Nanometric Colloidal Sols of CeO₂–ZrO₂ Solid Solution as Catalyst Modifiers. I. Preparation and Structure

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Stable nanometric colloidal sols consisting of fluorite-type metal oxides were prepared for use as chloride-free precursors for automotive catalysts. The aqueous solution containing metal carbonates and tetramethylammonium (TMA) ions was degassed and hydrothermally treated at 140–160 °C. Colloidal suspensions thus formed were purified by ultrafiltration to yield very stable and condensed sol solutions of CeO₂ (CE), ZrO₂ (ZR) and their solid solutions, CeO₂– ZrO_2 (CZ), which were stabilized by TMA. Each oxide sol contained 6–8 nm primary particles, but they formed aggregates larger than 40 nm. Local structural analysis by means of XAFS suggested that CZ sol exhibited two types of solid solution domains containing more or less Ce. The dried CZ sol exhibited higher thermal stability and oxygen storage capacity than CE and ZR sols.

In the current automotive three-way catalyst (TWC) formulation, metal oxides with fluorite-type structure play extremely important roles.¹⁻⁵ CeO₂-based oxides with varying oxygen stoichiometries are able to store a large amount of oxygen under an oxidizing atmosphere and release it under a reducing atmosphere and thus achieve a buffering effect on fluctuating air-to-fuel ratio.⁶⁻¹⁴ The uptake of oxygen allows NO conversion to continue during rich-to-lean transients, whereas the release of oxygen promotes oxidation of CO and hydrocarbons during lean-to-rich transients. CeO2-ZrO2 solid solutions are most widely used for this purpose because of large oxygen storage capacity (OSC) and high thermal stability.¹⁵ CeO₂ is also known as a useful support material to effectively suppress sintering for Pt and Pd.^{16,17} The interactions between these metals and CeO2 under oxidizing atmosphere promote the redispersion of metal crystallites and thus contribute to the sintering inhibition mechanism. Furthermore, CeO₂ shows catalytic activities for water-gas shift reactions,^{18,19} steam reforming,²⁰ and combustion of soot emitted from diesel engines,²¹⁻²⁷ Another type of fluorite-type oxide, ZrO₂, is utilized as a support oxide capable of anchoring highly-dispersed Rh particles, and thus recognized as an irreplaceable material to lessen the amount of this scarcest precious metal.28

The common procedure for preparing TWCs is by impregnating an aqueous solution containing salts of precious metals onto oxide support powders. The catalyst powders thus obtained are made into slurry for the monolith coating. During these procedures, Ce and/or Zr are added in forms of fine oxide powders or water-soluble salts. In the present study, however, we are interested in the use of colloidal oxide sols, which are expected to play critical roles as catalyst precursors because their nanoparticles of narrow size distribution and high reactivity are able to promote the catalytic performance. Easy handling of sols is another benefit suitable for the present catalyst preparation routes. Although traditional oxide sols such as Al₂O₃ and SiO₂ have been used as a binder in the slurry for preparation of monolithic honeycomb catalysts,²⁹ CeO₂based oxides in the form of sol have not been recognized as main catalyst precursors.

The present work aims to study preparation and structure of colloidal sols of fluorite-type metal oxides, CeO_2 , ZrO_2 , and their composite system (CeO_2 – ZrO_2) as precursors of automotive catalysts. The three types of nanometric and chloride-free colloidal suspensions were prepared by hydrothermal reactions followed by ultrafiltration. The local structure of as-prepared CeO_2 – ZrO_2 sols and their thermal behavior are especially highlighted, because of the practical importance as the most efficient oxygen storage material. The dynamic oxygen release–storage cycles were carried out to evaluate the oxygen storage property of dried sols.

