Catal Lett (2008) 124:68–73
DOI 10.1007/s10562-008-9501-x

Preferential Oxidation of CO in H_2-Rich Gas at Low Temperatures over Au Nanoparticles Supported on Metal Oxides

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Received: 6 February 2008 / Accepted: 25 April 2008 / Published online: 15 May 2008

Abstract We investigated Au catalysts supported on TiO_2, Fe_2O_3, and ZnO for their preferential oxidation of CO in a H_2-rich atmosphere. Both full conversion and selectivity were achieved over Au/Fe_2O_3 and Au/ZnO around room temperature, but at higher temperatures the CO conversion was suppressed due to competition between CO and H_2.

Keywords Au catalyst · CO oxidation · PROX · Au loading amount · Support effect · Low temperature

1 Introduction

Hydrogen has attracted much interest as an energy source for electric vehicles and residential power generators. During hydrogen generation by steam reforming or partial oxidation of hydrocarbon fuels, such as methanol or gasoline [1, 2], approximately 1 vol.% CO is simultaneously generated [3]. A CO content higher than 10 ppm is considered detrimental to the metal electrodes used in fuel cells, especially Pt, because these metals can be poisoned by CO adsorption. Preferential oxidation of CO (referred to herein as PROX) is an effective method for removing trace amounts of CO from H_2. In a H_2-rich atmosphere, H_2 competes with CO to react with O_2, leading to decreased hydrogen generation. To effectively remove CO from a H_2-rich atmosphere, a high amount of CO conversion with high selectivity at low temperatures is required. Ideally, a 100% CO conversion with 100% selectivity to CO_2 below 473 K is desired.

Au catalysts could be effective candidates for PROX, since well-dispersed Au nanoparticles on metal oxides exhibit high activity toward CO oxidation at low temperatures [4–6]. The activity of the Au catalysts toward CO oxidation is strongly affected by factors such as the catalyst preparation method [7, 8], the size of the Au particles [4], and the contact structure between the Au particles and the metal-oxide support [9, 10]. Some researchers have suggested that the high activity observed for Au catalysts supported on reducible metal oxides results from synergistic effects between the Au and the support material [5, 11, 12]; in particular, Au/TiO_2 and Au/Fe_2O_3 catalyst/support systems have been extensively investigated for simple CO oxidation [4, 13–17]. In addition to the activity toward CO oxidation, selectivity toward CO_2 and long-term stability are key features of the catalysts used for PROX.

CO oxidation over supported Au nanoparticle catalysts is intrinsically predominant over H_2 oxidation [6, 18, 19], and this behavior contrasts with that observed for CO oxidation over other noble-metal catalysts, such as Pt or Pd. In fact, Au catalysts supported on MnOx, TiO_2, CeO_2, and Fe_2O_3, have been suggested as suitable candidates for PROX at low temperatures [18, 20–35]. For example, CO conversion higher than 90% was obtained with Au/Fe_2O_3, even in the presence of H_2 [34]. In most cases in the

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literature, the molecular ratio of O_2 to CO in the reactant gas exceeds 1.0, which is twice the stoichiometric ratio for complete CO oxidation, and this imbalance might result in the combustion of H_2. Furthermore, inert gases, such as He and N_2, have been used to dilute H_2. More recently, the PROX reaction has been attempted over Au/MnOx/Al_2O_3, Au/MgO/Al_2O_3, and Au/ZrO_2 around room temperature [36–38]. However, full (100%) conversion with 100% selectivity has not been accomplished yet in H_2-rich atmospheres.

In this study, we carried out the PROX reaction over three catalysts, Au/TiO_2, Au/Fe_2O_3, and Au/ZnO, under severe conditions, i.e., only H_2 was added to the stoichiometric mixture of O_2 and CO, and the results were compared with those obtained from the oxidation of CO or H_2 individually in air. The effects of the support materials and the Au loading amount on the catalysts for CO oxidation in a H_2-rich atmosphere are presented and discussed. In addition, the effect of H_2 on both CO conversion and selectivity of the catalysts are also discussed. Since Au catalysts are known to undergo rapid deactivation during CO oxidation [13, 39–41], we also investigated the long-term stability of Au catalysts during the PROX reaction.

