Catal Lett (2008) 124:318–323
DOI 10.1007/s10562-008-9463-z

Study of the Redox Properties of Noble Metal/Co_3O_4 by Electrical Conductivity Measurements

Hongmin Duan · Dongyan Xu · Wenzhao Li · Hengyong Xu

Received: 25 January 2008 / Accepted: 7 March 2008

Abstract The noble metal (Ru, Rh, Pd, Pt)/Co_3O_4 system was studied by electrical conductivity measurements combined with temperature-programmed reduction (TPR). The results indicate that noble metals decrease the activation energy of Co_3O_4 and improve the reduction of Co_3O_4 due to hydrogen spillover. The promotional effect of Pt on the reduction of Co_3O_4 is most significant among the examined noble metals. By the electrical conductivity study of the unpromoted and the Pt promoted Co_3O_4 samples in oxygen and syngas, it can be drawn that the addition of the noble metal Pt can facilitate the oxidation of Co and the re-reduction of the cobalt oxides.

Keywords Electrical conductivity · Co_3O_4 · Noble metal · Reduction · Hydrogen spillover

1 Introduction

Noble metals, such as ruthenium, platinum and rhenium, represent a kind of important promoters which are often employed on cobalt-based Fischer-Tropsch synthesis catalysts. The addition of small amounts of noble metals can decrease the reduction temperature of cobalt species [1–6]. It was found that the addition of Ru and Pt decreased the reduction temperature of both the first peak and the second peak in the TPR profiles; however, the addition of Re mainly decreased the reduction temperature of the second peak in the TPR profiles because Re is reduced at a higher temperature than Ru or Pt [2, 4]. Furthermore, the addition of noble metals can increase the number of Co^0 active sites by promoting the reduction of cobalt oxides, and thus increase the Fischer-Tropsch synthesis activity of cobalt-based catalysts [1, 3, 7–13]. Hydrogen spillover from noble metal to cobalt particles is considered to be one reason for improving the reduction of cobalt oxides [1, 2, 5, 7, 8].

Electrical conductivity measurements are a useful tool to study the metal/metal oxide semiconductor system. Li et al. [14–17] investigated different noble metal/metal oxide semiconductor systems (Pt, Pd, Rh/TiO_2, SnO_2, ZnO, CeO_2, Co_3O_4) by electrical conductivity measurements, and suggested that the noble metal could activate the hydrogen molecule by dissociating it into two hydrogen atoms, which could spill over onto the metal oxide semicondutor. In conclusion, the hydrogen molecule acted as the electron donor, the semiconductor acted as the electron reservoir, and the noble metal acted as an intermediate accelerating the hydrogen atom transport from the hydrogen molecule to the semiconductor. Herrmann et al. [18] investigated Pt, Pd/CeO_2–ZrO_2 catalysts by electrical conductivity measurements to understand the relationship between oxygen vacancies and catalyst deactivation. Ionescu et al. [19, 20] studied the hydrogen spillover for the Pt/Al_2O_3 system by electrical conductivity measurements. In this paper, electrical conductivity measurements were conducted to study the effect of noble metals on the redox properties of Co_3O_4. Previously, the effect of Pt on Co_3O_4 reduction was discussed in brief [15]. The effect of noble metals (Ru, Rh, Pd and Pt) on Co_3O_4 reduction were investigated further in this article. Electrical conductivity measurements for the unpromoted and the Pt promoted Co_3O_4 samples in oxygen and syngas were iterated to shed light on the effect of the noble metal on cobalt oxidation and re-reduction.

H. Duan · D. Xu · W. Li · H. Xu (✉)
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China
e-mail: xuhy@dicp.ac.cn

2 Experimental

2.1 Sample Preparation

Co_3O_4 samples containing 1.0 wt.% noble metal (Ru, Rh, Pd, Pt) were prepared by the incipient wetness impregnation method. Co_3O_4 powder was first impregnated with different aqueous solutions, including ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$), rhodium chloride hydrate ($RhCl_3 \cdot 3H_2O$), palladium chloride ($PdCl_2$) and hydrogen chloroplatinate hydrate ($H_2PtCl_6 \cdot 6H_2O$). Then the samples were dried at 393 K for 16 h and calcined at 673 K for 4 h in air. In addition, an unpromoted Co_3O_4 sample was calcined at the same condition as noble metal promoted Co_3O_4 samples for comparison.

