Catal Lett (2008) 122:223–227
DOI 10.1007/s10562-008-9407-7

CO/FTIR Spectroscopic Characterization of $Pd/ZnO/Al_2O_3$ Catalysts for Methanol Steam Reforming

V. Lebarbier · R. Dagle · T. Conant · J. M. Vohs · A. K. Datye · Y. Wang

Received: 10 December 2007 / Accepted: 18 January 2008 / Published online: 12 February 2008

Abstract An as-synthesized 8.8wt% $Pd/ZnO/Al_2O_3$ catalyst was either pretreated under O_2 at 773 K followed by H_2 at 293 K or under H_2 at 773 K to obtain, respectively, a supported metallic Pd° catalyst ($Pd°/ZnO/Al_2O_3$) or a supported PdZn alloy catalyst ($PdZn/ZnO/Al_2O_3$). Both catalysts were studied by CO adsorption using FTIR spectroscopy. For the supported PdZn alloy catalyst ($PdZn/ZnO/Al_2O_3$), exposure to a mixture of methanol and steam, simulating methanol steam reforming reaction conditions, does not change the catalyst surface composition. This implies that the active sites are PdZn alloy like structures. The exposure of the catalyst to an oxidizing environment (O_2 at 623 K) results in the break up of PdZn alloy, forming a readily reducible PdO with its metallic form being known as much less active and selective for methanol steam reforming. However, for the metallic $Pd°/ZnO/Al_2O_3$ catalyst, FTIR results indicate that metallic Pd° can transform to PdZn alloy under methanol steam reforming conditions. These results suggest that PdZn alloy, even after an accidental exposure to oxygen, can self repair to form the active PdZn alloy phase under methanol steam reforming conditions. Catalytic behavior of the $PdZn/ZnO/Al_2O_3$ catalyst also correlates well with the surface composition characterizations by FTIR/CO spectroscopy.

Keywords FTIR spectroscopy · Pd catalyst · PdZn alloy catalyst · Methanol steam reforming

V. Lebarbier · R. Dagle · Y. Wang (✉)
Pacific Northwest National Laboratory, Richland, WA 99354, USA
e-mail: yongwang@pnl.gov

V. Lebarbier · T. Conant · A. K. Datye
Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, NM 87106, USA

J. M. Vohs
Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

1 Introduction

Based on the current rate of consumption of fossil fuels, most of these resources could be depleted in a few decades [1]. A movement toward the generation of renewable energy is imperative. Proton-Exchange Membrane Fuel Cells (PEMFCs) powered by hydrogen from renewable sources to produce electricity appear to be an alternative solution. Hydrogen fuel can be obtained from steam reforming of alcohols such as methanol. Methanol is an attractive candidate due to its high hydrogen/carbon ratio, low sulfur content [2, 3], low cost [3, 4], relatively low reforming temperature (473–623 K) [2–5], easy storage feasibility [6] and high availability [4, 7].

Methanol steam reforming is catalyzed by supported metals [8–15]. Many studies [16–28] have focused on copper-based catalysts which exhibit a high reactivity and favorable selectivity to CO_2 and H_2. However, the Cu-based catalysts can readily undergo deactivation at high temperature [29] ($\geq$553 K) due to metal sintering and their pyrophoric nature makes them undesirable for safe and efficient operation of PEM fuel cells. PdZn catalysts, on the other hand, do not have the disadvantages of Cu-based catalysts and have attracted much attention recently [9, 10, 12, 14, 30–38]. Iwasa et al. [11, 39] showed that Pd/ZnO catalysts reduced at high temperatures (>573 K) are very active and selective to H_2 and CO_2. The high catalytic performance of Pd/ZnO catalysts was attributed to the

