



Article Effect of High-Energy Milling on Ceria-Zirconia's Redox Properties

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Abstract: Series of ceria-zirconia (CZ)-based nano-materials with a d₅₀ in the range of 0.2 to 1.3 microns were made using the jar milling, Eiger milling, and steam jet milling (SJM) techniques. The effect of the milling conditions on the morphology and textural properties was studied. High-energy steam jet milling in a quasi-hydrothermal environment (with potential local temperature spikes over 500 °C) significantly impacted the CZ crystal structure by inducing lattice distortions. It was shown that the acquired lattice stress resulted in a significant increase in oxygen mobility, which was manifested by a TPR-H₂ T_{max} shift from 450–550 to 150–250 °C. CZ materials with fast oxygen mobility are metastable phases, and re-slurring nano-CZ powders in water and impregnation with precious metals had stabilizing effects on fast oxygen mobility. Efficiently enhancing the CZ redox activity milling process took place in the following order: Steam jet milling > Eiger milling > jar milling.

Keywords: ceria-zirconia-based mixed oxides; dry milling; wet milling; steam jet milling; crystal lattice distortions; redox properties; fast oxygen mobility

1. Introduction

Mixed cerium-zirconium-based oxides have many applications, like oxygen storage components in three–way catalysts (TWCs), oxygen sensors, fuel cell conductors, hydrogen generation, etc. This relates to cerium's ability to experience a fast–changing valence state from (IV) to (III): $2CeO_2 \leftrightarrow Ce_2O_3 + O$, depending on the environment [1]. In TWC applications, the reduction of CeO_2 provides oxygen for the oxidation of CO and hydrocarbons under rich fuel conditions, and Ce_2O_3 oxidation removes excess oxygen under lean conditions. The amount of absorbed/released oxygen was quantified as the oxygen storage capacity (OSC). A high available OSC, as well as facile oxygen mobility, are critical factors for CZ performance.

Dozens of preparation routes have been proposed and commercialized for making a wide range of CZ materials with tailored properties in the past three decades [2]. These include different types of co-precipitation [3–6], hydrothermal [7,8], sol–gel [9], impregnation [8], solid state [10], spray pyrolysis [11], and other routes. The mechanochemical route is one of these methods [12–14]. This route also includes the dry or wet milling of micronsize CZ materials to nano-size. Nano-materials are promising for different applications as they are characterized by a larger fraction of atoms located on the surface vs. located in the bulk of the particles. This makes them highly reactive. High-energy milling also induces mechanical stress that changes the physicochemical properties of the materials and can create structural and surface defects. Currently, mechanochemical routes are regarded as a powerful tool for making materials with enhanced properties. Among the promising applications of mechanochemically activated CZ materials are gasoline and diesel particulate filters (GPFs and DPFs, respectively), where the washcoat needs to comprise nano-particles that do not block the gas passage through the substrate [15-17]. Typically, CZ nano-slurries for GPFs/DPFs were made using wet milling techniques. They allow the achievement of a target particle size below 1 micron, and potentially toxic nano-particles formed during milling remain in the slurry.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The objective of this research was to study the effects of different milling techniques on the morphology, textural, and redox properties of mechanochemically treated CZ materials. Two wet milling techniques (jar and Eiger milling) and one dry milling technique (steam jet milling) were used. Even though wet milling techniques are more production-friendly, the main stress is given to the dry process, namely, steam jet milling, which provides the highest energy impact during milling, and, as we will show, this results in an unusual increase in oxygen mobility in milled CZ materials.

2. Results and Discussions

Several milling techniques were used for the evaluation of their effect on the textural and redox properties of the milled CZ materials. Most of the experiments were conducted with commercial CZ20, with a composition of 20%CeO₂–70%ZrO₂–5%La₂O₃–5%Pr₆O₁₁. A typical particle size distribution curve of the unmilled CZ material is presented in Figure 1a. Unmilled CZ20 has particles in a wide range from 5 microns up to 100 microns with a d₅₀ of ~28 microns. According to SEM, the CZ consisted of aggregates with rounded or irregular shapes. These aggregates appeared dense; however, they had a complex hierarchical structure. Primary particles (crystallites) with a 10–20 nm size were stuck together and formed first-order aggregates with a d₅₀ < 0.5 μ m. Further assembly resulted in second-and higher-order aggregates with larger sizes (Figure 2a).