Experimental

Preparation of Fluorite-Type Oxide Sols. Nanometric colloidal sols of three fluorite-type oxides, CeO₂, ZrO₂, and CeO₂–ZrO₂, were prepared as shown in Figure 1 using ZrO-(CO₃) (AMR Technologies, Inc.), Ce₂(CO₃)₃ (AMR Technologies, Inc.), [(CH₃)₄N]₂(CO₃) (TMAC, Tama Chemical Co., Ltd.), and H₂O₂ (Kanto Chemical Co., Inc.) as starting materials. Tetramethylammonium (TMA) ions ((CH₃)₄N⁺) act as a stabilizer for colloidal dispersion of oxide nanoparticles. The





Figure 1. Preparation flow of the fluorite-type oxide sol.

Figure 2. Photographs of as-prepared CE, CZ, and ZR sols in bottles.

detailed preparation procedures for each sol are described in the following.

ZrO₂ (ZR) Sol: In a 3-L glass vessel, 1306.1 g of an aqueous solution of TMAC (44.5 mass % as [(CH₃)₄N](OH)) and 995.7 g of water were mixed by stirring and 976.5 g of ZrO(CO₃) (40.2 mass % as ZrO₂) was slowly added. After stirring for 1 h, the mixture was heated at 105 °C for 6 h under reflux to completely dissolve the carbonate and degas CO₂. The resulting slurry containing 12.5 mass % ZrO₂ (pH 10.6) was transferred to a stainless steel autoclave vessel, where hydrothermal treatment was carried out at 140 °C for 3 h under stirring. The product was a stable and homogeneous colloidal suspension containing 12.5 mass % ZrO₂ (pH 9.8) containing no precipitation. Finally, ultrafiltration using a membrane filter (differential molecular weight 2×10^5) was applied to remove an excess amount of electrolytes to obtain a white ZR sol containing 40 mass % ZrO₂ (pH 9.6) as shown in Figure 2.

CeO₂ (CE) Sol: In a 3-L glass vessel, 1004.2 g of an aqueous solution of TMAC (44.5 mass % as $[(CH_3)_4N](OH)$) and 354.4 g of water were mixed by stirring and heated up to 80 °C, where 240.9 g of Ce₂(CO₃)₃ (50.0 mass % as CeO₂) was slowly added. To oxidize Ce³⁺ to Ce⁴⁺, 408.0 g of 35% H₂O₂ was added to the solution at a constant rate by use of a peristaltic tube pump. The mixture was then heated at 105 °C for 6 h under reflux to completely dissolve the carbonate and

degas CO₂. The resulting slurry containing 6.0 mass % of CeO₂ (pH 11.2) was hydrothermally treated at 140 °C for 6 h under stirring to convert into a sol containing 6.0 mass % CeO₂ (pH 10.9). As in the case of ZR sol above described, ultra-filtration of the product gave a stable yellowish CE sol containing 40 mass % CeO₂ (pH 9.4) as shown in Figure 2.

CeO₂-ZrO₂ (CZ) Sol: In a 3-L glass vessel, 819.8 g of an aqueous solution of TMAC (44.5 mass % as [(CH₃)₄N](OH)) and 435.5 g of water were mixed by stirring and heated up to 60 °C, where 172.1 g of $Ce_2(CO_3)_3$ and 183.9 g of $ZrO(CO_3)$ was slowly added (Ce/Zr molar ratio: 0.8). To oxidize Ce^{3+} to Ce^{4+} , 388.7 g of 35% H₂O₂ was added to the solution at a constant rate by use of a peristaltic tube pump. The mixture was then heated at 105 °C for 6 h under reflux to completely dissolve the carbonate and degas CO₂. The resulting slurry containing 8.0 mass % of CZ (pH 10.5) was hydrothermally treated at 140 °C for 6 h under stirring to convert into a sol containing 8.0 mass % CZ (pH 10.3). After ultrafiltration, a stable orange CZ sol containing 30 mass % CeO2-ZrO2 (pH 9.5) was obtained as shown in Figure 2. Because the Ce/Zr molar ratio of asprepared colloidal particles was confirmed to be unity, a part of Zr was lost by the ultrafiltration step.

