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Investigation of La^{3+}-modified Al_2O_3-supported CeO_2

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X-ray photoelectron spectroscopy measurements indicate that the Ce^{3+} fraction in Al_2O_3-supported CeO_2 can be decreased by the incorporation of La^{3+}. If La^{3+} is incorporated into the Al_2O_3 before CeO_2 is added, a higher CeO_2 dispersion and a greater range of reversible reducibility of the CeO_2 may also be obtained. These changes offer potential for improvement in the oxygen storage capacity provided by CeO_2 in three-way catalysts.

Keywords: Lanthana-modified alumina; alumina-supported ceria; oxygen storage; three-way catalyst; X-ray photoelectron spectroscopy

1. Introduction

It is well known that the addition of ceria (CeO_2) to automotive-exhaust-gas catalysts improves both performance and durability. A portion of this improvement in performance is thought to result from the ability of CeO_2 to easily undergo partial reduction and reoxidation, which thereby enlarges the window for three-way operation by providing a buffer against fluctuations in air-to-fuel ratio [1]. Reactions which transform CeO_2 into other more stable compounds, such as $CeAlO_3$, for example, would be expected to adversely affect such behavior by fixing one oxidation state.

The reaction between CeO_2 and Al_2O_3 to form $CeAlO_3$ normally requires a high-temperature reducing environment. According to Shyu et al., however, the high-temperature requirement is relaxed for small CeO_2 particles supported on γ-Al_2O_3 [2]. Furthermore, Shyu et al. also concluded that a sizable fraction of the cerium ions obtained upon the preparation of such a highly dispersed system is already in the trivalent state, even though the final step is calcination. Shyu et al. refer to this Ce^{3+} fraction as the $CeAlO_3$ precursor because it can be reduced to $CeAlO_3$ even more easily than the small CeO_2 particles on Al_2O_3.

In view of these results, a high CeO_2 dispersion on γ-Al_2O_3 would appear to be undesirable.

On the other hand, highly dispersed CeO_2, if it could be prevented from reacting with Al_2O_3, should favor faster and more complete oxygen exchange. Indeed, Nunan et al. have found that decreasing the CeO_2 crystallite size in Ce-containing three-way catalysts increases the activity [3]. A means of inhibiting the interaction between CeO_2 and Al_2O_3 responsible for the $CeAlO_3$ precursor as well as the formation of $CeAlO_3$ under reducing conditions would thus be desirable. To this end, the addition of La^{3+} as an Al_2O_3 modifier has been proposed, the idea being simply that these ions might block the reaction between Al_2O_3 and CeO_2 which leads to the stabilization of Ce^{3+} [4].

This same approach has also been applied to the problem of the loss of Rh activity, which appears to involve a reaction between Al_2O_3 and Rh_2O_3 under high-temperature oxidizing conditions [5]. It was found, however, that La^{3+} can also combine with Rh_2O_3, rendering the catalyst even less active. The possibility of La^{3+} combining with CeO_2 also exists, but in this case the result may be positive if extrinsic oxygen vacancies created by substitution of La^{3+} for Ce^{4+} in CeO_2 can improve the rate of oxygen exchange [6].

There is evidence, however, that the potential benefit of adding La^{3+} to CeO_2 may be negated by a surface effect. Shelef et al. found that when thin films of La_2O_3 are deposited on top of thin films of TiO_2, Nb_2O_5, or CeO_2, the reducibility of these latter oxides is impeded, apparently due to an effective blocking of the reducible-oxide surfaces [7]. The recent findings of Kubsh et al. of reduced three-way activity for catalysts made with La-stabilized CeO_2 when treated in such a way as to cause surface segregation of La^{3+} may possibly be explained in such terms [8]. Indeed, the propensity of La^{3+} from an aqueous solution of $La(NO_3)_3$ to spread over, or wet, the surface of γ-Al_2O_3 is well known [9], and similarly, La^{3+} may also tend to cover the surface of a reducible oxide.

The net result of combining La^{3+} with a mixture of CeO_2 and Al_2O_3 is thus not easy to anticipate. It has been observed, however, that the dispersion of La^{3+} on γ-Al_2O_3 is significantly greater than that of $Ce^{(4,3)+}$ upon impregnation from aqueous nitrate solutions [10]. In addition, Shelef et al. also found that high-surface-area Al_2O_3 competes reasonably well with CeO_2 for La^{3+}, even when the CeO_2 is sandwiched between films of Al_2O_3 and La_2O_3 [7]. These two bits of information suggest that it may indeed be possible to protect CeO_2 from reaction with Al_2O_3 and yet limit the risk of blocking the CeO_2 surface by incorporating La^{3+} into the Al_2O_3 first and then adding CeO_2.