Figure 1. (a) Particle size distribution curve of unmilled CZ20 ($d_{50} = 28$ microns). (b) Particle size distribution curve of CZ20 slurry after jar milling ($d_{50} = -0.2$ microns).



Figure 2. (a) SEM (left) and TEM (right) images of unmilled CZ20. (b) SEM (left) and TEM (right) images of jar-milled CZ20.

The first technique used was wet–ball jar milling. Despite relatively slow jar rotation, this process enabled the production nano-slurries in which the CZ particles could have a d_{50} of less than 0.20 microns. Jar milling efficiently destroyed large, high-order aggregates with the formation of rather soft and homogeneous by size first-order aggregates (Figures 1b and 2b). The size and shape of such powders allows us to conclude that the jar mill energy is not sufficient for producing nanomaterials consisting of individual crystallites. The process drawbacks are a very long milling time and re-agglomeration of the nanomaterials during drying.

Pore size distribution curves of the unmilled CZ20 and CZ20 milled to $d_{50} = 0.2$ microns are presented in Figure 3. There was no change in the pore diameter despite severe material deagglomeration. This suggests that first-order aggregates are the main structural blocks in the CZ powders. They bear the main features of the material's mesoporosity and are responsible for the overall thermal stability of the material.

The specific surface areas and pore volume of the values for fresh, aged-milled, and unmilled materials are summarized in Table 1. The data show that jar milling resulted in a decrease in the S_a and V_{pore} of the milled materials. However, despite severe deagglomeration, the decreases in S_a and V_{pore} were not drastic. The nano-CZ retained ~70–75% of its surface area and pore volume after slurry drying. The retention of a high specific surface area and porosity is extremely important during the catalyst substrate coating.



Figure 3. Pore diameter distributions of CZ20 materials calcined at 1000 $^{\circ}$ C: Unmilled powder (black) and after drying 20% aqueous nano-CZ20 slurry (d₅₀ = 0.2 μ m; red).

Table 1. Specific surface area and pore volume (calcination at 700 and 1000 °C) of unmilled CZ20 and the product after jar milling.

	S _a —700, m ² /g	V _{pore} —700, cc/g	S _a —1000, m ² /g	V _{pore} —1000, cc/g
Unmilled CZ20	101.7	0.60	57.7	0.45
Jar-milled CZ (20% slurry)	83.7	0.46	41.1	0.34
Eiger-milled CZ (20% slurry)	56.7	0.24	31.1	0.19

Further evaluation of the milling effect on the CZ properties included phase stability and redox properties. The XRD powder patterns presented in Figure 4 show that the unmilled CZ20 had a tetragonal crystalline structure and that jar milling did not change the CZ20 crystal phase.



Figure 4. XRD powder patterns of the reference CZ20 (black) and jar-milled CZ20 (red) after aging at 1100 $^{\circ}$ C for 6 h in air.

The redox activity of CZ materials was studied using the TPR-H₂ technique. TPR-H₂ allows to determine the available oxygen storage capacity (OSC) and, based on the T_{max} position, provides an indication of the CZ oxygen mobility. The OSC depends mainly on the composition and increases linearly with the increase in ceria in CZ up to ~30–35%CeO₂, and then it remains practically unchanged at 1.0–1.1 mM H₂/g for materials with higher CeO₂ content [18]. The oxygen mobility in CZ depends on the following factors, including:

The Ce/Zr molar ratio, the amount of trivalent RE dopants defining the concentration of oxygen defects in the crystal lattice, the type and size of the RE dopants influencing the lattice parameters and channel dimensions, the crystallite size determining the pathway that oxygen needs to take to reach the surface from the bulk, and the chaotic or ordered orientation of domains in the crystallites affecting the activation energy for grain–boundary oxygen diffusion.