2.2 Temperature-Programmed Reduction (TPR)

TPR experiments were carried out in a quartz reactor. The calcined sample (0.02 g) was first purged with an argon flow of 20 mL/min at a ramp rate of 10 K/min to 623 K for 30 min to remove the traces of water, followed by cooling to room temperature. Then the sample was reduced in 4 vol.% hydrogen and argon mixture (30 mL/min) at a temperature ramp rate of 5 K/min. The effluent gas was passed through a cooling trap to condense and collect the water produced during the reduction. A gas chromatograph (SHIMADZU GC-8A) equipped with a thermal conductivity detector (TCD) was used to measure hydrogen consumption.

2.3 Electrical Conductivity Measurements

The calcined sample was pressed into a disc of 11.38 mm in diameter and 1.0 mm in thickness at 20 MPa. The disc was fixed between two platinum electrodes connected with a multifunction meter to measure the electrical resistance. All of the samples were tested in nitrogen and hydrogen atmospheres. The sample was first heated in a nitrogen flow of 20 mL/min at a ramp rate of 10 K/min to 623 K for 30 min, followed by cooling below 323 K. Then hydrogen (30 mL/min) was switched on. When the measured electrical resistance was almost unchanged, which means that hydrogen nearly completely replaced nitrogen, the sample was heated at a ramp rate of 5 K/min.

The electrical resistance of the unpromoted Co_3O_4 and the Pt promoted Co_3O_4 samples were further measured in oxygen and syngas atmospheres. The sample was first heated in a hydrogen flow of 30 mL/min at a ramp rate of 5 K/min. When the measured electrical resistance decreased slowly, presenting a metallic conduction behavior, the temperature was decreased to 523 K for the unpromoted Co_3O_4 sample or kept at 523 K for the Pt promoted Co_3O_4 sample. Then the electrical resistance was measured in turn in oxygen (20 mL/min) and syngas (20 mL/min) whose composition was $n(H_2)/n(CO)/n(CO_2)/n(N_2) = 2/1/0.4/1$. The electrical conductivity of samples was calculated in terms of measured electrical resistance.

3 Results and Discussion

3.1 Electrical Conductivity in Nitrogen

Co_3O_4 is a spinel oxide whose cation distribution can be shown to be $Co^{2+}(Co^{3+})_2\,(O^{2-})_4$ [21]. Co^{2+} ions are localized in the tetrahedral sites and Co^{3+} ions are localized in the octahedral sites. The two ion charge states between the two sites can exchange in a small amount, explaining the electric properties of stoichiometric Co_3O_4 [22]. The temperature dependence of the electrical conductivity of unpromoted and noble metal promoted Co_3O_4 samples in nitrogen atmosphere are shown in Fig. 1. The electrical conductivity increases with increasing temperature for all samples, showing a typical semiconductor-like conduction behavior. Co_3O_4 is an intrinsic *p*-type semiconductor whose electrical conductivity is mainly in the form of hole free carriers [22]. The temperature increase induces more hole free carriers, thus increasing the electrical conductivity.

The Arrhenius plots of the electrical conductivity of unpromoted and noble metal promoted Co_3O_4 samples as a function of reciprocal temperature are shown in Fig. 2. The electrical conductivity-temperature behavior follows the equation [23, 24]:

$$\sigma T = A\exp(-E_a/kT)$$

In the equation, E_a is activation energy, k is the Boltzmann constant, T is absolute temperature, and A is the