2 Experimental

We deposited gold nanoparticles on titanium dioxide (P-25, Nippon Aerosil Co., Ltd) by the deposition–precipitation (DP) method using $HAuCl_4 \cdot 4H_2O$ [9]. Au/α-Fe_2O_3 and Au/ZnO catalysts were prepared from $FeNO_3$ and $Zn(NO_3)_2$ precursors, respectively, by the coprecipitation (CP) method as described elsewhere [5]. All of the samples were calcined at 673 K for 4 h in air. The actual loading amounts of Au in the catalyst samples were analyzed by inductively coupled plasma spectroscopy. We analyzed all the samples by X-ray diffraction (Miniflex, Rigaku) with Cu $K\alpha$ radiation and estimated the Au particle size with the Scherrer equation. The results of this characterization are listed in Table 1.

Catalytic activity was measured in a fixed-bed flow reactor under atmospheric pressure. The catalyst sample sieved with 70–120 mesh (212–125 μm) was placed in a quartz-tube and pretreated at 523 K for 30 min in an air stream, after which the reactant gas was passed through the catalytic bed at a flow rate of 33 mL/min (SV = 20,000 h^{-1} mL/g-catalyst). For the separate CO and H_2 oxidation reactions we used 1 vol.% of each gas in air, and for the selective oxidation of CO in excess H_2 we used a reactant gas mixture of 1 vol.% CO, 0.5 vol.% O_2, and 98.5 vol.% H_2. The catalyst temperature was monitored with a thermocouple covered by a quartz-tube sheath in contact with the inlet of the catalyst bed. The effluent gas was analyzed by on-line gas chromatography with a thermal conductivity detector (GC-8A and GC-14B, Shimadzu) for H_2, O_2, and CO. The selectivity toward CO_2 for the selective oxidation of CO was determined from the consumption of CO and O_2 according to the following formula:

$$\text{Selectivity }(\%) = \{([\mathrm{CO}]_0 - [\mathrm{CO}])/([\mathrm{O_2}]_0 - [\mathrm{O_2}])\} \times 100,$$

where [CO] and [O_2] are the CO and O_2 concentrations (vol.%), respectively, and the subscript ‘0’ denotes the initial concentration in the reactant gas.

3 Results and Discussion

Table 1 summarizes the catalytic properties of the three catalysts for the separate oxidation of CO or H_2 in terms of

Table 1 Au loading amounts, particle sizes and catalytic activities for CO and H_2 oxidation of the Au catalyst samples

Support	Preparation method	Au loading[c] (wt.%)	Au loading[c] (mol.%)	Au particle size[d] (nm)	$T_{1/2}$ (H_2) (K)	$T_{1/2}$ (CO) (K)	$\Delta T_{1/2}$ (H_2-CO) (K)
TiO_2	DP[a]	0.5	0.20	4.1	329	261	68
		0.7	0.29	4.2	329	248	81
		1.0	0.41	5.5	318	236	82
		1.3	0.53	5.7	315	<230	>85
Fe_2O_3	CP[b]	3.4	2.77	3.4	325	248	77
		10.1	8.35	3.8	306	234	72
ZnO	CP[b]	0.5	0.21	3.0	378	334	44
		4.9	2.1	3.0	309	202	107

[a] Deposition–precipitation

[b] Co-precipitation

[c] Determined by ICP measurements

[d] Estimated with Scherrer equation

the temperature at which 50% conversion ($T_{1/2}$) was achieved for each gas. All the catalysts had a higher activity (lower $T_{1/2}$ values) for CO oxidation than for H_2 oxidation. As the amount of Au increased, the $T_{1/2}$ values for both oxidation reactions decreased, and the difference between the $T_{1/2}$ values for CO and H_2 oxidations [$\Delta T_{1/2}$ (H_2 − CO)] over Au/TiO_2 increases. Among the tested catalysts, Au/TiO_2 was the most active toward CO oxidation, and this finding is consistent with previous reports [4, 5]. Complete CO oxidation in air was accomplished for Au/TiO_2 and Au/Fe_2O_3 even at 273 K, but the activity of Au/ZnO was relatively low.