Characterization. The particles size in as-prepared colloidal suspensions was determined by dynamic light scattering (DLS) measurements (Submicron Particle Size Analyzer N5, Beckman Coulter) using a He-Ne laser (25 mW, 632.8 nm) at a scattering angle of 90°. The sols were dried by evaporation to dryness under reduced pressures at ambient temperature for the following characterization. The powder X-ray diffraction (XRD) measurement was performed using monochromated $Cu K\alpha$ radiation (30 kV, 20 mA, Rigaku Multiflex). The size of crystallite was calculated by line-broadening analysis of XRD profiles using the (111) reflection. The microstructure of dried sols was observed by transmission electron microscopy (TEM, JEM1010, JEOL Ltd.) operating at 100 kV. The colloidal particles were mounted by immersing a Cu grid mesh covered with a microgrid carbon into sol solutions. TG/DTA measurement in a flow of air at the heating rate of 10 °C min⁻¹ was carried out with a Brucker TG-DTA2000SA instrument. The size of primary particle for each sol was calculated from BET surface area, which was determined from N₂ adsorption isotherms measured at 77 K (Macsorb Model-1201, Mountec Co., Ltd.). Prior to the measurement, each sol was dried at 105 °C in a drying oven and heated at 300 °C for 1 h. The surface areas of dried sols after calcination up to 1000 °C for 5 h in air were also measured.

Local structures around Zr and Ce atoms were studied by X-ray absorption fine structure (XAFS) of Zr and Ce K-edges, which were recorded on the NW10A station at Photon Factory for Advanced Ring (PF-AR), High Energy Accelerator Research Organization (KEK), Tsukuba (Proposal No. 2011G619). A Si(311) double-crystal monochromator was used. The spectra were recorded at ambient temperature in a transmission mode. The incident and transmitted X-rays in Ce K-edge EXAFS measurement were monitored in 17- and 31-cm-long ionization chambers filled with Ar and Kr, respectively. The ionization chambers for the incident and transmitted X-rays in Zr K-edge EXAFS measurement were filled with Ar 50% + N₂ 50%. The powder sample was pressed into a disk

of 10 mm in diameter after its volume was adjusted with boron nitride powders to give an appropriate absorbance at the edge energy for XAFS measurement. XAFS data were processed using a REX 2000 program (Rigaku). EXAFS oscillation was extracted by fitting a cubic spline function through the post edge region. The k^3 -weighted EXAFS oscillation in the 3.0–16.0 Å region was Fourier transformed for curve-fitting analysis. Phase shifts and backscattering amplitude functions for Ce–O, Ce–O–Ce, Zr–O, and Zr–O–Zr shells were extracted from the EXAFS data of CeO₂ and ZrO₂ (Rare Metallic Co., Ltd.). The curve-fitting analysis for Ce–O–Zr shell was performed using parameters calculated by FEFF code.

The powdered CZ sol was impregnated with an aqueous solution of $[Pt(NH_3)_2(NO_2)_2]$ (Tanaka Precious Metals) followed by drying and calcination at 600 °C for 3 h in air (1 mass % Pt) before evaluation of OSC. The measurement was done by use of microbalance (TG, Rigaku 8120), which was connected to a dual-gas supplying system. The catalyst (10 mg) was first heated in a stream of N₂ up to 800 °C, where a constant weight was attained within 30 min. The gas feed was then switched between 1.4% H₂ (120 min) and 0.7% O₂ (40 min) balanced by N₂ with recording the catalyst weight at this temperature.

Results and Discussion

Structure and Microstructure of Oxide Sols. As-prepared three types of alkaline sols maintained stable colloid dispersion without sedimentation or coagulation in spite of their high solid fractions (30–40 mass %). Figure 3 shows powder XRD patterns of oxide sols dried in vacuo at ambient temperature. The diffraction peaks could be assigned to fluorite-type structure with cubic (CE and CZ) and monoclinic (ZR) symmetries. As can be seen from broad diffraction peaks, their crystallinity was very low, but it is sufficient to detect the shift of diffraction peaks of CZ toward higher angles compared to CE. Because of the smaller ionic radius of Zr^{4+} (0.087 nm) than that of Ce⁴⁺ (0.102 nm), the shift is a clear indication of the formation of CeO₂–ZrO₂ solid solutions having smaller lattice constants.