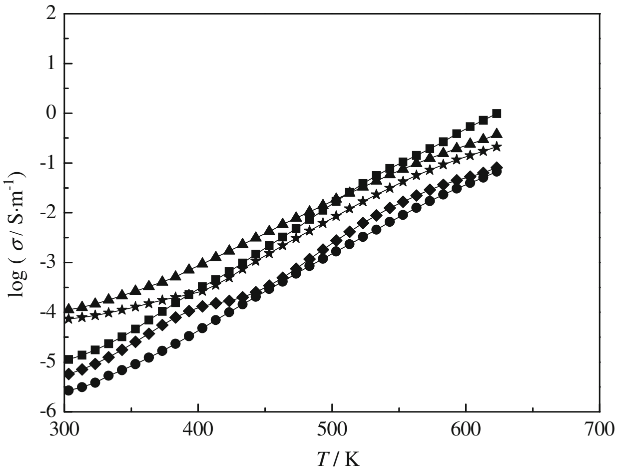

Fig. 1 The electrical conductivity of unpromoted and noble metals promoted Co_3O_4 samples in nitrogen. (■) Co_3O_4; (▲) Ru/Co_3O_4; (♦) Rh/Co_3O_4; (★) Pd/Co_3O_4; (●) Pt/Co_3O_4

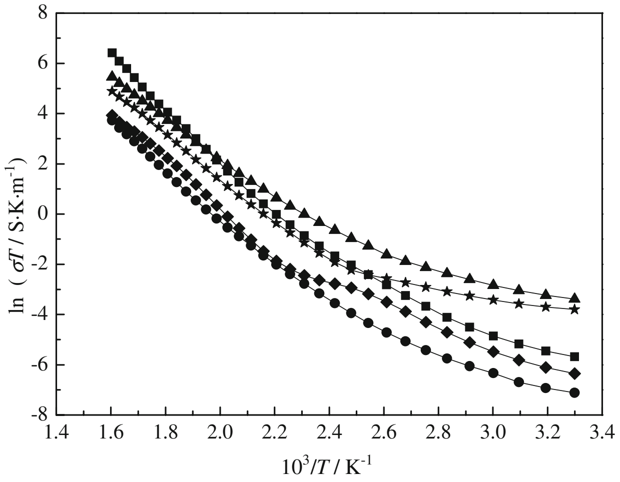

Fig. 2 The Arrhenius plots of the electrical conductivity of unpromoted and noble metals promoted Co_3O_4 samples. (■) Co_3O_4; (▲) Ru/Co_3O_4; (♦) Rh/Co_3O_4; (★) Pd/Co_3O_4; (●) Pt/Co_3O_4

pre-exponential factor. When the equation is placed in a linearized form, the activation energy E_a can be calculated using the slopes of lines. As shown in Fig. 2, the slopes of the lines increase with increasing temperature in the low temperature region, indicating that the activation energy E_a increases with increasing temperature. The slopes of the lines do not increase any more with increasing temperature in the high temperature region, indicating that the activation energy E_a becomes a constant. The activation energy E_{a1} for the low temperature region (303–333 K) and E_{a2} for the high temperature region (453–623 K) were calculated and the values are provided in Table 1. It can be seen that the activation energy of noble metal promoted Co_3O_4 samples are lower than that of the unpromoted sample, except for E_{a1} of the Rh promoted sample. The decrease in the activation energy is probably caused by the introduction of noble metal as a dopant, which likely increases the concentration of dislocations and imperfections.

3.2 Electrical Conductivity in Hydrogen

When temperature is a constant, the semiconductor material keeping *p*-type from Co_3O_4 to CoO, the electron holes are the charge carries and the amounts of them decrease; therefore, the electrical conductivity decreases. However, the semiconductor material changing to *n*-type from CoO to Co, the electrons become the charge carriers and the amounts of them increase; hence, the electrical conductivity increases. The influence of changes of the oxidation state of cobalt on electrical properties was also observed by Lee et al. [25]. The temperature dependence of the electrical conductivity of unpromoted and noble metal promoted Co_3O_4 samples in hydrogen atmosphere is shown in Fig. 3. As in nitrogen atmosphere, the electrical conductivity of the unpromoted Co_3O_4 sample in hydrogen increases with increasing temperature below 353 K. Nevertheless, the increasing rate of the electrical conductivity becomes slower between 353 K and 563 K. In this region of the profile, three factors may coexist. The increasing temperature causes the electrical conductivity increasing all the same. Moreover, the hydrogen molecule is dissociated to hydrogen atoms and the electrons transfer from hydrogen atoms to Co_3O_4, resulting in the reduction of Co_3O_4. If only the first reduction step (Co_3O_4 → CoO) occurs, the electrical conductivity will decrease. From the shape of the profile, the second reduction step (CoO → Co) can not be confirmed inexistent. As a result, the electrical conductivity increases slowly. When the temperature succeeds 563 K, Co_3O_4 is mainly reduced to CoO, resulting in a rapid decrease in the electrical conductivity, which reaches a minimum at 603 K. Subsequently, CoO is reduced to Co, the electrical conductivity increases sharply. Above 623 K, the electrical conductivity decreases slowly, showing a metallic conduction behavior, implying that Co_3O_4 is reduced to Co entirely.