The plots of CO conversion and selectivity toward CO_2 versus. temperature over Au/TiO_2 exhibited maxima (Fig. 1). The highest CO conversion (85% with a selectivity of 90%) was observed over 1.3 wt.% Au/TiO_2 at 295 K (Fig. 1a). CO conversion increased at lower temperatures with increasing Au loading, but at higher temperatures it appeared independent of Au loading. A similar tendency was observed for the selectivity toward CO_2. Notably, both conversion and selectivity were almost independent of the extent of Au loading at higher temperatures, and both decreased with increasing temperature. Compared to the condition of excess O_2 (Table 1), the oxidation of CO was suppressed in the PROX conditions and CO conversion did not reach 100% even at room temperature. When the H_2 balance in the reactant gas was substituted with Ar, the $T_{1/2}$ value for CO oxidation over 0.7 wt.% Au/TiO_2 increased from 248 to 287 K. However, CO conversion finally reached 100% at 303 K even under low partial pressure of O_2 (data not shown). CO conversion over supported Au catalysts has been reported to decrease when H_2 is introduced into the reaction mixture, due to competition between H_2 and CO for adsorption on the Au particles and reaction with oxygen [36, 37, 42]. These results suggest that CO oxidation at low temperatures is mainly influenced by the difference in partial pressure between O_2 and CO, whereas competition between CO and H_2 is more prevalent at higher temperatures.

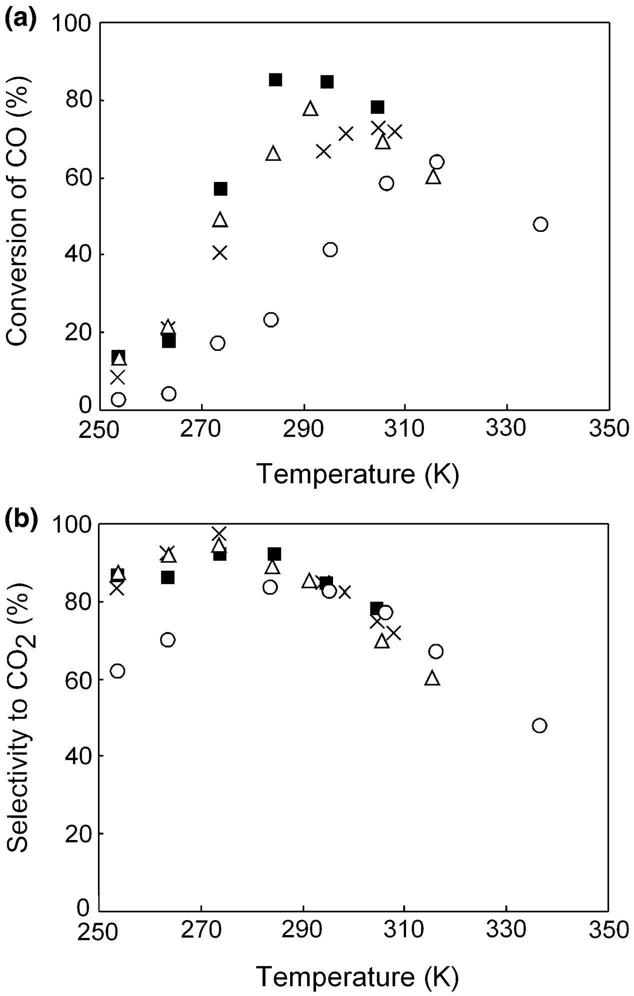

Fig. 1 (**a**) CO conversion and (**b**) selectivity toward CO_2 for CO oxidation in a H_2-rich atmosphere over Au/TiO_2 as a function of the reaction temperature for a reaction mixture containing 1 vol.% CO, 0.5 vol.% O_2, and balance H_2; SV = 20,000 h^{-1} mL/g-catalyst. (○) 0.5 wt.%, (×) 0.7 wt.%, (Δ) 1.0 wt.%, and (■) 1.3 wt.%