In this investigation, an attempt was made to assess some of these ideas using typical catalyst material and preparation procedures. In particular, the effects of impregnation order and oxidation/reduction treatments on the cerium oxidation state in La^{3+}-modified γ-Al_2O_3-supported CeO_2 were investigated using X-ray photoelectron spectroscopy.

2. Experimental

Four different samples were made by impregnation of γ-Al_2O_3 with various combinations of cerium and lanthanum nitrate solutions. The first contained only cerium at a nominal CeO_2 loading of 5 wt%, and the second, third, and fourth contained both cerium at a nominal CeO_2 loading of 5 wt% and lanthanum at a nominal La_2O_3 loading of 10 wt%. These particular loadings were chosen because they correspond to the transition in each case from highly dispersed to bulk forms of the rare-earth oxides on γ-Al_2O_3 (for γ-Al_2O_3 having a surface area of about 100 m^2/g) [2,11]. In the second and third samples, the impregnations were performed separately, first lanthanum and then cerium in the second sample and the reverse order in the third sample, with a cycle of drying and calcination at 450°C between impregnations. In the fourth sample, lanthanum and cerium were coimpregnated. After the final impregnation, all samples were dried and calcined at 450°C. Portions of each sample were pressed into pellet form (6 mm diameter, ≈ 1 mm thick) for subsequent treatment and analysis.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an M-Probe system manufactured by Surface Science Instruments/VG-Fisons, Mountain View, CA. Monochromatic Al Kα radiation (1486.6 eV), focussed to a 800 μm diameter spot and operated at 85 W, was used for all analyses. The analyzer was operated at a 150 eV pass energy for the acquisition of survey spectra, and a 50 eV pass energy during the acquisition of all high-resolution core level spectra. A low-energy flood gun and Ni charge neutralization screen were utilized to minimize charging effects. The base pressure of the spectrometer was 2×10^{-9} Torr. Core–level binding energies were referenced relative to the Al 2p line at 74.2 eV.

The data system used was also supplied by the instrument manufacturer. Atomic Ce/Al and La/Al ratios used for quantitation were obtained by integration of the Ce 3d, La 3d, and Al 2p spectra, with appropriate corrections made for photoionization cross-sections. An assessment of the relative amount of Ce^{4+} present in the samples was performed by measuring the area under the u‴ peak, denoted in fig. 1, relative to the total area under the Ce 3d spectral envelope, as described in greater detail below. Due to the proximity of the La 3d and Ce 3d regions, the background in the vicinity of the Ce 3d region slopes precipitously when La is present, thus rendering an evaluation of the u‴ peak area difficult when the relative Ce spectral intensity is low. To facilitate a more accurate measurement of the peak areas, a 5th degree polynomial was fitted to the background, which was subsequently subtracted from all the Ce 3d spectra. The Ce 3d spectra acquired for all samples, including those without La (and those used for fig. 1), were treated equivalently.

A PHI model 04-800 Catalytic Reactor System, attached directly to the sample preparation chamber, was used for in situ oxidation and reduction