presence of PdZn alloy, as revealed by the combination of XRD, XPS and TPR methods [9, 39]. According to Iwasa et al. [39] the PdZn alloy is formed during the reduction under H_2 at a temperature higher than 573 K. Metallic Pd°, on the other hand, predominantly produces CO and H_2 via methanol decomposition. Since their pioneering work, several papers [12, 31, 36, 40–43] have investigated the alloying effect on the reactivity of the Pd/ZnO catalysts. Chin et al. [44] studied the reactivity of a 16.7% Pd/ZnO catalyst which only has metallic Pd°. The results showed a continuous increase in methanol conversion during the first half hour to a steady state conversion of 32%. The corresponding CO selectivity decreased from 47% to 14% throughout the experiment. It was proposed that the bimetallic PdZn alloy, responsible for the activity changes, was formed under reaction conditions. In agreement with these findings, recent results from Conant et al. [45], illustrated a modification of the PdZn nanoparticle surface affected by the reducing/oxidizing environment and the reactions conditions. However, the surface compositions of either metallic Pd° or PdZn alloy under methanol steam reforming or oxidizing conditions have not been studied yet. The purpose of the present study is twofold: (1) to understand the influence of the methanol steam reforming and oxidizing conditions on the surface composition of PdZn alloy; and (2) to investigate the potential PdZn alloy formation from the metallic Pd° under methanol steam reforming conditions.

2 Experimental

2.1 Preparation of the Catalyst

An 8.8wt% $Pd/ZnO/Al_2O_3$ (Pd relative to $Pd/ZnO/Al_2O_3$) catalyst was prepared by multiple incipient wetness impregnations. Specifically, a palladium nitrate solution (4.4 wt% Pd, Aldrich) was mixed with a $Zn(NO_3)_2 \cdot 6H_2O$ (99.5%, Aldrich). The premixed Pd and Zn nitrate solution (Pd:Zn molar ratio 0.38) was added drop by drop to the alumina support (boehmite from Sasol) calcined at 1,123 K for 5 h prior to the multiple impregnations. A total of five impregnations were used. Between each impregnation step, the powder was dried at 353 K for 2 h. A Pd:Zn ratio of 0.38 was chosen since it is optimum ratio for methanol steam reforming based on our previous report [33].

2.2 Infrared Spectroscopy

IR spectra were recorded with a Nicolet Magna 750 spectrometer, equipped with a MCT detector (resolution: 4 cm^{-1}, 128 scans). The sample pressed into a pellet (ca. 30 mg for a 1.32 cm^2 pellet) was activated using two different pretreatment methods. The first pretreatment method reduces the catalyst under H_2 for 2 h at 773 K. The second pretreatment includes the calcination of catalyst under O_2 for 2 h at 773 K, followed by first cooling the sample under vacuum to 293 K and then reduced under H_2 at 293 K for 2 h. During the oxidation (or reduction) treatment, the sample was alternatively exposed to O_2 (or H_2) for 4 min and evacuated under vacuum for 2 min to simulate flow conditions. After these pretreatments, CO adsorption was conducted at 293 K. For some of the experiments, CO was then evacuated under vacuum at 623 K and a mixture of $H_2O + CH_3OH$ (molar ratio 1.8:1), was introduced into the cell for 30 min at 548 K (5 cycles: $H_2O + CH_3OH$ for 4 min and evacuation under vacuum for 2 min). This step was followed by an evacuation under vacuum at 623 K and a CO adsorption at 293 K. For each CO adsorption, 1.1 μmol of gas was introduced.

2.3 Reactivity

Methanol steam reforming activity was evaluated in a 4 mm I.D quartz tube reactor. Approximately 200 mg of catalyst was loaded between two layers of quartz wool inside the reactor. A thermocouple was placed in the middle of the catalyst bed. A pre-mixture feed of water/methanol (molar ratio of 1.8:1), was aerated through a vaporizer operating at 643 K and introduced into the reactor using a syringe pump. Nitrogen purge was fed into the system using a Brooks Mass Flow Controller (5850E series). The nitrogen consisted of 29% of the total vapor feed (molar). Total throughput was run at GHSV = 21,845 h^{-1} at a temperature of 548 K. Prior to activity tests, the catalyst was reduced in-situ under $10\%H_2/N_2$ at 623 K for 2 h. A glass condenser at 273 K was used to separate liquid products from gaseous products. The product gases, CO, CO_2 and H_2 were separated using MS-5A and PPQ columns and analyzed on-line by means of a MTI Quad Micro GC (Model Q30L) equipped with a TCD.