The microstructure of dried sols was observed by TEM. As shown in Figure 4, the secondary particles of several ten nm



Figure 3. XRD patterns of fluorite-type oxide sols after drying in vacuo at ambient temperature.

in size consist of aggregates of primary particles smaller than 10 nm. The size of particle aggregates of CZ sol was smallest $(\leq 20 \text{ nm})$, whereas those of CE and ZR sols were more than 30 nm. Table 1 shows physicochemical properties of three types of sols. The BET surface areas of dried sols were in a range of $130-160 \text{ m}^2 \text{ g}^{-1}$. The particle sizes calculated from the surface area are in the range of 6-8 nm, which is in accordance with TEM images. Because these values are close to crystallite sizes estimated by line-broadening analysis of XRD patterns, one primary particle should be composed of a single crystallite. The particle sizes in the colloidal suspensions were determined by dynamic light scattering. They ranged from about 50 to more than 100 nm in diameter, depending on the oxide composition. These values were larger than those observed in the TEM images in Figure 4, because of the occurrence of further aggregation in the sol solution.

Local Structure of CZ Sol. Although the XRD result in Figure 3 suggests the difference of lattice constants in accordance with the formation of CeO_2 -ZrO₂, several different types



Figure 4. TEM photographs of as-prepared fluorite-type oxide sols with low and high magnifications.

 Table 1. Physicochemical Properties of Fluorite-Type

 Oxide Sols

Sol	CE	CZ	ZR
Oxide	CeO ₂	CeO ₂ –ZrO ₂ ^{a)}	ZrO ₂
Oxide content/mass %	40	30	40
Stabilizer	TMAH ^{b)}	TMAH	TMAH
Specific gravity/g mL ⁻¹	1.56	1.36	1.53
Viscosity ^{c)} /mPa s ⁻¹	3	7	4
pH	9.4	9.5	9.6
$S_{\rm BET}/{\rm m}^2{\rm g}^{-1}$	130	157	160
Crystallite size ^{d)} /nm	9	7	6
Particle size ^{e)} /nm	8	6	7
Particle size ^{f)} /nm	110	49	90

a) Ce:Zr = 1:1. b) Tetramethylammonium hydroxide. c) Measured at 25 °C. d) Calculated from XRD line-broadening analysis using the (111) reflection. e) Calculated from BET surface area (S_{BET}) of dried sols. f) Determined by dynamic light scattering measurement of colloidal suspensions.



Figure 5. a) Fourier-transformed Zr K-edge EXAFS for CZ and ZrO₂. b) Fourier-transformed Ce K-edge EXAFS for CZ and cubic CeO₂.

of solid solutions with different local structures were known in the system.³⁰ The local environment around Ce and Zr atoms was therefore studied using XAFS. Figure 5a shows Fourier transforms of Zr K-edge EXAFS of dried CZ sol and monoclinic ZrO₂ as a reference without correction for phase shift. For CZ, one peak at around 1.7 Å can be assigned to Zr–O, whereas the other peak at around 3.1 Å is contributions from Zr–O–Zr and/or Zr–O–Ce shells, which is less intense than that of monoclinic ZrO₂. The second shell peak shifted to a longer distance than ZrO₂ implies the formation of solid solution and/ or ZrO₂ phases with different symmetries. We also measured Ce K-edge EXAFS of CZ and CeO₂ as a reference (Figure 5b). CZ showed a weak and broad second shell peak at around 3.5 Å, which was assigned to Ce–O–Ce and Ce–O–Zr.