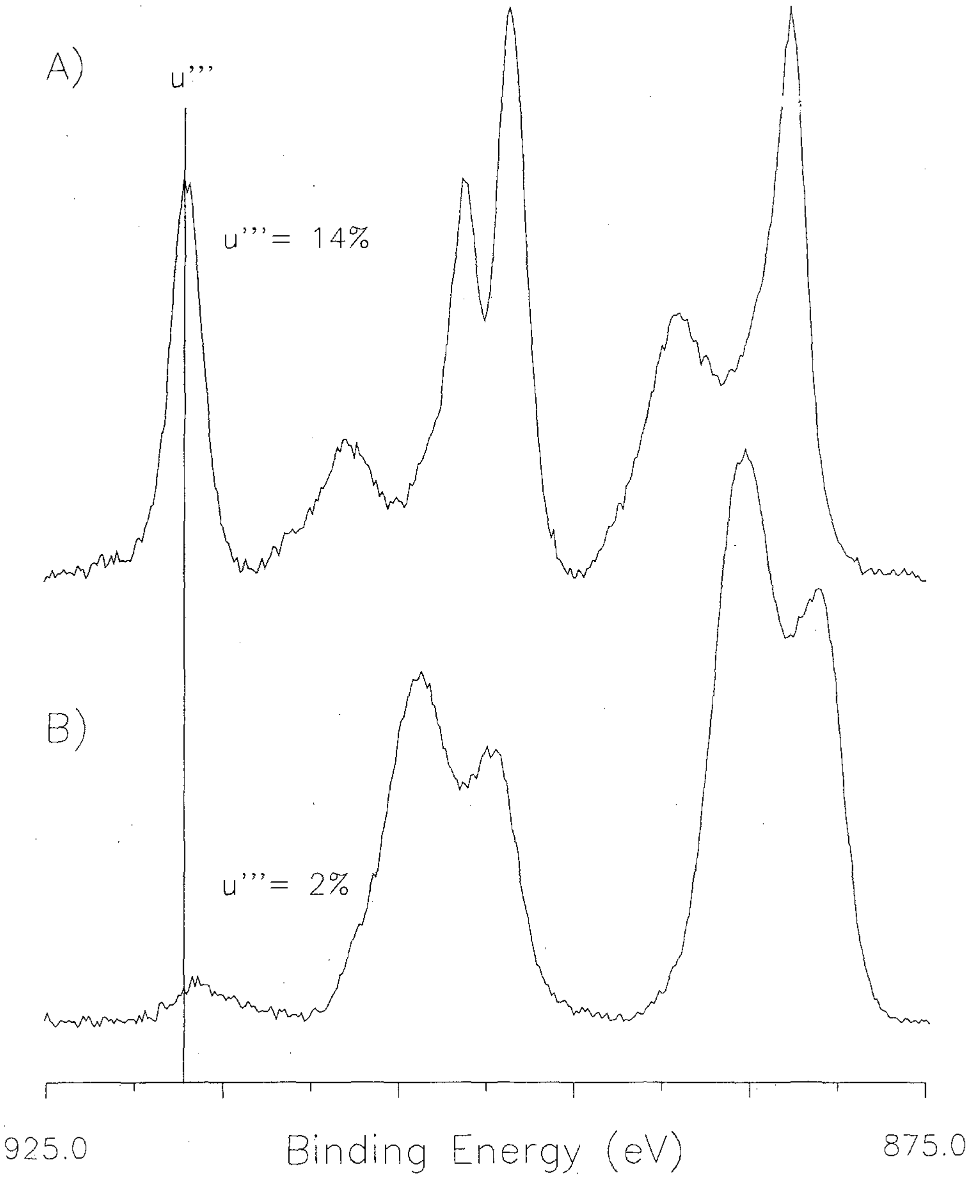

Fig. 1. Ce 3d spectra from thin films of oxidized cerium on sapphire [7]: (A) CeO_2 and (B) Ce_2O_3.

treatments. The base pressure of the preparation chamber and reactor were 1×10^{-9} Torr and 1×10^{-8} Torr, respectively. The reactor gases, obtained from Matheson, were O_2 (99.98%) for oxidation and H_2 (99.9995%) for reduction. Each treatment consisted of exposure to 1 atm of a given gas at a flow rate of about 100 cm^3/min at a given temperature for 1 h. Initially, the samples were oxidized at 450°C in order to reduce outgassing and to remove carbon contamination. Subsequently, the samples were reduced at 600°C and then oxidized at

25°C. XPS measurements were performed following each treatment after first transferring the samples from the reactor to the analyzer in vacuo in order to prevent contamination or oxidation due to air exposure.

3. Results and discussion

Examination of the survey spectra acquired following in situ oxidation and reduction treatments revealed the presence of Ce, La, Al, and O; no other elements were present at a detectable level. The Ce/Al and La/Al atomic ratios are summarized in table 1. A comparison of the Ce/Al ratio from the first sample, containing no La, with the La/Al ratio from any of the other samples, shows that the La/Ce ratio for these oxides in their highly dispersed forms is between 2 and 3, taking into account the difference in loadings. (The ratio of La/Al to Ce/Al is about 0.12 to 0.024, or 5 to 1, whereas the La/Ce ratio based on the loadings is only about 2 to 1.) This result is consistent with previous observations of the greater tendency of La^{3+} than $Ce^{(4,3)+}$ to disperse on γ-Al_2O_3 upon impregnation from aqueous nitrate solutions [10]. The Ce/Al ratios vary from sample to sample. The ratio measured for the first sample is somewhat larger than that based on the loading, 0.015, whereas the ratios for the third and fourth samples are somewhat smaller, possibly due to partial covering of Ce by La. The ratio measured for the second sample is about three