Typically, CZ materials with a higher CeO₂ content have faster oxygen mobility than zirconiarich CZ. The T_{max} position was in the range of 400 to 600 °C (after aging at 1000–1100 °C). The TPR-H₂ profiles for the reference and jar-milled CZ20 ($d_{50} = ~0.2$ microns) are presented in Figure 5. The data shows that jar milling did not improve or deteriorate the redox properties of CZ. The oxygen storage capacity in both materials after aging was close to the theoretical value (~0.7 mMol H₂/g), and the T_{max}, which characterizes how facile the oxygen mobility is, was in the range of 470–485 °C for both.



Figure 5. TPR-H₂ profiles of unmilled CZ20 (black) and jar-milled CZ20 with $d_{50} = 0.2$ microns (red). Before the TPR-H₂ tests, the samples were calcined at 1000 °C for 6 h in air.

Summarizing, it is possible to conclude that jar milling is a powerful tool for making CZ nano-slurries that retain the main features of the starting material after drying, namely, the phase stability, mesoporosity, high surface area, and pore volume, as well as the unchanged redox properties.

The second tested milling technique was Eiger milling, which is widely used in industry. This is also a form of wet ball milling, but differing from jar milling in that it employs a variable agitator speed (from hundreds of rotations per minute (RPM) to several thousands of RPM), resulting in the CZ deagglomeration to nano-size via attrition, shear, and direct impact being much faster. Another difference is that the collision energy of the milling media with CZ particles was significantly higher, which created local temperature spikes (quasi-hydrothermal environment). The efficiency of Eiger milling depends on several factors, including the bead size, agitator speed, duration, and CZ composition. The

data in Table 1 show a significant effect of milling on the surface area and pore volume of fresh and aged CZ. The deterioration of S_a and V_{pore} was much stronger in comparison to that of jar milling. The pore volume was affected the most severely, as it decreased by more than 50%. However, the pore diameter of the milled CZ remained practically unchanged, which supports the suggestion that first-order aggregates are the main structural blocks in CZ powders. Eiger milling also did not affect the CZ phase stability.

However, Eiger milling had a significant impact on the CZ redox properties. The TPR-H₂ profiles of unmilled CZ20 and CZ20 Eiger-milled to different depths are presented in Figure 6. Eiger milling did not affect the available oxygen storage capacity of CZ20, but it enhanced the oxygen mobility in CZ. There was a significant shift of the T_{max} to lower temperatures, which depended on the milling depth: T_{max} = 415 °C for CZ20 with $d_{50} = 1.35$ microns and T_{max} = 350 °C for CZ20 with $d_{50} = 0.54$ microns. This is clear evidence of the presence of mechanochemical activation of the CZ redox properties.



Figure 6. TPR-H₂ profiles of unmilled CZ20 (black) and Eiger-milled materials to $d_{50} = 1.34 \mu m$ (blue) and $d_{50} = 0.54 \mu m$ (red). Before the TPR-H₂ tests, all of the samples were calcined at 1000 °C for 6 h in air.

The last milling technique tested was steam jet milling. In this case, the grinding energy was provided by super-heated steam jets, with a temperature of ~280 °C and a pressure of ~10 bar. The use of super-heated steam in the milling process eliminated the possibility of CZ contamination with elements from the milling media (as in jar or Eiger milling), making the milling process fast and resulting in non-aggregated nano-size powders. In the steam jet milling experiments, we used two CZ compositions: CZ20 and CZ40 (40%CeO₂-50%ZrO₂-5%La₂O₃-5%Pr₆O₁₁). By changing the milling duration, two samples with different milling depths for each CZ composition were made and characterized similarly to the materials prepared via jar and Eiger milling.