Similar to the results for Au/TiO_2, the extent of CO conversion over Au/Fe_2O_3 and Au/ZnO under the PROX conditions depended on the amount of Au loading, but the selectivity was less affected by this parameter (Figs. 2, 3). Notably, around room temperature the selectivity over Au/Fe_2O_3 and Au/ZnO catalysts reached 100%, and 100% conversion was also achieved over 10.1 wt.% Au/Fe_2O_3 and 4.9 wt.% Au/ZnO. At higher temperatures both conversion and selectivity decreased over all catalysts due to competition between CO and H_2, as also seen over Au/TiO_2 (Fig. 1). In contrast with the behavior observed for CO oxidation, the oxidation rate of H_2 over Au catalysts is almost independent of the support material, and the activity is primarily related to the exposed surface area of gold [8]. This behavior is consistent with the trends of conversion and selectivity observed here. The differences in activity for CO oxidation are attributed to the different abilities of the support materials to supply reactive oxygen species [4, 5, 21, 43]. For example, the reducible metal oxides used here, namely TiO_2 and Fe_2O_3, are well known for their ability to store and supply oxygen for the oxidation reaction, and this property has been demonstrated for the PROX reaction over Au/Fe_2O_3 [44]. In the present study, however, we did not notice a substantial catalyst support effect. Notably, the competition between CO and H_2 was observed beginning at ~300 K and was substantially independent of the support oxide composition or loading amount of Au, whereas the CO conversion depended on the Au amount such that the best catalytic performance was obtained with a higher loading amount.

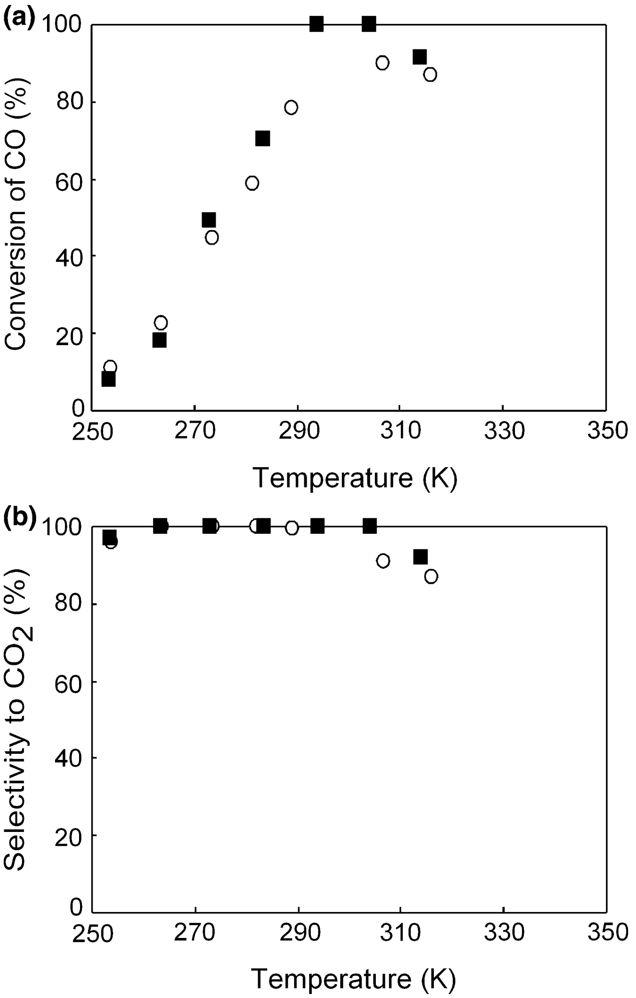

Fig. 2 (**a**) CO conversion and (**b**) selectivity to CO_2 for the CO oxidation in a H_2-rich atmosphere over Au/Fe_2O_3 as a function of reaction temperature; gas composition are the same as in Fig. 1. (○) 3.4 wt.% and (■) 10.1 wt.%