Compared with the unpromoted Co_3O_4 sample, the noble metal promoted samples display much lower temperatures at which the electrical conductivity exhibits corresponding

Table 1 The activation energy of unpromoted and noble metals promoted Co_3O_4 samples

Sample	E_{a1}/eV	E_{a2}/eV
Co_3O_4	0.209	0.923
Ru/Co_3O_4	0.142	0.694
Rh/Co_3O_4	0.225	0.850
Pd/Co_3O_4	0.095	0.769
Pt/Co_3O_4	0.177	0.836

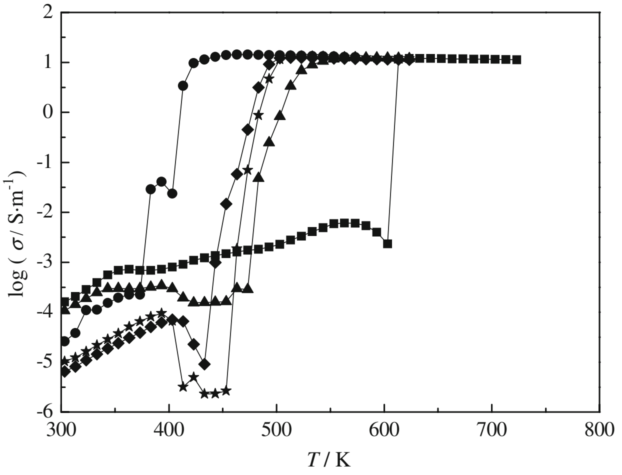

Fig. 3 The electrical conductivity of unpromoted and noble metals promoted Co_3O_4 samples in hydrogen. (■) Co_3O_4; (▲) Ru/Co_3O_4; (♦) Rh/Co_3O_4; (★) Pd/Co_3O_4; (●) Pt/Co_3O_4

changes. It can occur that the hydrogen molecule is adsorbed and dissociated to hydrogen atoms on noble metals at very low temperature; furthermore, hydrogen atoms spill over [19, 20, 26] from the noble metal particles to the Co_3O_4 particles. The electrons transfer from hydrogen atoms to Co_3O_4, thus Co_3O_4 can be reduced to CoO and Co at very low temperature in the presence of a noble metal promoter. From Fig. 3, it can be seen that for Ru, Rh and Pd promoted Co_3O_4 samples, the temperatures corresponding to the minimum of the electrical conductivity are lower by about 170 K relative to the unpromoted sample. Similarly, the temperatures at which Co_3O_4 is reduced to Co entirely on Ru, Rh and Pd promoted Co_3O_4 samples are lower by about 60, 110 and 100 K, respectively than that of the unpromoted sample. For the case of the Pt promoted sample, some Co_3O_4 is even reduced to CoO below 373 K and then the CoO is in turn reduced to Co quickly, presenting a sharp increase in electrical conductivity at 373 K. Then another fraction of Co_3O_4 is reduced to CoO and Co continuously, presenting a minimum at 403 K and then another sharp increase in electrical conductivity. It is obvious that the promotional effect of Pt on the reduction of Co_3O_4 is most significant among the examined noble metals.

