Effect of SO_2 on the oxygen storage capacity of ceria-based catalysts

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We have examined the effect of SO_2 poisoning on a series of catalysts having Pd supported on ceria, alumina, and ceria–zirconia. For pre-exposure of 20 ppm SO_2 at 673 K, we observed no changes in the light-off curves for CO oxidation on Pd/alumina. This pre-exposure of SO_2 to Pd/ceria resulted in a significant upward shift in the light-off curve, so that the poisoned Pd/ceria catalyst exhibited similar rates to that of Pd/alumina. Similar upward shifts were observed for the water–gas-shift reaction upon exposure of Pd/ceria or Pd/ceria–zirconia samples to SO_2. However, pulse-reactor data with alternating CO and O_2 pulses showed that SO_2 poisoning actually increased the amount of oxygen that could be transferred to and from the catalyst over the entire temperature range that was examined. The implication of these results for understanding the effect of SO_2 poisoning and the measurement of OSC are discussed.

Keywords: ceria, SO_2, oxygen storage capacity, CO oxidation, water–gas-shift reaction

1. Introduction

Ceria is a crucial component for automotive, three-way, emissions-control catalysis. While ceria has been shown to play a number of roles in this application, from the enhancement of water–gas-shift (WGS) activity [1] to stabilization of the alumina support [2,3], its primary function is that of providing oxygen storage capacity (OSC) [4–11]. Because three-way catalysts are not selective, it is important to maintain the air–fuel ratio at its stoichiometric value in order to simultaneously oxidize CO and hydrocarbons and reduce NO [4]. In the conventional view, the OSC component does this by releasing oxygen under rich conditions to oxidize unburned hydrocarbons and CO and taking up oxygen under lean conditions for the efficient removal of NO; however, the fact that reduced ceria is oxidized by water and CO_2 [12,13], major components in the exhaust, indicates that OSC is coupled with WGS and similar reactions.

Sulfur poisoning is a major problem in three-way catalysts. Beck and coworkers showed that CO_2, which is currently present at levels between 5 and 20 ppm in the typical exhaust, interacts strongly with the ceria in the catalytic converter and that it is this poisoning of ceria that appears to be the primary problem [14–18]. They reported that the improvement in activity found with Pd/ceria/alumina compared to Pd/alumina alone was cancelled by the addition of 30 ppm of SO_2 at 450 °C [14]. Interestingly, sulfur poisoning is reported to be partially reversible above 650 °C and its impact, at least in the short term, appears to be minimal for operation at 700 °C [16].

In the work to be described in this paper, we set out to investigate more closely the effect of SO_2 on the OSC component in three-way catalysts. In agreement with previous research, we will show that small amounts of SO_2 have a dramatic effect on the catalytic properties of ceria-supported precious metals, primarily by interacting with the ceria. What is surprising, however, is that these changes are not observed in pulse-reactor studies designed to measure the effect of oxygen storage. The results raise interesting questions for how one measures OSC and how one should view the role of ceria.

2. Experimental

The catalysts used in the experiments performed at the University of Pennsylvania were Pd supported on γ-Al_2O_3, CeO_2, and a 50 : 50 CeO_2–ZrO_2 mixed oxide. After wet impregnation to a loading of 1% Pd with $Pd(NH_4)_3(NO_3)_2$, each catalyst was dried, calcined for 2 h in flowing air at 673 K, and then pressed into wafers. The ceria and γ-Al_2O_3 samples were obtained from Alfa Aesar; the ceria–zirconia support was prepared by mixing aqueous solutions of $Ce(NO_3)_3$ and $Zr(NO_3)_2 \cdot xH_2O$, then drying and calcining in air to 673 K. BET measurements on the ceria showed that it had a surface area of 30 m^2/g. The surface areas of the ceria and the ceria–zirconia samples were also determined by measuring the gravimetric uptake of 2-propanol following exposure and evacuation at room temperature, according to procedures described elsewhere [19,20]. Assuming a saturation coverage of 5×10^{18} molecules/m^2, the surface areas were 34 m^2/g for ceria and 32 m^2/g for ceria–zirconia. Prior to the steady-state rate experiments, the wafers were reduced *in situ* in a stream of 10% CO in He at 673 K for 1 h. The catalyst used in the experiments performed at Ford Motor Company was 2% Pd supported

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on CZ3, a commercial support with a composition of 70% CeO_2 and 30% ZrO_2 [21].