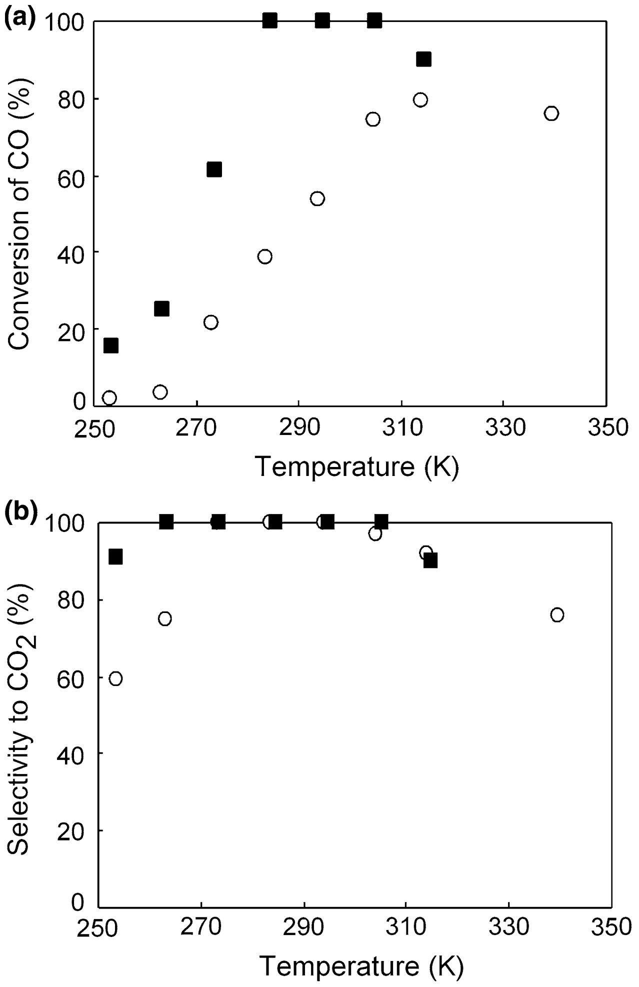

Fig. 3 (**a**) CO conversion and (**b**) selectivity toward CO_2 for CO oxidation in a H_2-rich atmosphere over Au/ZnO as a function of the reaction temperature; gas composition are the same as in Fig. 1. (○) 0.5 wt.% and (■) 4.9 wt.%

The dissociation of O_2 is generally believed to occur not directly on the Au particles, but at the periphery of the particle surface [10, 11, 45]. In addition, the activated oxygen reacts with CO adsorbed on Au particles to form an intermediate, which is immediately transformed to CO_2 [46]. Therefore, CO conversion might be governed by the number of specific sites available for CO oxidation at the interface between the Au nanoparticles and the support surface; the length of this interface depends on the Au particle size. However, H_2 also adsorbs on the surface of the Au particles to dissociate and react with molecular oxygen [47]. In fact, many highly reactive intermediates, such as H_2O_2, are involved in the reaction between H_2 and O_2 over Au catalysts [48]. Neutron experiments by Sivadinarayana et al. [49] provide evidence for the formation of H_2O_2 and hydroperoxo radicals (HOO·) from the reaction between H_2 and O_2 over supported Au nanoclusters. Thus, the reaction rate of H_2 oxidation may reflect the surface area of Au. Although different active sites are being considered for the separate oxidation of CO and H_2, a reaction mechanism model for CO oxidation was proposed by Bond and Thompson [11] in which H_2 is involved in forming intermediates such as hydroxy carbonyl (CO–Au–OH) or hydroperoxy carbonyl (CO–Au–OOH) at the particle-support interfaces. To further understand the reaction mechanisms, spectroscopic studies performed under the actual operating conditions of the reaction would be required.