3 Results and Discussion

3.1 CO Adsorption

Based on our previous work [33, 40] and that of others [39], reduction temperatures higher than 573 K are sufficient to reduce the supported and unsupported Pd/ZnO to form PdZn alloy. Therefore, a PdZn alloy catalyst, designated as $PdZn/ZnO/Al_2O_3$, was obtained by reducing the 8.8% $Pd/ZnO/Al_2O_3$ catalyst under H_2 at 773 K for 2 h. To identify the surface compositions of PdZn alloy that are

prevalent under the methanol steam reforming conditions, infrared spectra of CO adsorbed on the PdZn alloy catalyst before and after the exposure to a mixture of methanol and steam at 548 K were measured and are shown in Fig. 1 (spectra a and b). To study the potential surface composition change of PdZn alloy and its correlation with the stability of PdZn alloy in the presence of O_2 under a typical methanol steam reforming temperature, infrared spectrum of CO adsorbed on PdZn alloy catalyst after the exposure to O_2 at 623 K was also measured and is included in Fig. 1 (spectrum c).

In Fig. 1, both spectra a and b are similar. They both show a main band at 2,071 cm^{-1} characteristic of linear CO adsorption. A small band between 2,000–1,800 cm^{-1}, due to multibonded CO species, is also noted. According to our previous HREELS results on the Zn/Pd(111) alloy surfaces and the FTIR results on a similar high surface area PdZn/ZnO/Al_2O_3 catalyst [38], the band situated at 2,071 cm^{-1} is ascribed to the vibration of CO linearly adsorbed on the PdZn alloy particles. It is also worth noting that the area of the band at 2,071 cm^{-1} for both spectra a and b is almost identical. Therefore, these results indicate that the surface composition of the PdZn alloy catalyst is not affected by the exposure to a mixture of methanol and steam at a typical methanol steam reforming temperature of 548 K. In other words, the surface composition of the PdZn alloy is likely the active composition for methanol steam reforming.

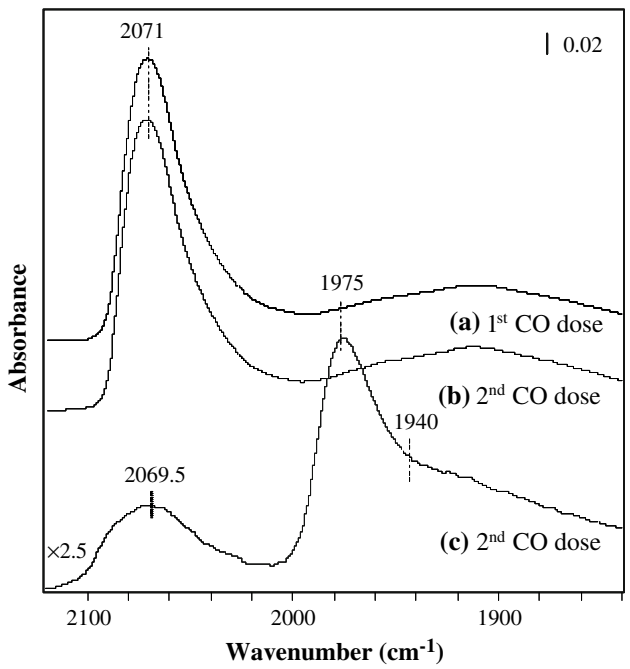

Fig. 1 FTIR spectra recorded after CO adsorption, (a) just after pretreatment under H_2, (b) after exposure to H_2O/CH_3OH and (c) after oxidation, for the PdZn/ZnO/Al_2O_3 catalyst. Spectra are normalized to a pellet of 100 mg