The WGS and CO oxidation reactions were monitored in a $\frac{1}{4}$ inch, quartz, tubular reactor at 1 atm, using 100 mg of catalyst. Before introducing CO to the reactor, it was passed through an activated carbon trap to remove carbonyls and a NaOH trap to remove CO_2. Water was fed to the reactor by bubbling He through deionized, distilled water. For CO oxidation, the composition was 23 Torr of CO and 23 Torr of O_2, with the balance made up by the He carrier. The WGS measurements used 23 Torr CO and 17 Torr of H_2O. In all cases, we simply measured the conversion of CO, using an on-line gas chromatograph (SRI model 8610C), as we ramped the temperature, holding the total flow rate at 120 cm^3/mm. The conversions were identical for ramping the temperature up or down and no hysteresis was observed in any of the measurements. The maximum conversions were always significantly less than 100% due to channeling of reactants around the small catalyst bed.

For those experiments involving sulfur poisoning in the WGS and CO oxidation reaction measurements, the catalysts were exposed to 100 ppm of SO_2 in He at 673 K for 2 h, then cooled to room temperature in pure He, before measuring the conversions. SO_2 was not maintained in the reactant gases during the measurements.

The transient-pulse experiments at Penn and Ford were performed on similar systems that have been described in earlier papers [13,21]. In both systems, the compositions leaving the reactor were monitored by quadrupole mass spectrometers, so that the time response to step changes in the reactant compositions could be determined. Integration of the partial pressures as a function of time allowed accurate determination of the amounts of oxygen which could be added or removed at different temperatures. The carrier gas in both the Penn and Ford systems was He, with only relatively dilute amounts of CO or O_2 added in the pulses. In the poisoning studies, the He contained 20 ppm of SO_2 in the Penn experiments and 10 ppm of SO_2 in the Ford experiments [13,21]. The catalysts were exposed to the SO_2 stream for at least 2 h before beginning the pulse measurements and SO_2 was maintained in the carrier. The amounts of catalyst used were 300 mg in the work at Penn and 81 mg at Ford.

3. Results

To determine the effect of SO_2 exposures to Pd, the conversion of CO in 23 Torr each of CO and O_2 was monitored as a function of temperature on Pd/γ-Al_2O_3, before and after exposure to 100 ppm of SO_2 for 2 h, with the results shown in figure 1. The reaction "lights off" at approximately 520 K on both the clean and poisoned catalysts. The fact that there are no measurable differences in the results for the poisoned and unpoisoned catalysts indicates either that sulfur is easily removed from the Pd surface in the reaction mixture at temperatures below 520 K or that exposure of Pd to SO_2 has little effect on CO oxidation under our conditions.

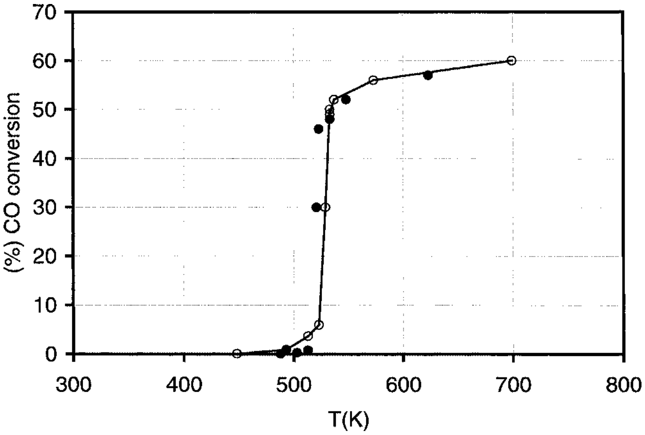

Figure 1. Light-off curves for CO oxidation on 1% Pd/alumina. Data are shown before (○) and after (●) exposure to SO_2.

