

Ceria-zirconia solid solutions as possible constituents for Three-way catalysts towards CO oxidation

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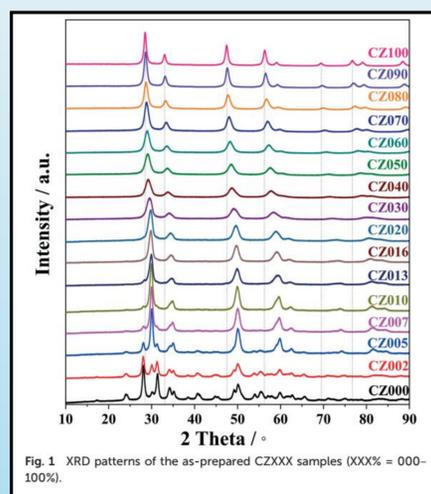
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INTRODUCTION

Heterogeneous catalysis can be considered as a surface phenomenon to a first approximation where the gas phase comes into contact with the solid catalyst surface to transform educts into desired products. However, besides electron exchange between the reactants and the catalyst, constituents of the catalyst from the bulk and the surface, such as oxygen ions of reducible oxides, may participate in oxidation catalysis that is commonly referred to as the Mars-van-Krevelen mechanism. The amount of oxygen that can be exchanged by a reducible oxide with the gas phase or with an active metal component is called the oxygen storage/release capacity (OSC). Oxygen storage in solid catalyst is very important for industrial oxidation reactions such as HCl oxidation reaction (Deacon process). Ceria nanoparticles act as promising catalysts for HCl oxidation reaction. Ceria possesses high OSC (oxygen storage capacity) which is a measure of the oxygen quantity that material can store and release. This makes ceria suitable for redox reactions which usually follow Mars-van Krevelen mechanism (surface oxygen atoms directly involved in reactions). $Ce_{1-x}Zr_xO_2$ solid solutions were prepared as a function of the composition x with constant specific surface area in order to explore the relationship between oxygen storage capacity (OSC) and activity of the oxidation reactions of CO. The as-prepared $Ce_{1-x}Zr_xO_2$ solid solutions were characterized by X-ray diffraction (XRD), Raman spectroscopy (Raman), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Ceria-zirconia solid solutions with different ratios of Ce/Zr were synthesized by the co-precipitation method. Hydrogen peroxide was first dropped into the $Ce(NO_3)_3 \cdot 6H_2O$ solution to obtain a molar ratio of H_2O_2/Ce of 1.5. The corresponding amount of $ZrO(NO_3)_2 \cdot nH_2O$ solution was then mixed with the solution to attain a molar ratio of $Ce/Zr = (1-x)/x$. The precipitation of ceria-zirconia precursor was achieved by dropping an ammonia solution into the solution keeping the pH at around 9.5. The precipitate was stirred for 18 h and then washed with deionized water several times until a pH value of around 7 was reached. The precipitate was then dried overnight at 393 K and calcined at various temperatures (between 700 and 800 °C) for 5 h in order to ensure a constant specific surface area among the various $Ce_{1-x}Zr_xO_2$, $x = 0, \dots, 1$ samples. The samples are referred to as CZXXX with XXX being the atomic percentage (% unit) of cerium.



The ceria-zirconia solid solutions, $Ce_{1-x}Zr_xO_2$, adopt three possible structures: monoclinic (m), tetragonal (t, t', t''), and cubic (c). There is a continuous transition from the mixed monoclinic + tetragonal phase of pure ZrO_2 towards the cubic phase of pure CeO_2 with increasing concentration of CeO_2 . All samples form a solid solution. There is no evidence for peak splitting due to phase separation in ceria-rich and zirconia-rich solutions. For pure ZrO_2 , Rietveld refinement reveals a mixture of 91% monoclinic and 9% tetragonal phase. The main reflections at $2\theta = 24.1^\circ, 28.2^\circ, 31.5^\circ, 34.2^\circ, 40.7^\circ, 49.3^\circ$ are assigned to the monoclinic phase (ICDD NO. 00-036-0420) and the reflections at $2\theta = 30.2^\circ, 35.3^\circ, 50.3^\circ$ are assigned to the tetragonal phase (ICDD NO. 01-079-1770). When the Ce concentration reaches 13–16 at%, the reflections of the monoclinic phase have vanished. For higher Ce concentrations than 16 at% the XRD scans do not change so that no further structural information can be obtained.