The spectrum c in Fig. 1 was recorded after the PdZn alloy catalyst was exposed to O_2 at 623 K. It has a main band at 1,975 cm^{-1} and a shoulder at 1,940 cm^{-1} in addition to a band at ~2,069.5 cm^{-1}, which are unlike the spectra a and b where the band at 2,071 cm^{-1} due to linear CO adsorption on PdZn alloy dominates. IR bands at similar positions were previously observed on a 2.77% Pd/Al_2O_3 catalyst (i.e. 2,069, 1,981 and 1,936 cm^{-1}) [46] and were assigned to the ν(CO) mode of CO adsorbed on Pd°. Our separate HREELS results on Pd(111) and FTIR results on a high surface area Pd catalysts also suggest that the bands at 1,975 cm^{-1} and 2,069.5 cm^{-1} are indicative of CO adsorbed in bridging and atop sties on the Pd, respectively. Therefore, we can deduce that the IR sample collected for spectrum c has the properties of metallic Pd°. Exposure of the PdZn alloy to oxygen at 623 K likely broke up the PdZn alloy to form PdO, which is known to be readily reduced to form the metallic Pd° either due to the evacuation of the IR sample at 623 K and/or because of the exposure of the IR sample to CO for the IR measurement. In other words, exposure of the PdZn alloy to oxygen under a methanol steam reforming temperature can lead to the break up of the active PdZn alloy phase to PdO, which can be readily reduced to form the metallic Pd°. As discussed above, metallic Pd° is known to dominate the decomposition of methanol.

To study the surface composition change of metallic Pd° under the methanol steam reforming reaction conditions, infrared spectra of CO adsorption on a supported metallic Pd° catalyst before and after the exposure to a mixture of methanol and steam at 548 K were measured and are shown in Fig. 2 (spectra a and b). The supported metallic Pd° catalyst, designated as Pd°/ZnO/Al_2O_3, was obtained by calcining the 8.8% Pd/ZnO/Al_2O_3 catalyst under O_2 at 773 K for 2 h followed by a reduction under H_2 at 293 K for 2 h. Based on our previous work [41] and that of others [13, 47], such a pretreatment Pd° results in the formation of a mostly metallic Pd°/ZnO/Al_2O_3 catalyst. The spectrum a in Fig. 2 has two bands at 2,062 and 1,980 cm^{-1} and a shoulder at 1,940 cm^{-1}. As discussed above on the spectrum c in Fig. 1, these bands are attributed to the vibration of CO coordinated to metallic Pd° supported on ZnO/Al_2O_3. Spectrum b in Fig. 2 recorded after introduction of the $H_2O + CH_3OH$ mixture is quite different than spectrum a. It has a main band at 2,073 cm^{-1}, characteristic of atop or linear CO adsorption, and a small band between 2,000 and 1,800 cm^{-1}, due to multibonded CO species. The band at 2,073 cm^{-1} is characteristic of bimetallic PdZn alloy, as discussed above, for spectra a and b in Fig. 1. Metallic Pd° catalyst can be formed by either a mild reduction as in the case of the Pd°/ZnO/Al_2O_3 catalyst or decomposition of PdZn alloy in the presence of O_2 followed by a mild reduction as in the case of the catalyst