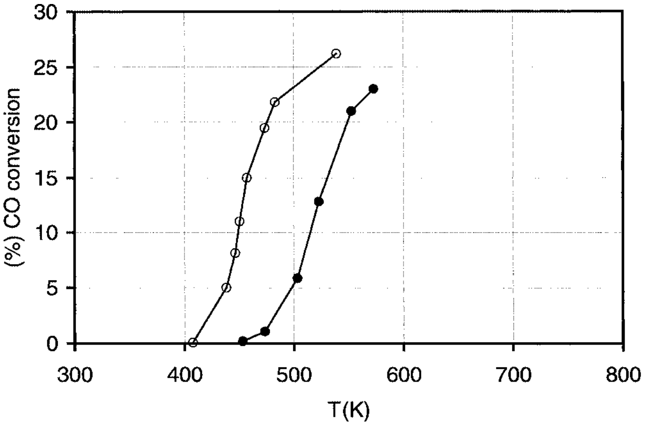

Figure 2. Light-off curves for CO oxidation on 1% Pd/ceria. Data are shown before (○) and after (●) exposure to SO_2.

Figure 2 shows the analogous light-off curves for CO oxidation on the Pd/ceria catalyst. In agreement with the work of others [11,22–24], light off of the reaction occurs at a significantly lower temperature, ~450 K, on the unpoisoned ceria-supported catalyst compared to its alumina-supported counterpart. The lower light-off temperature is likely due to a ceria-mediated reaction mechanism that is observed on ceria-supported catalysts [25–27]. This second mechanism, which involves oxygen from ceria reacting with CO adsorbed on the metal, has been shown to have a lower activation energy than the normal oxidation of CO on group VIII metals, where CO and oxygen adsorb competitively. Upon poisoning the catalyst with SO_2, the light-off temperature shifts up to ~520 K, the same temperature observed for Pd/γ-Al_2O_3. The obvious interpretation of the data in figure 2 in light of the results for Pd/γ-Al_2O_3 is that sulfur poisoning prevents ceria from transferring oxygen to the metal, so that only the Pd function is observable. The oxidation–reduction properties of ceria probably allow the SO_2 to be oxidized to sulfate groups on the ceria surface, and these sulfate groups either block oxygen trans-

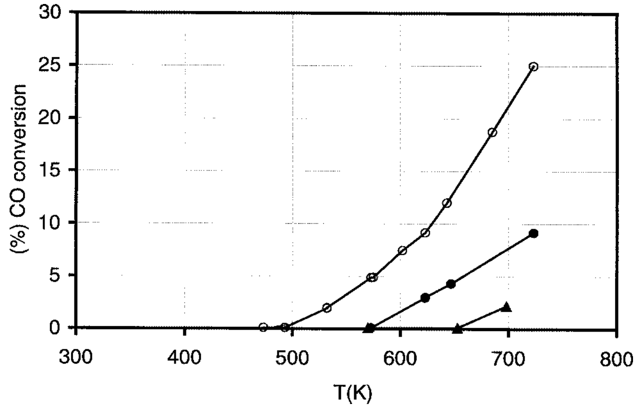

Figure 3. Light-off curves for the water–gas-shift reaction. Data are shown for 1% Pd/alumina (▲) and for 1% Pd/ceria before (○) and after (●) exposure to SO_2.