It was found that steam-jet milling efficiently destroyed large, high-order aggregates with the formation of sub-micron-sized powders. However, the maximum milling depth achieved by SJM milling (~0.5 microns) was somewhat lower than in the case of jar or Eiger milling. SEM and TEM images of SJM CZ20 are shown in Figure 7. SEM and TEM images of CZ40 before and after milling are shown in Figure 8a,b, respectively.



Figure 7. SEM (left) and TEM (right) images of steam jet-milled CZ20 (d50 = ~0.5 microns).



Figure 8. (a) SEM (left) and TEM (right) images of unmilled CZ40. (b) Steam jet-milled CZ40. The SEM image shows the morphology of CZ aggregates milled to $d_{50} = 0.55 \mu m$ (left), and the TEM image (right) shows the morphology of first-order aggregates.

The data on the surface areas and pore volumes of CZ20 and CZ40 before and after steam jet milling are summarized in Table 2, and the pore size distribution curves for the CZ40 samples are provided in Figure 9. As seen, steam jet milling led to a relatively minor shift in the CZ pore diameter from ~30 to ~25 nm, but resulted in the disappearance of a significant fraction of large pores (>40–50 nm). The large pores were derived from higher-order aggregates, which were removed by milling. The data in Table 2 shows a very negligent effect of milling on the surface area of fresh CZ20 and CZ40 independent of milling depth, but a substantial loss of surface area and especially of pore volume was observed after milling. Those CZ materials aged at 1000 and 1100 °C had lower S_a and V_{pore} values than the starting material, and their deterioration rates strongly depended on the milling depth. Milling to a d₅₀ of ~0.5 microns resulted in more than a 50% loss of pore volume and up to a 30–40% loss of surface area.

Table 2. CZ20 and CZ40 specific surface area and pore volume (calcination at 700, 1000, and 1100 °C) before and after steam jet milling.

Sample	700)°C	100	0 ° C	110	0 °C
	S_a , m^2/g	V _{pore} , cm ³ /g	S _a , m ² /g	V _{pore} , cm ³ /g	S _a , m ² /g	V _{pore} , cm ³ /g
CZ20, unmilled	101.7	0.60	57.7	0.45	31.5	0.23
CZ20 (d ₅₀ = 1.1 microns)	92.3	0.43	43.2	0.29	24.1	0.14
CZ20 ($d_{50} = 0.5$ microns)	85.8	0.27	32.8	0.14	18.8	0.09
CZ40, unmilled	87.8	0.63	56.8	0.45	24.3	0.18
CZ40 ($d_{50} = 0.8$ microns)	88.1	0.31	48.3	0.24	18.8	0.09
CZ40 ($d_{50} = 0.5$ microns)	85.1	0.25	34.0	0.16	17.0	0.07



Figure 9. Pore size distributions of CZ40 unmilled (black) and steam jet-milled to $d_{50} = 0.8 \mu m$ (red) after calcination at 1000 °C for 6 h.

According to the XRD data (Figure 10), steam jet milling does not change the CZ crystal phase. The steam jet-milled CZ materials retained their well-defined tetragonal structures after aging at 1100 °C.



Figure 10. XRD powder patterns of CZ40 and CZ20 before (black) and after (red) steam jet milling. All samples had been aged at 1100 °C for 6 h in air.