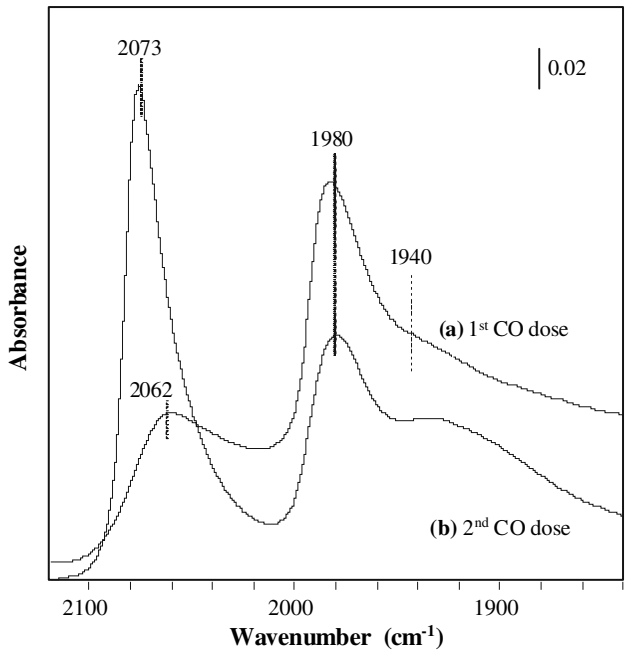

Fig. 2 FTIR spectra recorded after CO adsorption, (a) under O_2 at 773 K + H_2 at 293 K and (b) under H_2 at 773 K after exposure to H_2O/CH_3OH, for the metallic Pd°/ZnO/Al_2O_3 catalyst. Spectra are normalized to a pellet of 100 mg

measured in Fig. 1 spectrum c. The results in Fig. 2 indicate that under the methanol steam reforming conditions, metallic Pd can transform to the PdZn alloy which is the active phase for methanol steam reforming. Hydrogen produced during methanol steam reforming may facilitate the PdZn alloy formation. In our previous report, a continuous increase in methanol conversion accompanied with a continuous decrease in CO selectivity were observed on a supported metallic Pd°/ZnO catalyst [44], likely due to the PdZn alloy formation from Pd and ZnO under the methanol steam reforming conditions according to the FTIR results discussed here.

3.2 Reactivity

The above FTIR results suggest that in the presence of O_2 the active PdZn alloy phase can break up to form PdO, which is readily to be reduced to form the much less active and selective metallic Pd° while the metallic Pd° can self-repair and transform to the active PdZn alloy phase under methanol steam reforming conditions. To correlate these FTIR observations with the activity measurement, a supported PdZn alloy catalyst, PdZn/ZnO/Al_2O_3, was studied for methanol steam reforming. This catalyst was first studied in methanol steam reforming at 548 K for 2 h, then purposely exposed to an air flow at 623 K for 1/2 h, and followed by re-evaluating its methanol steam reforming activity at 548 K. Figure 3 shows the methanol conversion and CO selectivity as a function of time on stream. For the first 2 h time-on-stream (i.e. before oxidation), the CH_3OH conversion and the CO selectivity are ~77% and 2.3%, respectively, as expected from the catalytic performances on a PdZn alloy catalyst. The CO selectivity is below the equilibrium value (5.6%). These results are in agreement with the FTIR data displayed in Fig. 1a and b showing that the surface composition of PdZn alloy is not modified by the methanol steam reforming conditions.

After catalyst was exposed to air, a marked decrease in methanol conversion (60%) and an increase in CO selectivity (76%) were initially observed, which is in sharp contrast to those measured before the catalyst was exposed to air, i.e., 77% and 2.3%, respectively. The initial poor methanol conversion and CO selectivity are due to the presence of metallic Pd, which is formed from the PdZn alloy break up in the presence of oxygen followed by a mild reduction according to the FTIR results discussed above (spectrum c in Fig. 1), and metallic Pd° is well known to possess a poor methanol steam reforming activity [11, 15]. From Fig. 3 we can also see that methanol conversion increases and CO selectivity decreases with the time-on-stream. The gradual increase of the CH_3OH conversion and the corresponding decrease of the CO selectivity are attributed to the continuous formation of PdZn alloy from the metallic Pd° under methanol steam reforming as supported by the FTIR results in Fig. 2. Therefore, metallic Pd° formed due to the decomposition of PdZn alloy in the presence of oxygen can self-repair and re-form the active PdZn alloy phase under the methanol steam reforming conditions.