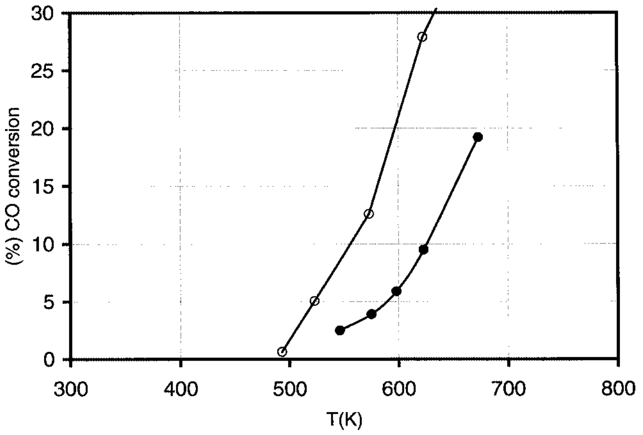

Figure 4. Light-off curves for the water–gas-shift reaction on Pd/ceria–zirconia. Data are shown before (○) and after (●) exposure to SO_2.

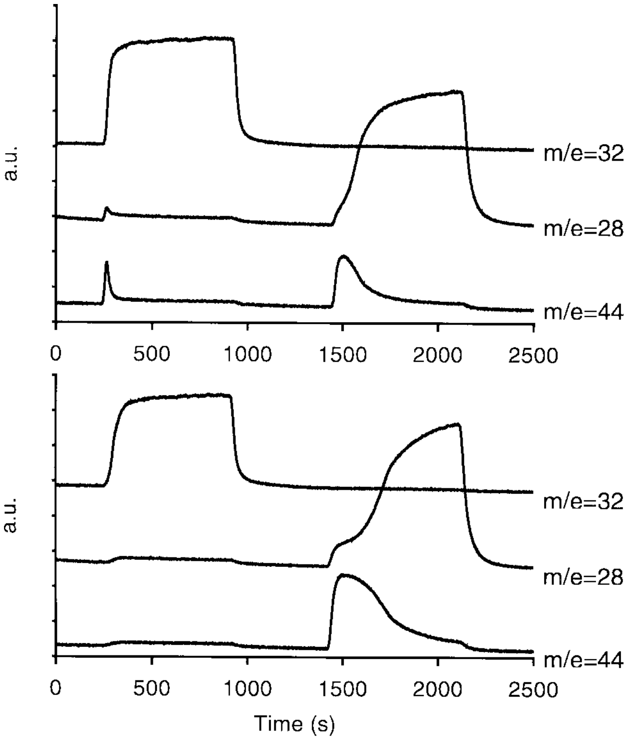

Figure 5. Results from the pulse-reactor data for O_2 and CO pulses at 773 K on the 1% Pd/ceria–zirconia catalyst, before an after exposure to SO_2. The data are part of a series of identical O_2 ($m/e = 32$) and CO ($m/e = 28$) pulses, so that the observed oxidation and reduction of the catalyst was reversible. In the top set of data taken before SO_2 exposure, a sharp CO_2 ($m/e = 44$ and 28) peak is observed upon exposure to O_2 and significantly more CO_2 was formed upon introduction of CO. The lower set of data shows the analogous results with 20 ppm of SO_2.

fer or prevent the oxidation and reduction of ceria. We have found that the poisoned catalyst can be restored to its initially active state in air, but only after above 950 K. High-temperature reduction can reactivate ceria-supported catalysts at somewhat lower temperatures, but not below 700 K [14–17].

Figures 3 and 4, which show conversion data for CO in WGS, lead to similar conclusions about the state of the catalyst. The data for figure 3 were obtained on Pd/alumina and on the Pd/ceria catalysts before and after poisoning with SO_2. Not surprisingly, Pd/alumina shows essentially no activity, even at the highest temperatures. By contrast, rates on Pd/ceria become significant above 500 K. Mechanistic studies of WGS on Pd/ceria suggested that the reaction involves oxidation of CO using oxygen from ceria and reoxidation of ceria by water [28,29]. Exposure of the catalyst to SO_2 shifts the conversion curve to much higher temperatures, by 50–100 K. The results are therefore consistent with the mechanism in which poisoning with SO_2 inhibits the ability of ceria to donate oxygen for the reaction of CO, leading to a significant increase in the temperature at which the reaction rates become important. Figure 4, which provides the analogous WGS data for Pd/ceria–zirconia, shows similar results, although the activity of this catalyst is higher than that of Pd/ceria. This is in agreement with the conclusion that rates for oxygen transfer are higher on Pd/ceria–zirconia compared to that on Pd/ceria [21].