The TPR-H₂ profiles for CZ20 and CZ40 unmilled and steam jet-milled to different depths are presented in Figures 11 and 12, respectively. The oxygen storage capacity of the unmilled CZ20 was 0.70 mMol H_2/g , and that of CZ40 was 1.05 mMol H_2/g , with the CeO₂ content being higher in CZ40. As seen, the T_{max} position of the CZ20 reference sample was 485 $^{\circ}$ C, which is typical for zirconium-rich CZ. The T_{max} of the steam jet-milled samples was significantly shifted to lower temperatures, and this shift depended on the milling depth: $T_{max} = 220$ °C for SJM-CZ with $d_{50} = 1.1$ microns and $T_{max} = 155$ °C for CZ with $d_{50} = 0.5$ microns. Such a significant T_{max} shift for 250–330 °C has only been reported previously in the case of CZ doping with precious metals (PGM) [1]. The OSC of CZ20 milled to 1.1 and 0.5 microns was 0.68 and 0.70 mMol H_2/g , respectively. A very similar situation was observed in the case of steam jet milling of CZ40. The T_{max} of the unmilled CZ40 was 495 °C. The material steam jet-milled to 0.8 microns had a bimodal TPR-H₂ profile with a high temperature peak at 490 °C and a low temperature peak at 350 °C. The third CZ sample, after longer milling ($d_{50} = 0.5$ microns), had a practically single modal TPR-H₂ profile with a T_{max} position of 200 °C. The OSC of the CZ40 milled to 0.8 and 0.5 microns was 1.03 and 0.99 mMol H_2/g , respectively. These data show that steam jet milling results in a significant shift of the T_{max} in milled materials but does not change the oxygen storage capacity.



Figure 11. TPR-H₂ profiles of unmilled CZ20 (black) and two steam jet-milled CZ20 with $d_{50} = 0.5$ microns (blue) and 1.1 microns (red). Before the TPR-H₂ tests, all of the samples were calcined at 1000 °C for 6 h in air.



Figure 12. TPR-H₂ profiles of unmilled CZ40 (black) and two steam jet-milled CZ40 with $d_{50} = 0.5$ microns (blue) and 0.8 microns (red). Before the TPR-H₂ tests, all of the samples were calcined at 1000 °C for 6 h in air.

The most plausible explanation for this phenomenon is that steam jet mechanochemical milling in a quasi-hydrothermal environment (with potential local temperature spikes over 500 °C) induces distinctive stress in the CZ lattice that facilitates oxygen mobility. This was confirmed by the HRTEM data of the unmilled and steam jet-milled CZ40. The HRTEM of unmilled CZ showed an almost perfect arrangement of atoms in all directions (Figure 13). A similar HRTEM image of the CZ crystallite after steam jet milling showed multiple lattice distortions spread non- homogeneously through the crystal (Figure 14). The d-values measured at multiple (hkl) locations for CZ40 and SJM-CZ40 are provided in Table 3. The d-values for the same (hkl) location for the SJM-CZ40 material varied from approximately 2 to 5% from the d-value measured for a reference cerium-zirconium material at the same (hkl) location. Such lattice distortions created by mechanical stress influence the metal–oxygen bonds, making them weaker and the oxygen more mobile in some cases.



Figure 13. Typical HRTEM image of unmilled CZ40 crystallite.



Figure 14. Typical HRTEM image of steam jet-milled CZ40 crystallite.

(hkl)	CZ40	SJM-CZ40
(112)	1.86 A	1.88 A 1.90 A
(211)	1.50 A	1.59 A
(101)	2.95 A 2.96 A	2.93 A 3.04 A 3.06 A
(110)	2.49 A 2.60 A	2.63 A
(200)	1.82 A	1.89 A
(202)	1.45 A 1.46 A 1.47 A	1.47 1.53

For coating the TWC substrate, mixed CZ oxides, together with other components (alumina and PGM), were used in the formation of aqueous slurry. Thus, the question arises if such a treatment can make an impact on the fast oxygen mobility. To check this, an aqueous SJM-CZ20 ($d_{50} = 0.5$ microns) slurry was made, mixed continuously for 1 day, and then dried and calcined at 1000 °C for 6 h. The characterization data of the textural

and redox properties are summarized in Table 4, and the TPR-H₂ profiles of the steam jet-milled CZ20 before and after re-slurring are presented in Figure 15. As seen, re-slurring did not change the specific surface area, but increased the pore volume by more than 35%. The latter could be related to nano-particle re-agglomeration during slurry drying, with the formation of higher order aggregates having large mesopores. The TPR-H₂ profiles of the two tested samples look similar: Very close T_{max} values (~160 °C) and identical OSCs of ~0.7 mM H₂/g equal to the theoretical values. This indicates that the dispersion of nano-SJM-CZ in water followed by drying and the formation of micron-sized aggregates did not release the lattice stresses, which are responsible for the fast oxygen mobility, caused by high-energy milling.