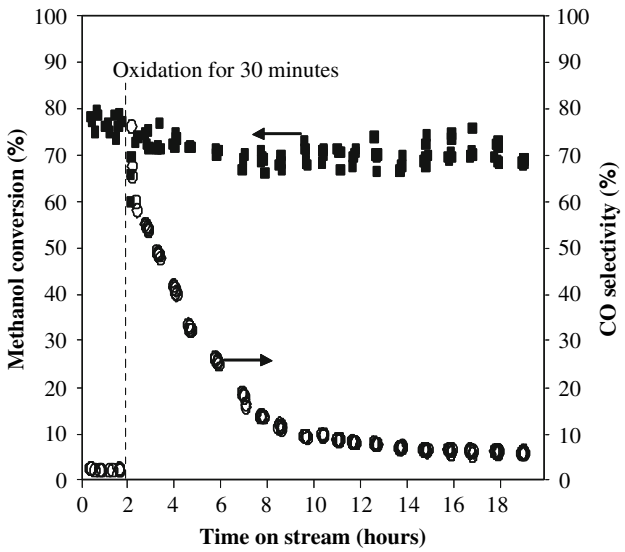

Fig. 3 Methanol conversion and CO selectivity versus time on stream (minutes) for a 8.8% Pd/ZnO/Al_2O_3 catalyst (T = 548 K, GHSV = 21,845 h^{-1})

4 Conclusion

In this study, we examined the effects of gaseous environment on the surface composition of a 8.8% Pd/ZnO/Al_2O_3 catalyst using CO-FTIR spectroscopy. The gaseous environment was chosen to simulate that during methanol steam reforming and after an accidental exposure to oxygen. It was found that the surface composition of the active PdZn alloy is not affected by the exposure to methanol steam reforming conditions, and the active phase in methanol steam reforming is likely the PdZn alloy. Exposure of the active PdZn alloy to oxygen can lead to the break up of PdZn alloy to readily reducible PdO with its metallic form being known as much less active and selective for methanol steam reforming. However, the metallic Pd° can form the active PdZn alloy phase again under the methanol steam reforming conditions.

Acknowledgments This work was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research, located at Pacific Northwest National Laboratory in Richland, WA. We greatly acknowledge funding for this work provided by the U.S. Department of Energy (Grant no. DE-FG02-05ER15712).

