of rare earths in Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst increases activities for WGS. The increasing extend, however, are discrepant with different rare earths in Ru-RE/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The activity was found in the following order: Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ru-Pr/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ru-La/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = Ru-Sm/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ru-Tb/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ru-Gd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Table 1. Effects of rare earths on catalytic activity of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Catalysts	CO conversion (%)						
	473 K	523 K	573 K	623 K	673 K	723 K	773 K
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	—	4.37	14.29	16.18	13.79	10.03	7.90
Ru-La/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.10	8.98	18.50	26.80	26.13	24.23	20.17
Ru-Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.31	9.34	19.79	38.10	37.70	37.40	34.31
Ru-Pr/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.23	9.30	19.98	37.18	36.98	35.10	31.31
Ru-Tb/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.63	8.34	16.16	23.13	21.32	18.89	16.10
Ru-Sm/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.13	9.13	18.50	26.76	26.01	25.99	20.59
Ru-Gd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.45	8.10	15.34	19.96	19.10	18.23	17.93

All the activity are influenced by temperature and increased with temperature raised from 473 to 623 K, but the conversion of CO dropped slightly when the reaction temperature was over 623 K. Because the shift reaction is exothermic, lower temperatures favour high CO conversion [6]. Compared to activities of the catalysts at 623 K, activities of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Pr/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at 773 K declined to 51.2 %, 10 % and 15.8 %, respectively. Addition of rare earth also enhances the stability of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and cerium achieves the best effects on both activity and stability.

The catalytic activities of the catalysts are associated with the difference of the ionization potentials between rare earths and ruthenium (Table 2). The greater the difference in ionization potential the better the activities. In the course of reduction, a part of RE<sup>n+</sup> ( $n = 3$  or 4) which migrated to the Ru surface are reduced to RE<sup>m+</sup> ( $m < 3$  or 4), 4d vacant levels of ruthenium atoms can simultaneously accept electrons [9], which causes the increase of the electronic density of ruthenium atom. The increase of the electron density promotes the dissociation of water and strengthens the interaction between water and adsorbed CO [11], both advantageous to WGS.

Table 2. The ionization potential ( $\Phi$ ) of RE and Ru.

Elements	$\Phi$ (eV)	$\Phi_{RE} - \Phi_{Ru}$ (eV)
Ru	7.37	0.00
La	5.58	-1.79
Ce	5.47	-1.90
Pr	5.42	-1.95
Tb	5.85	-1.52
Sm	5.63	-1.74
Gd	6.14	-1.23

*Effects of impregnation order and cerium contents on catalytic activity*

The activity of the ruthenium catalysts is also related to the metal dispersion and interaction between metal and support. Figure 1 shows that the activity of Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is higher than that of Ce-Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. For RuO<sub>2</sub>-CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was firstly impregnated with CeO<sub>2</sub>. It weakens the interaction of ruthenium and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, probably promotes dispersion of Ru particles and restrains the aggregation of Ru particles at high calcination temperatures [7]. Table 3 indicates that the addition of CeO<sub>2</sub> increases the number of active Ru atoms from  $2.44 \times 10^{19}$  to  $3.48 \times 10^{19}$  per g of catalyst, and the dispersion of Ru particles from 41 % to 58 %, as well. In Ce-Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, cerium may displace ruthenium from active sites.

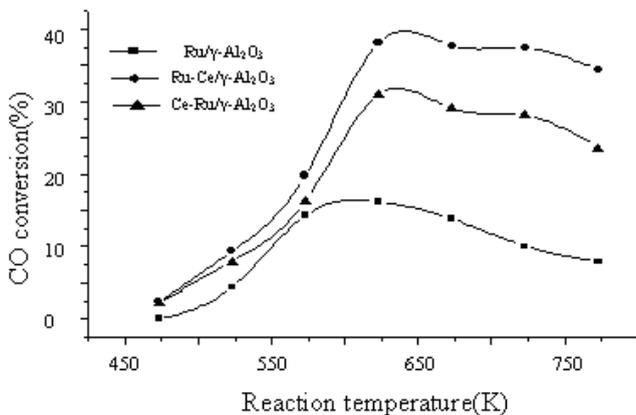


Figure 1. Effects of impregnation order on activities of the catalysts.