Table 4. Data on the textural and redox properties of steam jet-milled CZ20 ($d_{50} = 0.5$ microns) before and after re-slurring in water. Calcination at 1000 °C for 6 h.

	S _a , m ² /g	V _{pore} , cc/g	OSC, mM H ₂ /g	Tmax, °C
Nano-CZ powder	34.0	0.16	0.71	154
After re-slurring and drying	34.3	0.22	0.67	165



Figure 15. TPR-H₂ profiles of steam jet-milled CZ20 with $d_{50} = 0.5$ microns (black) and the same material after re-slurring in water and drying (red). Before the TPR-H₂ tests, both samples were calcined at 1000 °C for 6 h in air.

The tolerance of the fast oxygen mobility effect toward changes in the cerium oxidation state was studied in consecutive TPR-H₂ runs, mimicking changes in a rich-lean exhaust gas environment. Two materials were used in the experiment: Steam jet-milled nano-CZ20 with $d_{50} = 0.5 \mu m$ and the same material after re-slurring in water and drying. The TPR-H₂ profiles of six consecutive runs for nano-SJM-CZ20 are presented in Figure 16, and those for SJM-CZ20 after re-slurring are in Figure 17. In both cases, there were no changes in the available OSC. However, the consecutive TPR-H₂ runs had an impact on the TPR profiles. There was a gradual decrease in the low-temperature TPR peak at ~155–200 °C and an increase in the high-temperature peak at 400–450 °C. This shows that the fast oxygen mobility effect is not durable and the lattice distortions induced by high energy milling are metastable. Valence-state Ce^{IV} (0.097 nm) to Ce^{III} (0.114 nm) oscillations gradually released the lattice stresses.



Figure 16. Six consecutive TPR-H₂ profiles of steam jet-milled CZ20 powder ($d_{50} = 0.5$ microns).



Figure 17. Six consecutive TPR-H₂ profiles of steam jet-milled CZ20 ($d_{50} = 0.5$ microns) after reslurring in water, drying, and calcination at 1000 °C for 6 h in air.

However, these changes depend on the material. The data in Table 5 show that for nano-SJM-CZ20 in the first TPR-H₂ run, the fraction of available OSC at a temperature below 300 °C was ~83% and that below 400 °C was ~94%, but it fell rapidly and reached only 17% and 44%, respectively, on the sixth run. A similar but less pronounced decay effect was observed for SJM-CZ20 after re-slurring. The fraction of available OSC on the sixth TPR-H₂ run at a temperature below 300 °C was 50% and below 400 °C was 75%, which is still very high. The data indicate that the re-slurring and re-agglomeration of nano-SJM-CZ stabilized lattice distortions/stresses.

TPR-H ₂ Run	OSC below 400 °C, mM H ₂ /g		OSC below 300 °C, mM H ₂ /g		
	Nanomaterial	After Re-Slurring	Nanomaterial	After Re-Slurring	
1st run	94.3	93.5	82.6	83.6	
2nd run	60.9	96.4	39.5	89.5	
3rd run	52.2	93.2	25.1	80.4	
4th run	50.2	86.9	23.4	67.2	
5th run	48.9	91.4	19.2	68.0	
6th run	43.8	74.5	16.9	51.3	

Table 5. Fraction of OSC (in %) available below 300 and 400 °C for CZ20 nanomaterial ($d_{50} = 0.5$ microns) and for the same CZ after re-slurring in water and drying.