Since SO_2 appears to affect the ability of ceria to donate oxygen, we examined OSC on various catalysts using the pulse-reactor systems. Examples of the raw data for the Pd/ceria–zirconia measurements performed at Penn are shown in figure 5 for 773 K, with data for the unpoisoned catalyst shown on top and data for the poisoned catalyst on the bottom. Here, we only show two pulses of O_2 ($m/e = 32$) and CO ($m/e = 28$) from a long string of essentially identical, alternating pulses. Data for the pulse measurements at Ford were qualitatively similar, although the amounts on the commercial support were significantly larger. In the top figure for Pd/ceria–zirconia, one observes a sharp CO_2 peak ($m/e = 44$), corresponding to 100 μmol/g, upon introduction of O_2 following a CO pulse. A similar, but larger, CO_2 peak was observed in alternating CO–O_2 pulses over Pd/ceria; interestingly, no CO_2 peak was observed upon the introduction of O_2 over a Pd/zirconia [13]. The CO_2 desorption event on Pd/ceria during the O_2 pulse was interpreted as resulting from the decomposition of surface carbonates that are only stable on reduced ceria, but not on zirconia or oxidized ceria [13]. Based on these results, we suggest that the smaller amount of CO_2 formed by the introduction of O_2 for Pd/ceria–zirconia is due to the fact that less ceria is present on the surface of the mixed oxide. Upon introduction of CO at 1500 s, much more CO_2 is formed, approximately 700 μmol/g, due to reduction of the oxidized support. As stated above, the oxidation–reduction cycle in this pulse sequence was completely reversible.

After introduction of SO_2, no CO_2 peak was observed upon the introduction of O_2, probably because sulfate species prevent formation of a surface carbonate. However, the amount of CO_2 formed upon pulsing CO increases dramatically, from 700 to 1000 μmol/g. In the experiments carried out at Ford, both the amount of CO_2 formed upon pulsing CO and the amount of oxygen consumed in the subsequent O_2 pulse also increased with the addition of SO_2. A likely explanation for the increased amount of oxygen which can be added and removed from the poisoned catalyst involves oxidation and reduction of sulfate species. For a catalyst with 30 m^2/g of surface area, 250 μmol/g corresponds to 5×10^{18} oxygen atoms/m^2, which could reasonably be expected for a monolayer coverage of the sulfate.

We did not attempt to fit the shapes of the pulses; however, it does not appear that there are significant differences in the "apparent" rates observed in the CO_2 evolution from the poisoned and unpoisoned catalysts. Because transient pulse data, like data for temperature-programmed desorption from porous materials [30,31], is complex and depends on rates of diffusion, adsorption, and dispersion, one should not draw the conclusion that the rates of intrinsic, surface processes are unaffected by the presence of sulfates.

The temperature dependence for the amount of oxygen transferred in the CO–O_2 pulses is shown in figure 6 for both the Penn (lozenges) and the Ford (circles) data, with and without poisoning. In the Penn experiments, the data show that the oxygen transferred on the poisoned catalyst is higher at all temperatures, so that the increased oxygen in figure 5 is not simply an artifact of the temperature conditions we used to make the measurements. The data taken on the commercial support at Ford shows a similar increase in the oxygen transfer for the sulfated sample at high temperatures, although the unpoisoned catalyst actually transfers slightly more oxygen at the lower temperatures. If one assumes that the slope of the lines in figure 6 provides an "activation energy" for oxygen storage, the activation energy for oxygen transfer is lower for the unpoisoned catalyst. (Since oxygen transfer in our measurements is not a rate, the "apparent activation energy" must be viewed cautiously.) This may suggest that sulfate species provide an increased barrier to removing oxygen, although a significant amount of oxygen can still be transferred at the lowest temperatures of our measurements in both the Penn and Ford studies.