To obtain detailed structural parameters, we performed curve-fitting analysis of first and second shells of Zr and Ce K-edge EXAFS. Structural parameters obtained from the curve-fitting are summarized in Table 2. The second shell of Zr K-edge EXAFS for CZ yielded the best fit when two shells of Zr-O-Zr (3.56 Å) and Zr-O-Ce (3.59 Å) were taken into consideration. Similarly, Ce K-edge EXAFS for CZ also suggests the presence of Ce-O-Zr with the very close atomic distance (3.60 Å) in addition to Ce-O-Ce (3.81 Å). The theoretical coordination number (CN) of the Ce-O-Ce in cubic fluorite-type structure is 12, but the sum of CN of the second shell in the present analysis is less than 12, probably because of the very small size of colloidal particles (<10 nm) as shown by TEM (Figure 4). Moreover, it should be noted that the ratios of CNs for Zr-O-Ce to Zr-O-Zr or Ce-O-Zr to Ce-O-Ce were less than unity. It was reported that Ce and Zr K-edge EXAFS for completely homogenous equimolar CeO2-ZrO2 solid solution demonstrated the CN ratios equal to unity.³⁰ The present solid solution with lower CN ratios (ca. 0.5) suggests the formation of two different domains containing more or less Ce with the size of around the unit cell. Taking these results into consideration, the present CZ sol can be identified as a solid solution, but its local structure consists of two different domains. It is well-known that the CeO₂-ZrO₂ phase diagram has unresolved and complex problems due to the presence of metastable phases arising from compositional fluctuation.³¹

 Table 2. Fitting Results Obtained from Zr K-edge and Ce K-edge EXAFS Analysis^{a)}

Oxide sol	Shell	CN ^{b)} (±0.3)	$r^{c)}$ /Å (±0.02)	$\sigma^{2 d)} / 10^{-2} \text{\AA}^2 \ (\pm 0.02)$	R factor /%
Zr K-edge					
CZ	Zr–O	6.9	2.15	0.53	1.4
	Zr-O-Zr	6.1	3.56	0.46	0.23
	Zr-O-Ce	3.3	3.59	0.49	0.23
ZrO_2	Zr–O	2.0	2.05	0.14	3.3
	Zr–O	3.0	2.15	0.10	3.3
	Zr–O	2.0	2.25	0.10	3.3
	Zr-O-Zr	7.0	3.46	0.64	1.0
	Zr-O-Zr	4.0	3.98	0.69	2.4
Ce K-edge					
CZ	Ce–O	4.9	2.34	0.40	1.7
	Се-О-Се	5.6	3.81	0.15	0.49
	Ce-O-Zr	2.9	3.60	0.49	0.49
CeO ₂	Ce–O	8.0	2.34	0.40	3.5
	Се-О-Се	12.0	3.82	0.12	2.3

a) Interval of *k*-space to *r*-space of FT is 3.0–16.0 Å⁻¹.
b) Coordination number. c) Atomic distance. d) Debye–Waller factor.

Local inhomogeneities of the CeO_2 –ZrO₂ solid solutions lead to Ce-rich and Zr-rich domains, which are undetectable by conventional XRD.³² The two-domain structure of CZ sol in the present work is therefore very similar to those of the equimolar solid solutions.

Thermal Stability and OSC of Dried Sols. Figure 6 shows the TG/DTA profile of CZ sol dried at $110 \,^{\circ}$ C in air. The sol exhibited three steps of weight losses at <150, 150–400, and >400 $^{\circ}$ C, which would be assigned to desorption of physisorbed water, decomposition of organic stabilizer (TMA) and dehydroxylation, respectively. A DTA profile shows a strong exothermic peak in the second step of weight loss as a result of combustion of organic moiety. Therefore, thermal



Figure 6. A TG/DTA profile of CZ sol measured in a flow of air.



Figure 7. BET surface areas of dried sols after heating at elevated temperatures. CZ: CeO_2 –ZrO₂ sol prepared as shown in Figure 1. CZ_{copre} : CeO_2 –ZrO₂ prepared by conventional coprecipitation method.

treatment of dried sols at \geq 400 °C yielded pure oxide phases without residual contaminants arising from the organic stabilizer. Such a low-temperature decomposition behavior is suitable for use as catalyst precursors.

