



## Effect of promoters on physical properties of nano porous crystalline Ni loaded ZrO<sub>2</sub> supported mixed oxide

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### ABSTRACT

Nano sized crystallites of Ni loaded ZrO<sub>2</sub> supported oxides were synthesized by cost effective co-precipitation method. Effect of promoter on crystallinity and surface area was screened by addition of Ce, Co, Ca, K, with respective nitrates. Crystallinity of synthesized mixed oxides were confirmed by X-ray diffractions and surface area and porosity was analyzed by BET method. NiO is fully reduced to metallic Ni and all the particles are in nano sizes. Morphology of Ce promoted Ni/ZrO<sub>2</sub> oxide was tested by HRTEM analysis. Addition of promoters shows significant increase in crystallinity as well as surface area. Characterization results that among all mixed oxide materials the Ce promoter greatly enhances the structural properties compare to NZ. The order of physical properties is: NCeZ > NCoZ > NCaZ > NKZ > NZ.

### 1. Introduction

Nanoporous materials are highly useful materials in various industrial processes due to their unique physical and chemical characteristics<sup>[1]</sup>. A nanoporous material consists of either an organic and/or inorganic framework, which maintains a porous structure with a typically large surface area to assess the reactants. Nanoporous materials are highly versatile and can be used in various industrial applications ranging from unique properties, making nanoporous materials useful for industrially important applications such as gas storage, separations, catalytic reactions (alkylation, oxidation, methanation, acid base reactions, rearrangements, dehydrogenation, hydrogenation and esterification), adsorption and environmental processes due to the presence of voids and controllable dimension at the atomic, molecular and nanometer scales<sup>[2]</sup>. As such, they are of interest to both chemical and environmental engineers, and with rising environmental concerns worldwide, the use of nanoporous materials in the removal of polluting species from different media as well as the recovery of useful ones has become more significant. A vast number of unique nanoporous materials can be synthesized, varying in chemical composition and pore topology. conventional solid state reaction methods involve heating of precursor materials (in the form of oxides or carbonates or organic derivatives) at higher temperatures, which results in inhomogeneity, bigger crystallite, poor stoichiometry, phase impurity, etc<sup>[3]</sup>. Synthesis and stabilization of nanostructures with required properties are the challenging task, since nano scale materials have large surface area and high reactivity, which tend to react themselves to form necking and hence, agglomerate into large secondary particles<sup>[4]</sup>. Hence, synthesis process plays an

important tool for the design of nanostructures with required properties such as crystallite size, size distribution, shape, homogeneity, etc., in order to meet the requirement for desired specific catalytical applications. Various preparation techniques, such as sol-gel pyrolysis method, hydrothermal technique and mechanical alloying has been used to prepare nanoparticles. But co-precipitation method is considered to be an economical way of producing fine particles<sup>[5]</sup>. Water is an excellent solvent for many ionic compounds. It can dissolve even non-ionic compounds under high pressure and high temperature. In hydrothermal synthesis, the above property of water has been effectively exploited for the preparation of fine powders of metal oxides<sup>[6-8]</sup>.

Under these hydrothermal conditions, water plays two roles as pressure transmitting medium and solvent for the precursors. Such hydrothermal conditions effectively brings down the activation energy for the formation of final phase, which can also speed up the reaction between the precursors, otherwise it would occur only at very high temperatures<sup>[9,10]</sup>. An autoclave is invariably employed to achieve hydrothermal conditions. Powders are either crystalline or amorphous depending on chosen hydrothermal conditions<sup>[11-15]</sup>. Co-precipitation process required to control the concentration of the solution, pH, temperature and stirring speed of the mixture in order to obtain the final product with required properties<sup>[16]</sup>. The advantages of hydrothermal process; 1. Powders are formed directly from the solution, 2. It is possible to control particle size and shapes by using different starting materials and hydrothermal conditions and 3. Resulting powders are highly reactive, which aid in low temperature sintering. The physical properties of nanoparticles are of current interest due to the size-dependent behavior observed in the

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nanometer length scale and high crystallinity. Cost effective Ni-based catalysts have been industrially well practiced because of their excellent catalytic properties. To enhance the catalytically properties of different promoters are loaded to synthesis nanocrystalline porous materials. Synthesis of nanocrystalline porous materials are needed to overcome the shortcomings of Ni catalyst, such as Ni particle sintering and coke deposition, which result in catalyst deactivation. The deactivation can be suppressed significantly when ZrO<sub>2</sub> is used as a catalyst support because the tetragonal phase of ZrO<sub>2</sub> enhances the thermal stability of the Ni catalysts by helping them endure the increased temperature at hot spots, that approximately 100°C higher than operating temperature of the system is most economical way<sup>[17]</sup>. Promoters are commonly introduced as a catalysts<sup>[18-20]</sup> to enhance the activity and metal dispersion such as CeO<sub>2</sub><sup>[21]</sup> and La<sup>[22]</sup> on Ni/Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> on Ni/ZrO<sub>2</sub><sup>[23,24]</sup>.