Table 3. The surface performance of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

Catalysts	Active surface area (m <sup>2</sup> g <sup>-1</sup> )	Active atom number <sup>a</sup>	Dispersion degree (%)
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.18	$2.44 \times 10^{19}$	41.0
Ru-Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	3.10	$3.48 \times 10^{19}$	58.5
Ce-Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	3.01	$3.37 \times 10^{19}$	56.6

<sup>a</sup>From CO adsorption.

Figure 2 presents the effects of cerium content on the activities of Ru-Ce/ $\gamma$ -Al<sub>2</sub>O catalysts. Addition of cerium increases the catalytic activity and the effect is maximum at 1.4 mol %. Under the condition of higher loadings, crystalline particles of cerium oxide occupy active sites and reduce the surface area (Table 4).

The XRD diffraction peaks of RuO<sub>2</sub> and CeO<sub>2</sub> was not observed in Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (Figure 3.), which indicates that RuO<sub>2</sub> and CeO<sub>2</sub> are highly dispersed on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier [12].

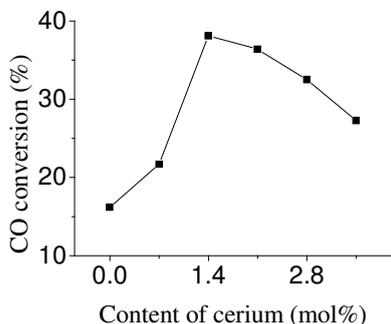


Figure 2. Effects of content of cerium on the activity of Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

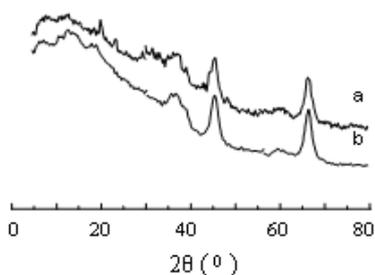


Figure 3. The XRD patterns of catalysts a: Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> b: Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Table 4. Effects of cerium contents on the performance of Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

Cerium contents (mol %)	Active surface area (m <sup>2</sup> g <sup>-1</sup> )	Active atom number	Dispersion degree (%)
0	2.18	$2.44 \times 10^{19}$	41.0
0.7	2.40	$2.70 \times 10^{19}$	45.3
1.4	3.10	$3.48 \times 10^{19}$	58.5
2.1	2.85	$3.21 \times 10^{19}$	53.7
2.8	2.73	$3.08 \times 10^{19}$	51.8
3.5	2.54	$2.90 \times 10^{19}$	48.3

#### Effects of cerium on surface properties of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The TPR profiles of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Figure 4. The TPR curves of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst shows one peak at 587 K whereas the reduction of bulk RuO<sub>2</sub> displays only one peak at about 490 K [13]. H<sub>2</sub>-consuming peaks at about 753 K and 913 K can be related to the reduction of surface and lattice oxygen of CeO<sub>2</sub>, respectively. [14]. The peaks at 510 and 602 K in the TPR curve of the Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be attributed to reduction of RuO<sub>2</sub> and CeO<sub>2</sub>. Reduction of RuO<sub>2</sub> in Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> occurs at lower temperature than that in Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, showing that the addition of CeO<sub>2</sub> decreases the interaction between the ruthenium and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The presence of ruthenium also promotes the reduction of CeO<sub>2</sub>, therefore the peaks of CeO<sub>2</sub> are shifted to lower temperature.

The desorptions of dissociative, coordinated, hydrogen-bonded and physically adsorbed water are given in previous work as at > 573 K, 473-573 K, 373-473 K and 373 K, respectively [15]. Figure 5 shows that there are four forms of dissociative, coordinated and hydrogen-bonded desorption on the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Because the samples were dried at 383 K before the TPD experiments, so that physical desorption can be excluded. The addition of cerium causes the temperature of the H<sub>2</sub>O desorption peak shift to higher temperature. The higher the temperature of H<sub>2</sub>O desorption is, the stronger the Ru-OH<sub>2</sub> bond at the surface of the catalysts and the greater the dissociation of H<sub>2</sub>O become. The shift reaction needs the dissociative of adsorption H<sub>2</sub>O to break OH-H and O-H bonds. Therefore the increase of the adsorbing intensity of H<sub>2</sub>O is associated with greater catalytic activity.