Nano-CZ20 with $d_{50} = 50$ microns was also impregnated with different amounts (from 0.01% to 0.1%) of rhodium or palladium. The data in Table 6 show that the non-impregnated nano-CZ20 had a very low T_{max} of 165 °C and that the presence of PGM resulted in a further shift of the T_{max} to even lower temperatures. Only 100 ppm of Rh was sufficient to move the T_{max} to below 100 °C.

Table 6. T_{max} of steam jet-milled CZ20 (d₅₀ = 0.5 microns) after impregnation with different amounts of Rh and Pd. Calcination at 1000 °C for 6 h.

PGM Loading	T_{max} , °C
0%	165
0.01% Rh	97
0.1% Rh	67
0.1% Pd	84

The typical TPR-H₂ profiles of SJM-CZ20, SJM-CZ20 doped with 0.1%Rh, and unmilled CZ20 doped with 0.1%Rh are presented in Figure 18. It is known that the impregnation of CZ with PGM results in a significant shift in T_{max} from 450–550 to 150–250 °C. As seen, the impregnation of CZ20 with 0.1%Rh shifted the T_{max} to ~150–200 °C. The CZ20-0.1%Rh TPR-H₂ profile and the T_{max} value were very similar to that of the SJM-CZ20 nanomaterial without Rh. The impregnation of nano-CZ20 with 0.1%Rh shifted the T_{max} to 67 °C and changed the TPR profile to bimodal with two distinct sharp peaks.



Figure 18. TPR-H₂ profiles of CZ20 nanomaterial (black), nano-CZ20 doped with 0.1%Rh (red), and unmilled CZ20 doped with 0.1%Rh (blue).

The TPR-H₂ profiles of SJM-CZ20 impregnated with 0.1%Pd after five consecutive runs are shown in Figure 19. There were no changes in the available OSC (~0.7 mM H₂/g), peak shape, or T_{max} , which indicates that the PGM impregnation had a stabilizing effect on the fast oxygen mobility.



Figure 19. TPR-H₂ profiles of CZ20 nanomaterial after impregnation with 0.1%Pd in five consecutive TPR runs.

3. Materials and Methods

3.1. CZ Materials and Aging Conditions

Two types of PIDC commercially available CZ materials with a compositions of 20%CeO₂–70%ZrO₂–5%La₂O₃–5%Pr₆O₁₁ (CZ20) and 40%CeO₂–50%ZrO₂–5%La₂O₃–5%Pr₆O₁₁ (CZ40) were used in the milling experiments. "Fresh" or starting CZ20 and CZ40 materials were calcined at 700 °C for 2 h in air. All of the milled materials were dried at 110–130 °C and then calcined at 700 °C for 2 h in air before aging. The aging of the unmilled and milled CZ20 and CZ40 was carried out at 1000 or 1100 °C for 6 h in air.

3.2. Milling Techniques Used in the Experiments

Steam jet milling. Milling was carried out using the S-Jet 25 Netsch system, in which super-heated steam jets, with a temperature of ~280 °C and pressure of ~10 bar, provided grinding energy. By changing the milling duration (typically from 30 min to 2 h) and the feed rate, different grades of CZ materials with a d_{50} in the range from 0.5 to 1.1 microns were made. The use of super-heated steam in the milling process eliminated CZ contamination with elements from the milling media and resulted in non-aggregated nanosized powders.

Jar milling A 3 L ceramic jar filled with CZ material, milling media (1 mm YSZ beads), and deionized water at a volume ratio of 1:2:5, respectively, was placed onto a U.S. Stoneware roller and the aqueous slurry was mixed under slow rotation (10 RPM) for 48 h. The resultant slurry was freeze-dried to prevent re-agglomeration of the nano-CZ particles.

An Eiger mill (model number M2000 VSZ TEFC I.S.) was used for wet ball milling of CZ. CZ milling was carried out at 2500 RPM in a mill camber filled to 80% with milling beads. YSZ milling beads (0.7 mm) were used as the milling media. After reaching the target particle size, the CZ slurry was separated from the milling beads, dried, and calcined.