Table 1
Ce/Al and La/Al ratios

	Ce/Al	La/Al
sample 1 (CeO_2/Al_2O_3)		
calcined (450°C)	0.024	
reduced (H_2/600°C)	0.021	
reoxidized (O_2/25°C)	0.027	
sample 2 ($CeO_2/La_2O_3/Al_2O_3$)		
calcined	0.040	0.11
reduced	0.054	0.11
reoxidized	0.051	0.12
sample 3 ($La_2O_3/CeO_2/Al_2O_3$)		
calcined	0.015	0.12
reduced	0.018	0.12
reoxidized	0.020	0.12
sample 4 ($La_2O_3+CeO_2/Al_2O_3$)		
calcined	0.011	0.12
reduced	0.006 [a]	0.11
reoxidized	0.016	0.12

[a] Large experimental uncertainty in this value due to interference from the Ni screen.

times that based on the loading, however. This probably corresponds to a significant reduction in the size of CeO_2 particles which results from the initial incorporation of La^{3+}. Such behavior has also been observed in both XRD and Raman measurements from similar samples [12].

The u‴ peak in the Ce 3d spectrum has previously been used to assess the oxidation state of cerium [2,7,13,14]. For CeO_2, which contains only Ce^{4+}, the contribution of u‴ to the total area under the Ce 3d spectral envelope is 13–14%, and for the sesquioxide (Ce_2O_3), which contains only Ce^{3+}, it approaches 0%. This is shown in fig. 1 with reference spectra [7] of oxidized and partially reduced films of cerium on sapphire, which are representative of Ce^{4+} and Ce^{3+}, respectively. In the work of Shyu et al., it was assumed that the relative magnitude of u‴ and the $Ce^{4+}/(Ce^{3+} + Ce^{4+})$ ratio are directly proportional, and the percent contribution of u‴ was used to assess the extent of $CeAlO_3$ (and the $CeAlO_3$ precursor) formation [2]. The same assumption is made in the present investigation, although questions raised recently about the nature of the Ce^{3+} fraction cast some doubt on its validity [15].

The Ce^{3+} fraction was thus found to vary both from sample to sample and with the kind of treatment. The Ce 3d spectra acquired after the initial oxidation treatment, for example, are shown in fig. 2. The contribution of u‴ for the first sample, containing no La^{3+}, is $10 \pm 1\%$, substantially lower than the 14% found for CeO_2. This is consistent with the results of Shyu et al. in that a significant fraction of the cerium ions already appears to be in the trivalent state prior to any reduction treatment [2]. All of the samples containing La^{3+} have a higher percentage of Ce^{4+} than the sample without La^{3+}. Furthermore, the percent contribution of u‴ is roughly independent of the order of impregnation. (Although the signal-to-noise ratio of the spectra obtained for the third and fourth samples is lower than for the second sample, due to the apparent attenuation of the Ce 3d signal by the La as well as the background contribution from the La 3d region as mentioned previously, the spectral features from the third and fourth samples are comparable with those from the second sample.)

It was hoped that the extent to which La^{3+} is able to interfere with the formation of $CeAlO_3$ under reducing conditions would be evident from the degree to which the percent contribution of u‴ can be reversibly cycled with alternate reduction and oxidation treatments. Conditions for the reduction treatment were chosen in order to attain complete reaction of the highly dispersed CeO_2 which is free to combine with Al_2O_3 to form $CeAlO_3$ [2]. Unfortunately, this treatment may also be harsh enough to partially reduce any CeO_2 for which the surface has been blocked by La^{3+} [7]. During the reduction treatment, then, all CeO_2 and any of the $CeAlO_3$ precursor present should be converted to Ce_2O_3 and/or $CeAlO_3$ [2]. In order to differentiate the Ce_2O_3 from the $CeAlO_3$, subsequent oxidation was performed at 25°C with the expectation that the Ce_2O_3 will be converted back to CeO_2 while the $CeAlO_3$ will be unaffected [2]. This “quasi-cycle” thus should allow for the effect of La^{3+} on the