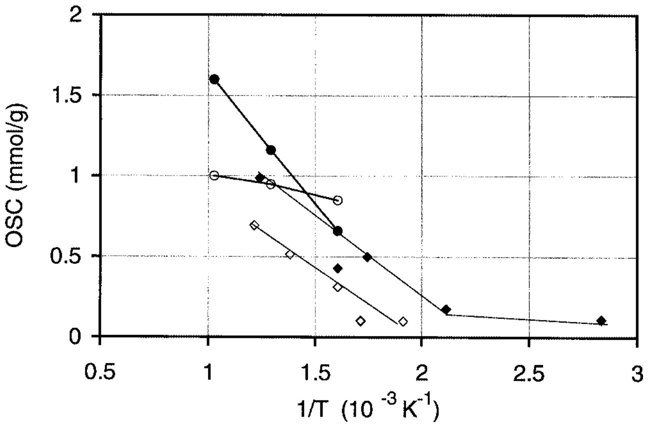

Figure 6. The reversible oxygen transferred in the pulse studies as a function of temperature. The data shown were taken at Penn on the 1% Pd/ceria–zirconia before (◇) and after (◆) SO_2 exposure and at Ford on the 2% Pd/CZ3 before (○) and after (●) SO_2 exposure.

4. Discussion

It is well known that SO_2 poisoning in automotive three-way catalysts severely affects the catalytic properties of the precious-metal catalysts, primarily by interacting with the oxygen-storage component. The shift in the light-off curves for both CO oxidation and WGS upon pre-exposure to SO_2 simply confirms this. It was, perhaps, somewhat unanticipated that SO_2 does not affect Pd/alumina, at least for CO oxidation under the conditions of our measurements; but this result further emphasizes that sulfur has its primary effect on ceria.

What is most surprising is the fact that the pulse measurements show an actual *increase* in the amount of oxygen transferred in the catalysts containing ceria and that this increase is observed even in the temperature range in which reaction measurements show severe deactivation. This apparent discrepancy can be rationalized by assuming that some of the oxidation and reduction in the poisoned catalyst is due to redox of a sulfate species and that the *rate* of oxygen transfer is much slower for the sulfated catalyst than it is for the unpoisoned sample. In the CO oxidation and WGS measurements, the rate can be no faster than this transfer of oxygen for the ceria-mediated rate processes. However, the pulse measurements are unable to measure the rate of this transfer process. A mathematical model to completely describe the transient kinetics in a pulse reactor would be very similar to that used to describe temperature-programmed desorption (TPD) from a packed bed [30,31], with the exception of the initial conditions. Analysis of TPD from a packed bed demonstrates that diffusion, dispersion, and adsorption are coupled to the desorption process, so that obtaining rates for the intrinsic surface properties is essentially impossible. The fact that the shape of the CO_2 peak in the pulse data does not change with SO_2 poisoning suggests that the rate-limiting step is not that of oxygen transfer.

While one can rationalize the pulse-reactor data by arguing that oxidation and reduction involve the sulfate species, the implications of these results could be very important for understanding OSC and for the characterization methods that we use to compare materials. The poisoned samples obviously do not have better OSC than the unpoisoned samples. While pulse-reactor measurements are not common, temperature-programmed reduction (TPR) measurements are commonly used to measure OSC. However, one can view the TPR data as being analogous to the differential with respect to temperature of the OSC measured in the pulse reactor. The fact that OSC in our measurements was higher for the sulfated catalyst at all temperatures indicates that there should be no upward shift in the TPR peak temperatures and no decrease in the area of the TPR peaks.

Based on the fact that the WGS data relates so well with what we would expect the catalytic performance of these materials to be, we suggest that light-off curves for WGS may be a very effective means for initial screening of catalysts. Ultimately, of course, only testing under realistic conditions which capture the cyclic changes in concentration of the exhaust and include all of the components of that exhaust can really be used to describe the catalytic performance.