References

1. DIREM/Industrie pétrolière en (2005) http://www.industrie.gouv.fr/energie/petrole/textes/explo-pro-monde05.html
2. Brown LF (2001) Int J Hydrogen Energy 243:420–427
3. Rostrup-Nielsen JR (2001) Phys Chem Chem Phys 3:283–288
4. Lindström B, Pettersson LJ (2001) Int J Hydrogen Energy 26:923–933
5. Peters R, Düsterwald HG, Höhlein B (2000) J Power Sources 86:507–514
6. Yong ST, Hidajat K, Kawi S (2004) J Power Sources 131: 91–95
7. Lindström B, Pettersson LJ (2002) J Power Sources 106:264–273
8. Takahashi K, Kobayashi H, Takezawa N (1985) Chem Lett 759–762
9. Iwasa N, Mayanagi T, Nomura W, Arai M, Takezawa N (2003) Appl Catal A Gen 248:153–160
10. Iwasa N, Yoshikawa M, Nomura W, Arai M (2005) Appl Catal A Gen 292:215–222
11. Iwasa N, Kudo S, Takahashi H, Masuda S, Takezawa N (1993) Catal Lett 19:211–216
12. Ranganathan ES, Bej SK, Thompson LT (2005) Appl Catal A Gen 289:153–162
13. Takezawa N, Iwasa N (1997) Catal Today 36:45–56
14. Suwa Y, Ito S-I, Kameoka S, Tomishige K, Kunimori K (2004) Appl Catal A Gen 267:9–16
15. Iwasa N, Takezawa N (2003) Top Catal 22:215
16. Agrell J, Bigersson H, Boutonnet M (2002) J Power Sources 106:249–257
17. Pour V, Barton J, Benda A (1975) Collect Czech Chem Commun 40:2923
18. Barton J, Pour V (1980) Collect Czech Chem Commun 45:3402
19. Kobayashi H, Takezawa N, Minochi C (1981) J Catal 69:487
20. Takahashi H, Takezawa N, Kobayashi H (1982) Appl Catal 2:363
21. Santacesaria E, Carrà S (1983) Appl Catal 5:345
22. Jiang CJ, Trimm MS, Wainwright NW (1993) Appl Catal A Gen 97:145
23. Breen JP, Ross JRH (1999) Catal Today 51:521
24. Peppley BA, Amphlett JC, Kearns LM, Mann RF (1999) Appl Catal A Gen 179:21–29
25. Agarwal V, Patel S, Pant KK (2005) Appl Catal A Gen 279: 155–164
26. Yu X, Tu S-T, Wang Z, Qi Y (2005) J Power Sources 150:57–66
27. Frank B, Jentoft FC, Soerijanto H, Kröhnert J, Schlögl R, Schomäcker R (2007) J Catal 246:177–192
28. Mastalir A, Patzkó A, Frank B, Schomäcker R, Ressler T, Schlögl R (2007) Catal Commun 8:1684–1690
29. Twigg M, Spencer M (2003) Top Catal 22:192
30. Hong C-T, Yeh C-T, Yu F-H (1989) Appl Catal 48:385–396
31. Kim C-H, Lee JS, Trimm DL (2003) Top Catal 22:319
32. Cao C, Xia G, Holladay J, Jones E, Wang Y (2004) Appl Catal A Gen 262:19–29
33. Xia G, Holladay JD, Dagle RA, Jones EO, Wang Y (2005) Chem Eng Technol 28:515
34. Valdés-Solís T, Marbán G, Fuertes AB (2006) Catal Today 116:354–360
35. Lenarda M, Moretti E, Storaro L, Patrono P, Pinzari F, Rodríguez-Casellón E, Jiménez-López A, Busca G, Finocchio E, Montanari T, Frattini R (2006) Appl Catal A Gen 312:220–228
36. Dagle RA, Chin Y-H, Wang Y (2007) Top Catal. doi: 10.1007/s11244-007-9009-4
37. Palo DR, Dagle RA, Holladay JD (2007) Chem Rev accepted
38. Jeroro E, Lebarbier V, Datye A, Wang Y, Vohs J-M (2007) Surf Sci 601:5546–5554
39. Iwasa N, Masuda S, Ogawa N, Takezawa N (1995) Appl Catal A Gen 125:145–157
40. Hu J, Wang Y, Vanderwiel D, Chin C, Palo D, Rozmiarek R, Dagle R, Cao J, LHolladay J, Baker E (2003) Chem Eng J 93: 55–60
41. Chin Y-H, Dagle R, Hu J, Dohnalkova AC, Wang Y (2002) Catal Today 77:79–88
42. Karim A, Conant T, Datye A (2006) J Catal 243:420–427
43. Karim A (2006) PhD Thesis. University of New Mexico, New Mexico
44. Chin Y-H, Wang Y, Dagle R, Li XS (2003) Fuel Process Technol 83:193–201
45. Conant T, Karim A, Lebarbier V, Wang Y, Girgsdies F, Schlögl R, Datye A (2007) J Catal submitted
46. Skotak M, Karpinski Z, Juszczyk W, Pielaszek J, Kepinski L, Kazachkin DV, Kovalchuk VI, d'Itri JL (2004) J Catal 227:11–25
47. Iwasa N, Ogawa N, Masuda S, Takezawa N (1998) Bull Chem Soc Jpn 71:1451–1455