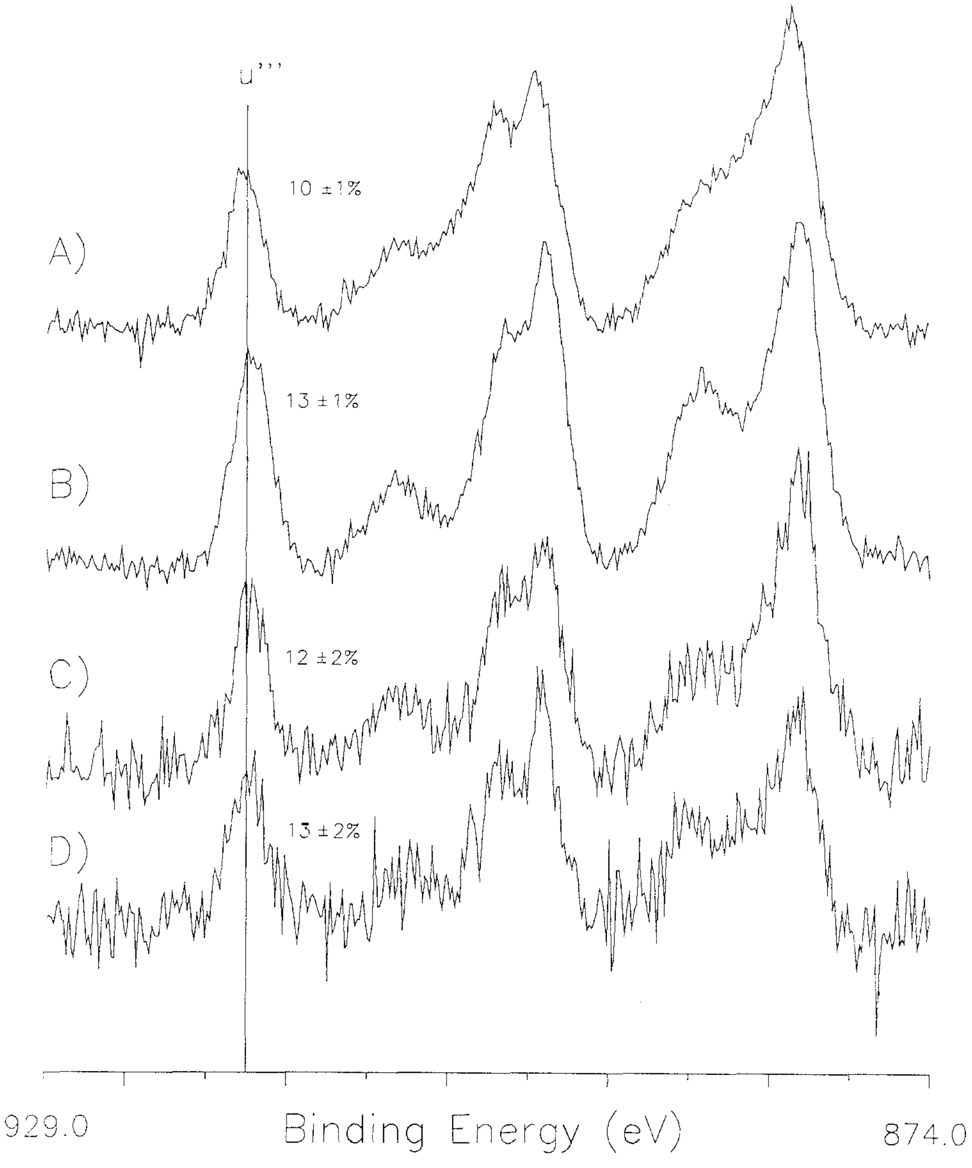

Fig. 2. Ce 3d spectra from samples calcined at 450°C: (A) sample 1 (CeO_2/Al_2O_3), (B) sample 2 ($CeO_2/La_2O_3/Al_2O_3$), (C) sample 3 ($La_2O_3/CeO_2/Al_2O_3$), and (D) sample 4 ($La_2O_3+CeO_2/Al_2O_3$).

reversible reducibility of the CeO_2 to be assessed, although without discriminating against the potential effect of La^{3+} which might be blocking the surface of CeO_2. Further investigation of this latter effect may be possible by means of additional, milder reduction treatments.