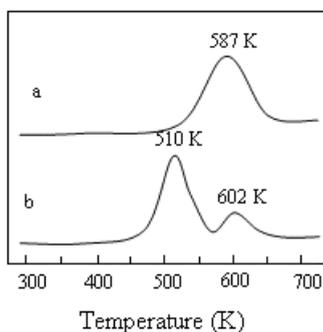


Figure 4. The TPR profiles of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, a: Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and b: Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

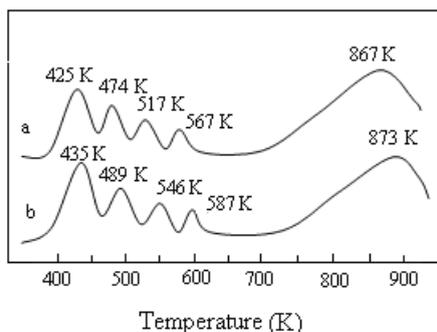


Figure 5. The TPD profiles of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, a: Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and b: Ru-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## CONCLUSIONS

This study showed that the catalytic activity of a Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be improved by the addition of rare earths (Ce, Pr, La, Sm, Tb or Gd) and of which modification effect of cerium is the best. The addition of cerium increases the active surface area and the dispersion of ruthenium, and impairs the interaction between ruthenium and the support. Cerium also has effect on the adsorption and reduction properties of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Consequently it can be understood that cerium acts as both electrical and morphological promoter.

## REFERENCES

1. Kappen, P.; Grunwaldt, J.D.; Hammershøi, B.S.; Tröger, L.; Clausen, B.S. *J. Catal.* **2001**, *198*, 56.
2. Costa, J.L.R., Marchetti, G.S.; Rangel, M.C. *Catal. Today* **2002**, *77*, 205.
3. Tanaka, Y.; Utaka, T.; Kikuchi, R.; Takeguchi, T.; Sasaki, K.; Eguchi, K. *J. Catal.* **2003**, *215*, 271.

4. Marban, G.B.; Fuertes, A. *Appl. Catal. B.* **2005**, 57, 43.
5. Utaka, T.; Okanishi, T.; Takeguchi, T.; Kikuchi R.; Eguchi, K. *Appl. Catal. A.* **2003**, 245, 343.
6. Zerva, C.; Philippopoulos, C.J. *Appl. Catal. B.* **2006**, 67, 105.
7. Yang, S.X.; Feng, Y.J.; Wan, J.F.; Zhu, W.P.; Jiang, Z.P. *Appl. Surf. Sci.* **2005**, 246, 222.
8. Luukkanen, S.; Homanen, P.; Haukka, M.; Pakkanen, T.A.; Deronzier, A. *Appl. Catal. A* **1999**, 185, 157.
9. Hua, N.P.; Wang, H.T.; Du, Y.K.; Shen, M.; Yang, P. *Catal. Commun.* **2005**, 6, 491.
10. Gaspar, A.B.; Dieguez, L.C. *Appl. Catal. A.* **2000**, 201, 241.
11. Jaktetchai, O.; Nakajima, T. *J. Mol. Struct. (Theochem)* **2002**, 619, 51.
12. Luo, L.T.; Guo, J.J.; Gu, Zh.H. *Chin. Environ. Chem.* **2004**, 23, 366.
13. Betancourt, P.; Rives, A.; Hubaut, R.; Scott, C.E.; Goldwasser J. *Appl. Catal. A.* **1998**, 170, 307.
14. Wang, J.A.; Chen, L.F.; Li, Ch.L. *J. Mol. Catal. A* **1999**, 139, 315.
15. Luo, L.T.; Li, K.; Li, F.Y. *Chin. Rare Earths* **1997**, 18, 45.