3.3 TPR

TPR profiles of unpromoted and noble metal promoted Co_3O_4 samples are shown in Fig. 4. Only one unsymmetrical peak with the temperature maximum located at 634 K is detected during Co_3O_4 reduction, as shown in Fig. 4. This peak corresponds to the reduction of bulk Co_3O_4 to Co via CoO [27, 28]. On the other hand, two major reduction peaks are detected during the reduction of the noble metal promoted Co_3O_4 samples. The peak located at low temperature is assigned to the reduction of the Co_3O_4 contacted with the noble metal particles, and the peak located at high temperature is assigned to the reduction of the large Co_3O_4 particles apart from the noble metal particles. Since noble metal oxides can be reduced at very low temperature and the amounts of the noble metal in samples are small, the reduction peak of the noble metal is overlaped by the first reduction peak of Co_3O_4. It can be seen from Fig. 4, that not only the low temperature peaks but the high temperature peaks of the noble metal promoted Co_3O_4 samples locate at lower temperature than the peak of the unpromoted sample. The decrease of the reduction temperature for noble metal promoted samples is ascribed to the hydrogen spillover from the pre-reduced noble metal particles to the Co_3O_4 particles contacted with the noble metal particles [1, 2], and the second hydrogen spillover further onto the large Co_3O_4 particles apart from the noble metal particles [29]. The low temperature reduction peak of the Rh promoted Co_3O_4 sample locates at higher temperature than that of other noble metal promoted samples, which may be caused by the higher reduction temperature of Rh oxide than other noble metal oxides. The high temperature peak of the Pt promoted Co_3O_4 sample just presents a shoulder peak. According to the decrease extent of the reduction temperature and the area of the low temperature reduction peak, it can be concluded that the promotional effect of Pt on the reduction of Co_3O_4 is most significant among the examined noble metals. This is well consistent with the result of the electrical conductivity in hydrogen atmosphere.

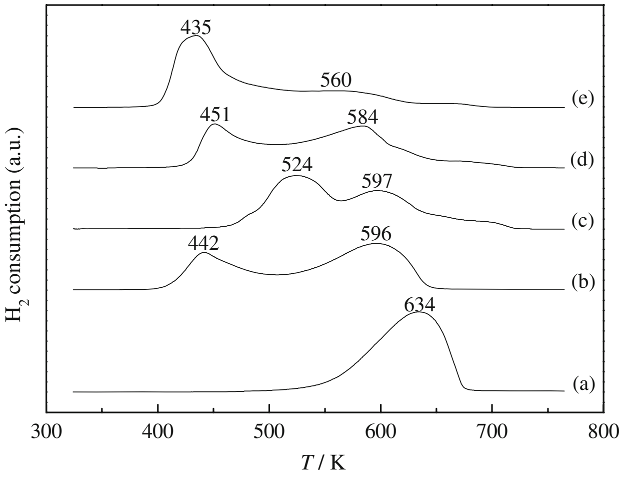

Fig. 4 TPR profiles of unpromoted and noble metals promoted Co_3O_4 samples. (**a**) Co_3O_4; (**b**) Ru/Co_3O_4; (**c**) Rh/Co_3O_4; (**d**) Pd/Co_3O_4; (**e**) Pt/Co_3O_4

3.4 Electrical Conductivity in Oxygen and Syngas

Some researchers found that the presence of the water produced during FTS reaction could result in the oxidation of the active cobalt metal and consequently the deactivation of the catalyst [13, 30, 31]. In order to reveal the influence of noble metals on the oxidation and the re-reduction of cobalt, the electrical conductivity of the unpromoted and the Pt promoted Co_3O_4 samples were investigated consecutively in hydrogen, oxygen and syngas atmospheres, corresponding to the reduction, the oxidation, and the re-reduction process, respectively. Pt was selected as an example of noble metals since the promotional effect of Pt is most significant among the examined noble metals as concluded in Chapt. 3.2 and 3.3. To enhance the oxidation of cobalt, the oxygen was chosen rather than the water as the oxidation agent in the test.