As though many reports, still synthesis of highly crystalline, nano porous and nano sized Ni is decisive. A major focus of research has been in development of newer methods of synthesis of these materials and also fabrication processes leading to their better performance. In present research work cost effective methods of co-precipitation method was tried to synthesize Ni loaded ZrO<sub>2</sub> supported with different promoter to screen the physical properties. In the following sections, mixed oxides employ a number of physical characterizations are elucidated to distinguish the interesting effects of the promoters.

## 2. Experimental

### 2.1. Catalyst preparation

The bimetallic mixed oxide with addition of a promoter was synthesized by a co-precipitation method. The metallic precursors of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Sigma-Aldrich, 98%), Zr(NO<sub>3</sub>)<sub>4</sub> (Sigma-Aldrich, 99%), Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Sigma-Aldrich, 98%), Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O (Sigma-Aldrich, 99.9%), Ca(NO<sub>3</sub>)<sub>2</sub> (Sigma-Aldrich, 99%) and KNO<sub>3</sub> (Sigma-Aldrich, 99.9%), dissolved in deionized water were used as reagents and a solution of KOH was used as a precipitating reagent. The precipitation was carried out at a room temperature with continuous stirring and the KOH of 0.5M was added to obtain optimum basic side of controlled pH and stirring rate. Catalysts metal compositions are listed in Table 1. The obtained precipitate was filtered, washed and dried at 90°C for 24h. These materials were calcined at 850°C for 4h.

**TABLE 1.** Metallic compositions of the mixed oxides prepared by co-precipitation method

Sample code	mixed oxides	Metal composition (wt.%)		
		Ni	Promoter	ZrO <sub>2</sub>
NCeZ	Ni-Ce-Zr-O	10	5	85
NCoZ	Ni-Co-Zr-O	10	5	85
NCaZ	Ni-Ca-Zr-O	10	5	85
NKZ	Ni-K-Zr-O	10	5	85
NZ	Ni-Zr-O	10	-	90

### 2.2. Characterization

The analysis of crystal phases was performed using the powder X-ray diffraction (XRD) technique. The XRD patterns were recorded on a DX-1000 diffractometer using Cu K $\alpha$  radiation between 20° and 80° with a continuous mode. The voltage and anode current were 40kV and 25 mA, respectively, and the scan step was 0.06 o/s. The size of crystal particles was calculated by applying the Scherrer equation to the half-width of the main XRD peaks. All the characterization method is illustrated in our previous report<sup>[25]</sup>.

The BET surface area and pore size distribution of the samples were obtained from the N<sub>2</sub> adsorption-desorption isotherms at -196 °C using Micromeritics 2010 sorptometer. Prior to the experiments, catalysts were outgassed at 350 °C for 12h under vacuum. The BJH method was applied for determination of pore size distribution.

High resolution transmission electron microscopy (HR-TEM) studies were performed on the NCeZ catalyst in order to examine the particle size, distribution and morphology. All fresh catalysts were first calcined in air at 850 °C for 4h and then reduced in H<sub>2</sub> (1 bar) at 500 °C for 2h before HR-TEM measurements. A 10 mg powder sample was dispersed in 5 mL of pure ethanol and kept in an ultrasonic bath for 20 min. Droplets of the sample were then deposited onto a carbon-covered copper grid and left to dry at room temperature. A JEOL 2100F transmission electron microscope with a field emission gun (FEG) and a point resolution of 0.19 nm were used.

## 3. Result and Discussion

In general, co-precipitation method required metal cations, taken as soluble salts (e.g. nitrates), are co-precipitated from a common medium, usually as hydroxides, carbonates, oxalates or citrates. In actual practice, one takes oxides or carbonates of the relevant metals, digests them with an acid and then the precipitating reagent is added to the solution. In this process, controlling the pH of starting solution is very much important to avoid the precipitation as well as to form the homogenous gel, which can achieved by the addition of base or acidic solutions<sup>[26]</sup>. Physical properties of all the mixed oxides prepared by the co-precipitation method are listed in Table 2.

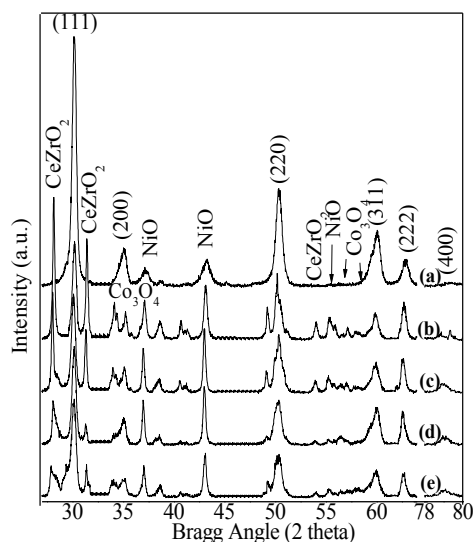
**TABLE 2.** Physical properties of with and without promoter added mixed oxides