3.3. Characterization Methods

 N_2 adsorption–desorption isotherms were measured at 77 K using an automatic Micromeritics ASAP 2020 analyzer after outgassing the sample at 300 °C for 2 h. The specific

surface area (S_a), total pore volume (V_{pore}), and pore size distribution were determined by the BET and BJH methods.

A laser diffraction particle size analyzer Horiba LA-930 was used for the characterization of the milled and unmilled CZ samples. The measurements were carried out in CZ aqueous slurries after 2 min of ultra-sonification and without the addition of surfactants. The average particle size was calculated from the cumulative particle size distribution curve and was reported as d₅₀.

Phase characterization was performed using a Rigaku Mini Flex II X-Ray diffractometer with Cu K α radiation (λ = 1.5406 Å) between 25 and 65 degrees (2 θ), a scan rate of 1 degree per minute, and a step size of 0.04 degrees.

Scanning electron microscopy (SEM) with EDS capabilities was performed using a Carl Zeiss EVO MA10 scanning electron microscope after sputtering the samples with platinum for 60 s.

A JEOL JEM-2100 200 Kv microscope was used to obtain high-resolution TEM images of the single CZ crystals. The crystallographic structure of the ceria-zirconia materials was evaluated using the selected area electron diffraction (SAED).

The TPR-H₂ experiments were conducted using a Micromeritics AutoChem II chemisorption analyzer (Norcross, GA, USA). The CZ sample was first pre-treated in an O₂ atmosphere at 500 °C for 1 h and then cooled to room temperature. The sample was then exposed to a flow of 10% H₂/Ar (5 mL/min) while the temperature was ramped from room temperature to 900 °C at a rate of 10 °C/min. Two consecutive runs were performed for each sample, and the results from the second run were used for characterization of the CZ redox properties.

3.4. CZ Impregnation with Precious Metals (PGM)

A total of 10 g of CZ powder was added to a beaker with 20 mL of water and mixed to make an aqueous slurry. After this, 5% rhodium or platinum nitrate was added to the CZ slurry. The CZ/PGM slurry was then transferred to a 100 mL Teflon bottle with 30 cm³ of 2 mm YSZ milling media, closed, and placed on a jar mill for 30 min of rotation (20 RPM). Then, the resultant slurry was then separated from the milling media and dried in an electric oven at 110 °C. The dry CZ/PGM powder was calcined at the target temperature (700 and 1000 °C).

4. Conclusions

Sub-micron-size CZ materials with a d_{50} in the range of 0.2 to 1.3 microns were prepared using wet (jar and Eiger milling) and dry (steam jet milling) milling techniques. Steam jet milling directly provided dry non-aggregated nano-CZ powders with a d_{50} of ~0.5 microns. The effects of milling type and milling conditions on the morphology and textural properties of CZ were studied. It was found that milling destroyed high-order CZ aggregates, which results in the disappearance of large mesopores and a significant drop in pore volume. Jar milling had the lowest/smallest impact on porosity, while the highest S_a/V_{pore} deterioration was observed after Eiger milling. High-energy steam jet milling under in a quasi-hydrothermal environment (with potential local temperature spikes over 500 °C) significantly impacted the crystal structure of CZ by inducing lattice distortions. It was shown that the acquired lattice stress resulted in a significant increase in the oxygen mobility, which was manifested by a T_{max} shift in TPR-H_2 from ~500 to 150–250 $^\circ C.~CZ$ materials with fast oxygen mobility are metastable phases, and nano-CZ re-slurring in water and/or impregnation with precious metals had a stabilizing effect on the fast oxygen mobility. The mechanochemical activation of ceria-zirconia-based materials depends on the technique and milling conditions. No activation was observed in the case of wet ball jar milling under any circumstances. Eiger milling substantially enhanced the oxygen mobility, but not to a such extent as steam jet milling.

Nano-CZ materials with fast oxygen mobility can be used for making catalysts with a low light-off temperature ("cold start") and PGM thrifting in both gasoline and diesel particulate filters.

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