The electrical conductivity as a function of time at 523 K in oxygen is shown in Fig. 5. The unpromoted and the Pt promoted Co_3O_4 samples were first reduced to Co in hydrogen atmosphere, presenting the electrical conductivity increasing to a level of the metal Co. When the oxygen was

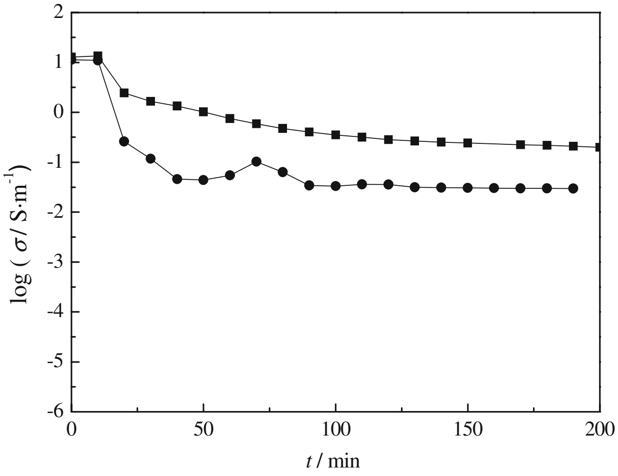

Fig. 5 The electrical conductivity of unpromoted and Pt promoted Co_3O_4 samples in oxygen. (■) Co_3O_4; (●) Pt/Co_3O_4

introduced, the electrical conductivity decreased as expected, suggesting that partial Co metal was oxidized to CoO. During the initial 40 min, the electrical conductivity decreased much more for the Pt promoted sample, indicating that the amounts of Co oxidized to CoO were larger relative to the unpromoted sample. After 40 min, the electrical conductivity of the Pt promoted sample increased and then decreased again, indicating that the pre-oxidized CoO were further oxidized to Co_3O_4 and then more Co were oxidized to CoO. It can be drawn that Co is more susceptible to oxidation in the presence of the noble metal Pt. The most reasonable explanation should be related to the oxygen spillover from the noble metals to cobalt phase [26], which could enhance the oxidation of cobalt metals.

After about 200 min in oxygen, the syngas was switched on. The electrical conductivity as a function of time at 523 K in syngas is shown in Fig. 6. As expected, the electrical conductivity of the unpromoted sample increased due to the reduction of CoO to Co metal. However, until 250 min in syngas, the electrical conductivity did not restore the initial value before the oxygen was introduced, which indicates that CoO was not reduced to Co entirely. In contrast, the electrical conductivity of the Pt promoted sample shows a sharp decrease primarily, which means that Co_3O_4 was reduced to CoO. Subsequently, a sharp increase is observed, and then the electrical conductivity restored to the initial value before the oxygen was introduced, indicating that CoO was reduced to Co entirely. It can be concluded that the cobalt oxides can be re-reduced to Co metal by syngas in the presence of the noble metal Pt.

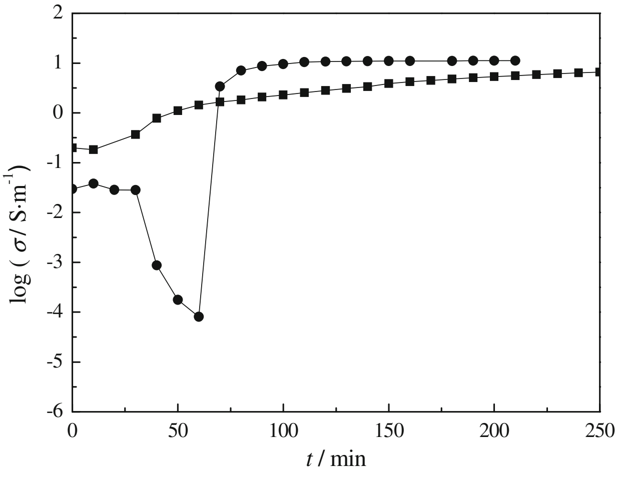

Fig. 6 The electrical conductivity of unpromoted and Pt promoted Co_3O_4 samples in syngas. (■) Co_3O_4; (●) Pt/Co_3O_4

4 Conclusion

The results of the electrical conductivity in nitrogen atmosphere shows that the introduction of noble metals decreases the activation energy of Co_3O_4. Through the results of the electrical conductivity in hydrogen atmosphere and TPR, it can be drawn that the noble metals improve the reduction of Co_3O_4 due to hydrogen spillover. The promotional effect of Pt is most significant among the examined noble metals. By conducting the electrical conductivity measurements on the unpromoted and the Pt promoted Co_3O_4 samples in oxygen and syngas, it is found that the addition of the noble metal Pt can facilitate the oxidation of Co and the cobalt oxides can be re-reduced to Co entirely by syngas.