Figure 7 plots the BET surface area of dried sols after calcination at elevated temperatures in air. The large surface areas of as-prepared sols $(>130 \text{ m}^2 \text{ g}^{-1})$ decreased monotonically with an increase of temperature, depending the oxide composition. The ZR sol steeply lost its surface area at \geq 500 °C and CE sol also showed significant sintering at >700 °C. By contrast, the CZ sol was found to retain the highest values at \geq 700 °C, suggesting that the formation of solid solution is an efficient way to prevent sintering. This behavior seems to be associated with a slow particle growth rate resulting from the structural complexity due to local inhomogeneities described above.³¹ It should be noted that such a thermal stability was not achieved when CeO₂-ZrO₂ was prepared by coprecipitation from an aqueous solution of nitrates, which yielded a mixture of CeO_2 and ZrO_2 after calcination. The present preparation route enabling the formation of CeO2-ZrO2 solid solution in a



Figure 8. Weight changes during reduction–oxidation cycles of 1 mass % Pt loaded CZ and CE measured at 300 and 500 °C. a) CE, 300, b) CE, 500, c) CZ, 300, and d) CZ, 500 °C.

liquid phase is a key for higher thermal stability at elevated temperatures.

Finally, the oxygen storage performance was evaluated under oscillating feed stream conditions, where reducing and oxidizing gas feeds were cycled. Figure 8 shows the weight changes of Pt-loaded dried sols of CZ and CE under a cycled feed stream condition (0.7% O₂ or 1.4% H₂, He balance) at 300 and 500 °C. CZ exhibited larger weight changes than CE at each temperature in accordance with the formation of solid solutions in the CZ sol. The weight change of about 1 mass % at 500 °C corresponds to 92.6 mmol- $O_2 \cdot (mol-Ce)^{-1}$, which is about 40% of the theoretical OSC according to the stoichiometric reaction, CeO_2 -Zr O_2 = $CeO_{1.5}$ -Zr O_2 + 0.25 O_2 . This is quite larger than 14.5 mmol- $O_2 \cdot (mol-Ce)^{-1}$ for CE, which is only 6% of the theoretical OSC of CeO₂. The measurement was also performed on Pt-unloaded sols at 300 °C, but OSC values were too small to be evaluated because of very slow kinetics. Loading Pt or any other precious metals are necessary for oxygen release in a low-concentration H_2 (1.4 vol %).

Conclusion

The present study successfully prepared stable and chloridefree colloidal suspensions of fluorite-type oxides, ZrO₂, CeO₂, and CeO₂–ZrO₂, which can be useful as catalyst precursors. The sols consisted of uniform primary particles as large as 6-8 nm, which form aggregates about 50-110 nm in size. EXAFS analysis proved that the binary oxide sol of CeO₂-ZrO₂ was composed of solid solutions having Zr-rich and Ce-rich domains. The organic stabilizer, tetramethylammonium ions, can easily be removed by heating at 400 °C in air. Large BET surface areas of dried sol more than 100 m² g⁻¹ decreased steeply upon calcination, but the CeO₂-ZrO₂ could retain a larger value than CeO₂ and ZrO₂ alone, because the formation of solid solution achieved tolerance against sintering. The dried sol of CeO2-ZrO₂ also exhibited a much larger oxygen storage capacity than CeO₂. These features of fluorite-type oxide sols are suitable for use in catalyst preparation. A further study on the characteristics as catalyst precursors is now under investigation.

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References

1 M. Shelef, Catal. Rev.: Sci. Eng. 1975, 11, 1.

- 2 K. C. Taylor, Catal. Rev.: Sci. Eng. 1993, 35, 457.
- 3 R. M. Heck, R. J. Farrauto, S. T. Gulati, *Catalytic Air Pollution Control: Commercial Technology*, Wiley, Hoboken, **1995**.

4 R. J. Farrauto, R. M. Heck, Catal. Today 1999, 51, 351.

5 H. S. Gandhi, G. W. Graham, R. W. McCabe, J. Catal. 2003, 216, 433.

6 G. Balducci, P. Fornasiero, R. Di Monte, J. Kaspar, S. Meriani, M. Graziani, *Catal. Lett.* **1995**, *33*, 193.

- J. Kašpar, P. Fornasiero, J. Solid State Chem. 2003, 171, 19.
 M. Ozawa, M. Kimura, A. Isogai, J. Alloys Compd. 1993, 193, 73.
- 9 M. Pijolat, M. Prin, M. Soustelle, O. Touret, P. Nortier, J. Chem. Soc., Faraday Trans. 1995, 91, 3941.
- 10 F. Zamar, A. Trovarelli, C. de Leitenburg, G. Dolcetti, J. Chem. Soc., Chem. Commun. **1995**, 965.