As shown in fig. 3, substantial reduction occurred in all the samples, the most in the case of the second sample for which the potential effect of La^{3+} which

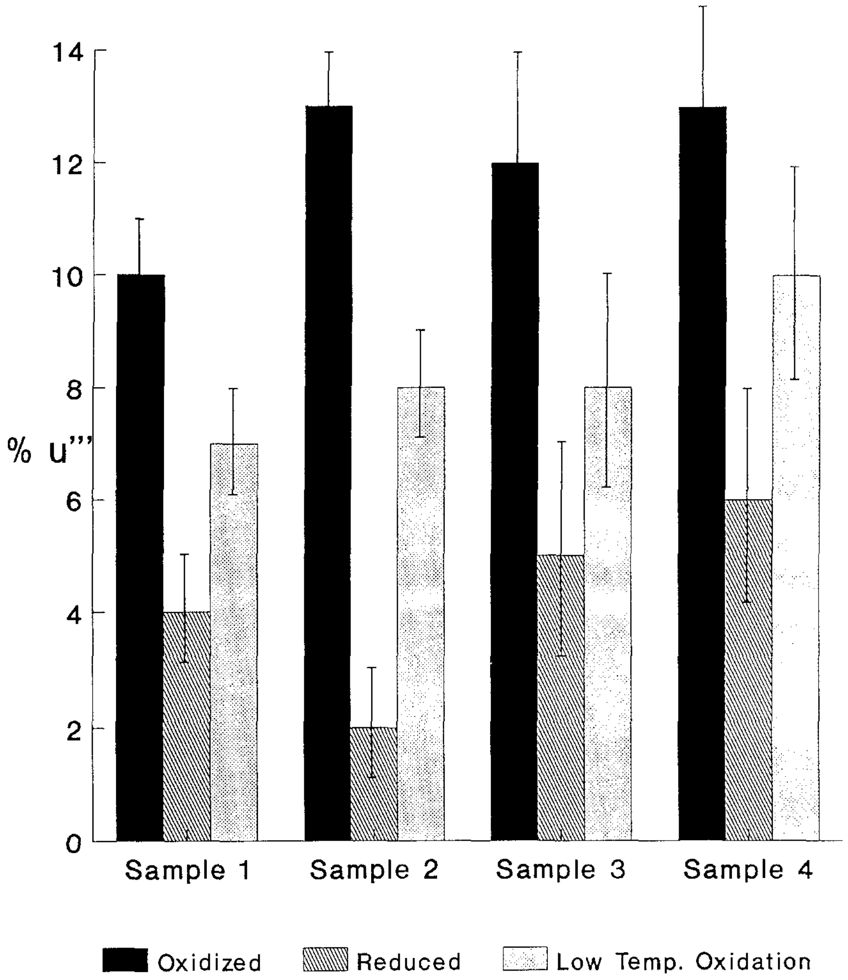

Fig. 3. u''' for each sample following the various treatments.

might be blocking the surface of CeO_2 should be minimal. The larger values of the percent contribution of u''' following reduction in the cases of the third and fourth samples may reflect incomplete reduction due to this effect, but they may also be the result of error in the area measurement of the u''' peak due to the lower signal-to-noise ratio in these spectra. Neither of these explanations would apply to the first sample, however, where the value of 4% indicates that some of the CeO_2 has not been reduced to Ce_2O_3. In this case, it may be that some CeO_2 has become inaccessible through redistribution of Al_2O_3 during impregnation with the cerium nitrate solution. (Such phenomena could also influence the apparent effects of La^{3+} in the other samples.) Another possibility is that all of the CeO_2 was in fact reduced to Ce_2O_3, but that some reoxidization occurred during transfer between the reactor and the analysis chamber. Upon subsequent oxidation at 25°C, the percent contribution of u''' increases for all samples, although it does not return to its initial value in any case. The largest changes in this quantity between successive treatments, particularly between reduction and low-temperature oxidation, corresponding to the greatest absolute amount of oxygen exchange, occur for the second sample.

Analogous measurements were also carried out on a complementary set of samples with nominal loadings of 10 wt% CeO_2 and 10 wt% La_2O_3, and all observations were consistent with those reported here for the lower CeO_2 loading.

4. Conclusions

Results of this investigation indicate that the Ce^{3+} fraction in Al_2O_3-supported CeO_2 can be decreased by the incorporation of La^{3+}. If La^{3+} is incorporated into the Al_2O_3 before CeO_2 is added, a higher CeO_2 dispersion and a greater range of reversible reducibility of the CeO_2 may also be obtained. All three changes offer potential for improvement in the oxygen storage capacity provided by CeO_2 in three-way catalysts, and the decreased Ce^{3+} fraction may, in addition, positively influence the maintenance of this oxygen storage capacity. The extent to which these changes translate into a real improvement in performance needs to be evaluated in a fully formulated catalyst, and tests involving the addition of Pt to La^{3+}-modified γ-Al_2O_3-supported CeO_2 are planned.

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