The best performance for the PROX reaction was obtained with 4.9 wt.% Au/ZnO, and we examined this catalyst's stability under the PROX condition. We note that full conversion and selectivity were maintained for more than 400 min and also when the reaction was repeated four times. The deactivation of Au catalysts has been reported to occur in the PROX atmosphere due to the formation of carbonates on Au particles, blocking the special sites for CO oxidation, but without decrease in the selectivity to CO_2 [50]. In this work, no deactivation of the catalytic activity was observed, and this behavior might be due to decomposition of the carbonate species by H_2O or hydroxyl species formed through the reaction between H_2 and O_2 on Au particles [51].

4 Conclusions

This work deals with the preferential oxidation of CO in a H_2-rich atmosphere over Au catalysts supported by TiO_2, Fe_2O_3, and ZnO, which exhibited a higher activity for oxidation of CO than of H_2. We prepared the samples by DP or CP methods and investigated the PROX reaction by using the reactant gas containing stoichiometric mixture of CO and O_2 balanced with H_2. At low temperatures, the conversion of CO in the PROX reaction was mainly dependent on the Au loading amount. In contrast, at high temperatures, the CO conversion was suppressed by the competition between CO and H_2 for adsorption and subsequent reaction with O_2 on the surface of Au particles, which was almost independent of the support materials or Au loading amount. The selectivity toward CO_2 at low temperatures reached 100% over Au/Fe_2O_3 and Au/ZnO catalysts, regardless of the Au loading amount. A combination of full conversion and selectivity was achieved around room temperature for 10.1 wt.% Au/Fe_2O_3 and 4.9 wt.% Au/ZnO. The Au/ZnO catalyst retained full conversion and selectivity for long-term PROX reactions and for repetitions of the PROX reaction. Finally, we concluded that the Au loading amount was an important parameter for obtaining a highly active gold catalyst for the PROX reaction under the present conditions.

Acknowledgments We would like to thank Prof. Masatake Haruta of Tokyo Metropolitan University and Dr Tadahiro Fujitani of AIST for their advice and encouragement.