11 S. Bernal, J. Kaspar, A. Trovarelli, *Catal. Today* **1999**, *50*, 173.

12 M. Shelef, G. W. Graham, R. W. McCabe, in *Catalysis by Ceria and Related Materials* in *Catalytic Science Series*, ed. by A. Trovarelli, Imperial College Press, London, **2002**, Vol. 2, p. 343. doi:10.1142/9781860949654_0010.

13 A. Trovarelli, Catal. Rev., Sci. Eng. 1996, 38, 439.

14 T. Masui, K. Minami, K. Koyabu, N. Imanaka, *Catal. Today* **2006**, *117*, 187.

15 M. Haneda, O. Houshito, T. Sato, H. Takagi, K. Shinoda, Y. Nakahara, K. Hiroe, H. Hamada, *Catal. Commun.* **2010**, *11*, 317.

16 Y. Nagai, K. Dohmae, Y. Ikeda, N. Takagi, T. Tanabe, N. Hara, G. Guilera, S. Pascarelli, M. A. Newton, O. Kuno, H. Jiang, H. Shinjoh, S. Matsumoto, *Angew. Chem., Int. Ed.* **2008**, *47*, 9303.

17 Y. Nagai, T. Hirabayashi, K. Dohmae, N. Takagi, T. Minami, H. Shinjoh, S. Matsumoto, J. Catal. **2006**, 242, 103.

- 18 P. Djinović, J. Batista, J. Levec, A. Pintar, *Appl. Catal.*, *A* **2009**, *364*, 156.
- 19 I. D. González, R. M. Navarro, W. Wen, N. Marinkovic, J. A. Rodriguéz, F. Rosa, J. L. G. Fierro, *Catal. Today* **2010**, *149*, 372.
- 20 R. Craciun, W. Daniell, H. Knözinger, *Appl. Catal., A* 2002, 230, 153.
- 21 E. Aneggi, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Catal. Today* **2006**, *114*, 40.

22 K. Krishna, A. Bueno-López, M. Makkee, J. A. Moulijn, *Appl. Catal.*, *B* **2007**, *75*, 189.

23 E. E. Miró, F. Ravelli, M. A. Ulla, L. M. Cornaglia, C. A. Querini, *Catal. Today* **1999**, *53*, 631.

24 G. Neri, G. Rizzo, S. Galvagno, M. G. Musolino, A. Donato, R. Pietropaolo, *Thermochim. Acta* **2002**, *381*, 165.

25 M. L. Pisarello, V. Milt, M. A. Peralta, C. A. Querini, E. E. Miró, *Catal. Today* **2002**, *75*, 465.

26 A. Setiabudi, J. Chen, G. Mul, M. Makkee, J. A. Moulijn, *Appl. Catal.*, *B* **2004**, *51*, 9.

27 M. Machida, Y. Murata, K. Kishikawa, D. Zhang, K. Ikeue, *Chem. Mater.* **2008**, *20*, 4489.

28 R. Burch, P. K. Loader, Appl. Catal., A 1996, 143, 317.

29 L. L. Murrell, Catal. Today 1997, 35, 225.

30 M. Breysse, M. Guenin, B. Claudel, H. Latreille, J. Véron, *J. Catal.* **1972**, *27*, 275.

31 J. Kašpar, P. Fornasiero, in *Catalysis by Ceria and Related Materials* in *Catalytic Science Series*, ed. by A. Trovarelli, Imperial College Press, London, **2002**, Vol. 2, p. 217. doi:10. 1142/9781860949654_0006.

32 T. Egami, W. Dmowski, R. Brenzny, SAE Paper 1997, 970461.