Acknowledgements The authors gratefully acknowledge Chunying Yu, Yanxin Chen and Qingjie Ge for their helps on the electrical conductivity measurements and the helpful discussions about this article.

References

1. Xu DY, Li WZ, Duan HM, Ge QJ, Xu HY (2005) Catal Lett 102:229
2. Jacobs G, Chaney JA, Patterson PM, Das TK, Davis BH (2004) Appl Catal A 264:203
3. Das TK, Jacobs G, Patterson PM, Conner WA, Li JL, Davis BH (2003) Fuel 82:805
4. Jacobs G, Das TK, Zhang YQ, Li JL, Racoillet G, Davis BH (2002) Appl Catal A 233:263
5. Rygh LES, Nielsen CJ (2000) J Catal 194:401
6. Bianchi CL (2001) Catal Lett 76:155
7. Hosseini SA, Taeb A, Feyzi F, Yaripour F (2004) Catal Comm 5:137
8. Martinez A, Lopez C, Marquez F, Diaz I (2003) J Catal 220:486
9. Li JL, Jacobs G, Zhang YQ, Das T, Davis BH (2002) Appl Catal A 223:195
10. Sun S, Fujimoto K, Yoneyama Y, Tsubaki N (2002) Fuel 81:1583
11. Tsubaki N, Sun SL, Fujimoto K (2001) J Catal 199:236
12. Kogelbauer A, Goodwin JG Jr., Oukaci R (1996) J Catal 160:125

13. Jacobs G, Patterson PM, Zhang YQ, Das T, Li JL, Davis BH (2002) Appl Catal A 233:215
14. Wang R, Xu HY, Liu XB, Ge QJ, Li WZ (2006) Appl Catal A 305:204
15. Xu DY, Duan HM, Li WZ, Ge QJ, Yu CY, Xu HY (2006) Chem J Chinese Univ 27:1746
16. Wang J, Li WZ, Yu CY, Chen YX, Zhang YZ (1997) React Kinet Catal Lett 62:217
17. Li WZ, Chen YX, Yu CY, Wang XZ, Hong ZP, Wei ZB (1984) In: Proceedings of 8th International Congress Catal., Verlag Chemie, Weinheim, vol 5. p 205
18. Bozo C, Guilhaume N, Herrmann J (2001) J Catal 203:393
19. Stoica M, Caldararu M, Ionescu NI, Auroux A (2000) Appl Surf Sci 153:218
20. Stoica M, Caldararu M, Rusu F, Ionescu NI (1999) Appl Catal A 183:287
21. Svegl F, Orel B, Grabec-Svegl I, Kaucic V (2000) Electrochim Acta 45:4359
22. Windisch CF Jr., Ferris KF, Exarhos GJ, Sharma SK (2002) Thin Solid Films 420–421:89
23. Ji Y, Kilner JA, Carolan MF (2004) J Eur Ceram Soc 24:3613
24. Trofimenko NE, Ullmann H (2000) J Eur Ceram Soc 20:1241
25. Lee JH, Yoo HI (1994) J Electrochem Soc 141:2789
26. Meng M, Lin PY, Fu YL (1997) Catal Lett 48:213
27. Wang WJ, Chen YW (1991) Appl Catal 77:223
28. Arnoldy P, Moulijn JA (1985) J Catal 93:38
29. Conner WC Jr., Falconer JL (1995) Chem Rev 95:759
30. van Berge PJ, van de Loosdrecht J, Barradas S, van der Kraan AM (2000) Catal Today 58:321
31. Hilmen AM, Schanke D, Hanssen KF, Holmen A (1999) Appl Catal A 186:169