References

1. Lemons RA (1990) J Power Sources 29:251
2. Kumar R, Ahmed S (1995) Fuels processing for transportation fuel systems. Presented at the First International symposium on New Materials for Fuel Cell Systems. Montreal, Canada
3. Mann RF, Amphlett JC, Peppley BA (1993) Front Sci Ser 7:613
4. Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet M, Delmon B (1993) J Catal 144:175
5. Haruta M, Yamada N, Kobayashi T, Iijima S (1989) J Catal 115:301
6. Linn SD, Bollinger M, Vannice MA (1993) Catal Lett 17:245
7. Bamwneda GR, Tsubota S, Nakamura T, Haruta M (1997) Catal Lett 44:83
8. Okumura M, Tsubota S, Haruta M (2003) J Mol Catal A 199:73
9. Tsubota S, Cunningham DAH, Bando Y, Haruta M (1995) In: Poncelet G et al. (ed) Preparation of catalysts, vol 6. Elsevier, Amsterdam, pp 227–235
10. Tsubota S, Nakamura T, Haruta M (1998) Catal Lett 56:131
11. Bond GC, Thompson DT (2000) Gold Bull 33:41
12. Haruta M (2003) Chem Rec 3:75
13. Bollinger MA, Vannice MA (1996) Appl Catal B 8:417
14. Grunwaldt JD, Maciejewski M, Becker OS, Fabrizioli P, Baiker A (1999) J Catal 186:458
15. Kozlov AI, Kozlova AP, Liu H, Iwasawa Y (1999) Appl Catal 182:9
16. Visco AM, Donato A, Milone C, Galvagno S (1997) React Kinet Catal Lett 61:219
17. Horvath D, Toth L, Guczi L (2000) Catal Lett 67:117
18. Torres Sanchez RM, Ueda A, Tanaka K, Haruta M (1997) J Catal 168:125
19. Okumura M, Nakamura S, Tsubota S, Nakamura T, Azuma M, Haruta M (1998) Catal Lett 51:93
20. Kahlich MJ, Gasteiger HA, Behm RJ (1999) J Catal 182:430
21. Shubert MM, Kahlich MJ, Gasteiger HAHA, Behm RJ (1999) J Power Sources 84:175
22. Landon P, Ferguson J, Solsona BE, Garcia T, Al-Sayari S, Carley AF, Herzing AA, Kiely CJ, Makkee M, Moulijin JA, Overweg A, Golunskie SE, Hutchings GJ (2006) J Mater Chem 16:199
23. Panzera G, Modafferi V, Candamano S, Donato A, Frusteri F, Antonucci PL (2004) J Power Sources 177:135
24. Carrettin S, Concepcion P, Corma A, Nieto JML, Puntes VF (2004) Angew Chem Int Ed 43:2538
25. Luengnaruemitchai A, Osuwan S, Gulari E (2004) Int J Hydrogen Energy 29:429
26. Yan Z, Chinta S, Mohamed AA, Frackler JP Jr, Goodman DW (2006) Catal Lett 111:15
27. Yu WY, Yang CP, Lin JN, Kuo CN, Wan BZ (2005) Chem Commun 354
28. Schumacher B, Denkwitz Y, Plzak V, Kinne M, Behm RJ (2004) J Catal 224:449
29. Galletti C, Fiorot S, Specchia S, Saracco G, Specchia V (2007) Chem Eng J 134:45
30. Arena F, Famulari P, Trunfio G, Bonura G, Frusteri F, Spadaro L (2006) Appl Catal B 66:81
31. Azar M, Caps V, Morfin F, Rousset J-L, Piednoir A, Bertolini J-C, Piccolo L (2006) J Catal 239:307
32. Schubert MM, Venugopal A, Kahlich MJ, Plzak V, Behm RJ (2004) J Catal 222:32
33. Qiao BT, Deng YQ (2003) Chem Commun 2192
34. Avgouropoulos G, Ioannides T, Papadopoulou Ch, Batista J, Hocevar S, Matralis HK (2002) Catal Today 75:157
35. Landon P, Ferguson J, Solsona BE, Garcia T, Carley AF, Herzing AA, Kiely CJ, Golunskie SE, Hutchings GJ (2005) Chem Commun 3385
36. Grisel RJH, Weststrate CJ, Goossens A, Crajè MWJ, van der Kraan AM, Nieuwenhuys BE (2002) Catal Today 72:123
37. Grisel RJH, Nieuwenhuys BE (2001) J Catal 199:48
38. Rossignol C, Arri S, Morfin F, Piccolo L, Caps V, Rousset JL (2005) J Catal 230:476
39. Valden M, Pak S, Lai X, Goodman DW (1998) Catal Lett 56:7
40. Bond GC, Thompson DT (1999) Catal Rev Sci Eng 41:319
41. Choudhary TV, Goodman DW (2002) Top Catal 21:25
42. Schumacher B, Derkwitz Y, Plzak V, Kinne M, Behm RJ (2004) J Catal 224:449
43. Dekkers MAP, Lippits MJ, Nieuwenhuys BE (1999) Catal Today 54:381
44. Schubert MM, Hackenberg S, van Veen AC, Muhler M, Plzak V, Behm RJ (2001) J Catal 197:113
45. Haruta M (1997) Catal Today 36:153

46. Boccuzzi F, Chiorino A, Manzoli M, Lu P, Akita T, Ichikawa S, Haruta M (2001) J Catal 202:256
47. Naito S, Tanimoto M (1988) J Chem Soc, Chem Commun 832
48. Okumura M, Kitagawa Y, Yamaguchi K, Akita T, Tsubota S, Haruta M (2003) Chem Lett 32:822
49. Sivadinaraya C, Choudhary TV, Daemon LL, Eckert J, Goodman DW (2004) J Am Chem Soc 126:38
50. Schubert MM, Plzak V, Garche J, Behm RJ (2001) Catal Lett 76:143
51. Daté M, Okumura M, Tsubota S, Haruta M (2004) Angew Chem Int Ed 43:2129