5. Conclusion

Poisoning of automotive, three-way catalysts by SO_2 occurs primarily through formation of sulfate species on the oxygen-storage component. These sulfate species can undergo oxidation and reduction in the same temperature range as that observed for ceria or ceria–zirconia supports; however, the rate of oxygen transfer, as measured by CO oxidation and water–gas-shift reaction rates is significantly decreased by the presence of sulfate species.

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References

[1] T. Shido and Y. Iwasawa, J. Catal. 136 (1992) 493.
[2] B. Harrison, A.F. Diwell and C. Hallett, Platinum Metals Rev. 32 (1988) 73.
[3] M. Ozawa and M. Kimura, J. Mater. Sci. Lett. 9 (1990) 291.
[4] R.W. McCabe and J.M. Kisenyi, Chem. Ind. 15 (1995) 605.
[5] K. Otsuka, M. Hatano and A. Morikawa, J. Catal. 79 (1983) 493.
[6] H.S. Gandhi and M. Shelef, Stud. Surf. Sci. Catal. 30 (1987) 199.
[7] R.K. Herz and J.A. Sell, J. Catal. 94 (1985) 199.
[8] G.B. Fisher, J.R. Theis, M.V. Casarella and S.T. Mahan, SAE Paper No. 931034 (1993).
[9] J.G. Nunan, H.J. Robota, M.J. Cohn and S.A. Bradley, J. Catal. 133 (1992) 309.
[10] M. Shelef and G.W. Graham, Catal. Rev. Sci. Eng. 36 (1994) 433.
[11] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439.
[12] T. Jin, T. Okuhara, G.J. Mains and J.M. White, J. Phys. Chem. 91 (1987) 3310.
[13] S. Sharma, S. Hilaire, J.M. Vohs, R.J. Gorte and H.-W. Jen, J. Catal. 190 (2000) 199.
[14] D.D. Beck, J.W. Sommers and C.L. Dimaggio, Appl. Catal. B 3 (1994) 205.
[15] D.D. Beck, J.W. Sommers and C.L. Dimaggio, Appl. Catal. B 11 (1997) 273.
[16] D.D. Beck and J.W. Sommers, Appl. Catal. B 6 (1995) 185.
[17] D.D. Beck, Catalyst Deactivation 111 (1997) 21.
[18] D.D. Beck and J.W. Sommers, Catalyst and Automotive Pollution Control III 96 (1995) 721.
[19] C.R. Narayanan, S. Srinivasan, A.K. Datye, R.J. Gorte and A. Biaglow, J. Catal. 138 (1992) 659.
[20] A.I. Biaglow, R.J. Gorte, S. Srinivasan and A.K. Datye, Catal. Lett. 13 (1992) 313.
[21] H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.-P. Cuif, S.E. Deutsch and O. Touret, Catal. Today 50 (1999) 309.
[22] M.F. Luo and X.M. Zheng, Appl. Catal. A 189 (1999) 15.
[23] C.H. Lee and Y.W. Chen, Ind. Eng. Chem. Res. 36 (1997) 1498.
[24] M. Fernandez-Garcia, A. Martinez-Arias, L.N. Salamanca, J.M. Coronado, J.A. Anderson, J.C. Conesa and J. Soria, J. Catal. 187 (1999) 474.
[25] H. Cordatos, T. Bunluesin, J. Stubenrauch, J.M. Vohs and R.J. Gorte, J. Phys. Chem. 100 (1996) 785.
[26] E.S. Putna, T. Bunluesin, X.L. Fan, R.J. Gorte, J.M. Vohs, R.E. Lakis and T. Egami, Catal. Today 50 (1999) 343.
[27] G.S. Zafiris and R.J. Gorte, J. Catal. 143 (1993) 86.
[28] T. Bunluesin, R.J. Gorte and G.W. Graham, Appl. Catal. B 15 (1998) 107.
[29] C. Padeste, M.W. Cant and D.L. Trimm, Catal. Lett. 18 (1993) 305.
[30] R.J. Gorte, J. Catal. 75 (1982) 164.
[31] R.A. Demmin and R.J. Gorte, J. Catal. 90 (1984) 32.