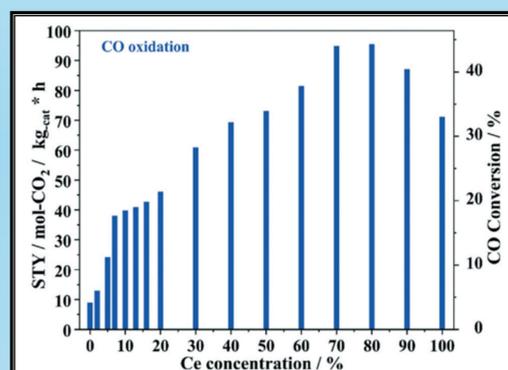
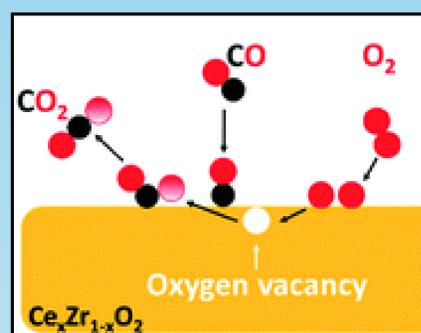


Fig. 4. Space-time yield (STY) per kilogram of catalyst in the CO oxidation for as-prepared CZXXX samples (XXX% = 000-100%). The reaction temperature during the reaction was 430 °C and the reaction condition: $N_2 : CO : O_2 = 89 : 1 : 10$. A total flow rate of 90 sccm was applied.

The activity in Fig. 4. shows a clear trend with increasing concentration of Ce. Starting from ZrO_2 , the activity increases again with increasing Ce concentration up to 80%. CZ070 and CZ080 exhibit highest catalytic activity $STY = 95 \text{ mol}_{CO_2} \text{ kg}_{cat}^{-1} \text{ h}^{-1}$.



RESULTS AND DISCUSSION

Table 1 Physicochemical properties of $Ce_xZr_{1-x}O_2$ (CZXXX: XXX atomic percentage of Ce): BET surface area and textural and structural characterization as determined by XRD: M = monoclinic, T = tetragonal, C = cubic phase

Samples	BET surface area ($m^2 g^{-1}$) ^a		Calcination temperature (°C)	Crystalline size (nm) ^b			M% ^c	T% ^c
	1st time	2nd time		D(M)	D(T)	D(C)		
CZ000	46	45	615	11.8	7.7		91	9
CZ002	48	48	650	11.3	9.2		76	24
CZ005	45	46	700	11.8	10.3		30	70
CZ007	45	47	700	8.0	10.3		18	82
CZ010	46	46	730	8.8	10.0		10	90
CZ013	47	46	730	11.1	8.5		1	99
CZ016	48	45	790		8.0		0	100
CZ020	47	45	780		7.1			
CZ030	47	44	750		6.0			
CZ040	48	48	760		5.2			
CZ050	46	45	730		5.1			
CZ060	46	46	740		5.3			
CZ070	46	47	750		6.4			
CZ080	47	45	720			6.8		
CZ090	48	47	710			8.4		
CZ100	46	47	540			10.0		

^a Determined by BET method. ^b Determined by Rietveld refinement. ^c The percentage of monoclinic phase (M%) and tetragonal phase (T%) were determined by Rietveld refinement.

There are five Raman bands at around 139, 253, 311, 462, 626 cm^{-1} indicating the existence of the t phase in the CZ016, CZ020 and CZ030 samples, even though the exact peak positions vary with the ceria content. The Raman resonances at 129, 300, 470 and 620 cm^{-1} are indicative of the formation of t'' form. For the CZXXX (XXX% = 050–070%), the peak position shifts and decreases from 470.7 to 472.5 cm^{-1} due to variation of the ratio between t'' phase and cubic phase.

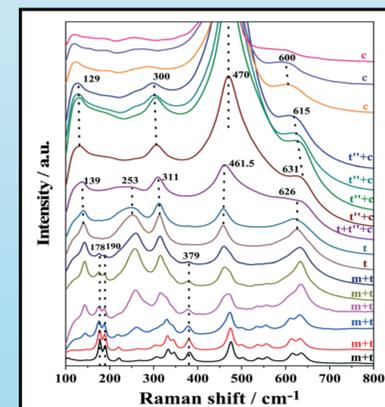


Fig. 2. Raman spectra of as-prepared CZXXX samples (XXX% = 000-100 atomic percent of Ce). Color code is identical to that of Fig. 1.

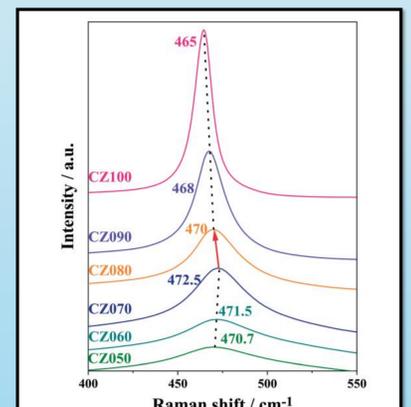


Fig. 3. Raman spectra of as-prepared CZXXX samples (XXX% = 050-100%) with the Raman shift between 400 and 550 cm^{-1} .

CONCLUSIONS

With specifically prepared $Ce_xZr_{1-x}O_2$ solid solutions we compared the OSC with the activity of CO oxidation reaction at the reaction temperature of 430 °C. It turns out that trends in the CO oxidation activity and in OSC as a function of the composition x are virtually identical, thus being compatible with the expected Mars-van-Krevelen mechanism.