Sample code	Surface area m <sup>2</sup> /g	Pore volume (ml/g)	Average pore diameter (nm)	Particle size of NiO nm) <sup>a</sup>
NCeZ	49.2	0.245	14.82	7.1
NCoZ	37.8	0.216	13.06	8.6
NCaZ	35.9	0.206	12.83	9.4
NKZ	33.7	0.184	12.59	12.6
NZ	29.6	0.164	10.54	14.2

<sup>a</sup>Particle size is measured from Scherrer equation by XRD pattern

The BET specific surface areas and pore size distributions of the catalysts showed comparable results. The surface area of unprompted NZ catalyst was 29.6 m<sup>2</sup>/g with a pore volume of 0.164 ml/g. Addition of promoters Ce, Co, Ca, K to NZ catalyst showed remarkable improvement in surface areas and pore volumes. Compared with other catalysts, the NCeZ catalyst showed the highest surface area of 49.4 m<sup>2</sup>/g with pore volume of 0.245 ml/g, and the NKZ catalyst showed the lowest surface area of 33.7 m<sup>2</sup>/g with pore volume of 0.184. These results clearly indicates that every promoter as significant role as a bimetallic and influenced the textural surface properties markedly. Fig. 1 illustrates the XRD patterns of oxides with and without a promoters, calcined at 850°C. Main broad diffraction lines are due to a cubic fluorite type phase corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 0 0) planes of ZrO<sub>2</sub> supports (PDF-ICDD 28-0271). The XRD profiles exhibited that nickel oxide (NiO) species did not affect the cubic phase structure of ZrO<sub>2</sub><sup>[25]</sup>. The diffraction peaks of NiO were intense at 31.9° and broader at 36° and 43.2° over NCeZ catalyst but their intensity decreased for other promoters NCoZ, NCaZ and NKZ as shown

in Fig. 1a–d. The unpromoted NZ mixed oxide showed weak peaks of Ni in Fig. 1e. The same trend could be observed for NiO phase. This clearly indicates that the type of promoter plays a unique role on crystallinity of other phases. Among bimetallic oxide the NCeZ catalyst shows more noticeable reflections of NiO compared with NCoZ catalyst<sup>[7]</sup>. However, doping of ceria with aliovalent cations, probably introduced into the network of the fluorite type oxide, has been an efficient way to generate oxygen vacancies, permitting a high mobility of oxygen from bulk to surface.

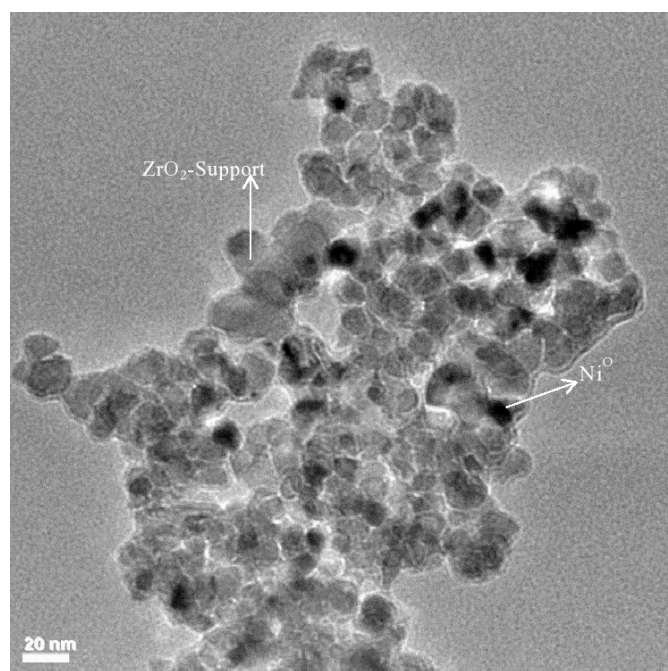


**Fig. 1.** XRD patterns of mixed oxides (a) NCoZ, (b) NCoZ, (c) NCoZ, (d) NKZ and (e) NZ, after 850°C of calcination.

In addition, the doping of ceria positively influences the thermal stability and the surface area of the compound in comparison to the pure oxides<sup>[27,28]</sup>. In Table 2 crystal sizes of Ni were calculated for all the samples by the Scherrer equation;  $D = K/\cos$ , where  $D$  is the active metal particle size,  $K$  is the Scherrer constant (0.89),  $\lambda$  is the wavelength of X-ray (1.5408 Å),  $\theta$  is the diffraction angle, and  $\beta$  is the half-peak width (radian)<sup>[29]</sup>. The particle sizes of NiO in Ce and Co-promoted oxide were smaller than those for Ca, K promoted oxide, suggesting that promoters could improve the dispersion of the nano-sized NiO species. Better dispersed NiO species were noticed when the mixed oxides were prepared by co-precipitation method than wet-impregnation method on Zr-support. The Mn phase was not detected. It appears that Ce has a better effect than Ca and K in promoting activity of the Ni catalyst. Since promoter is in low quantity (2 wt.%) of metals in all catalysts is kept the same, the result represents a synergistic effect of the three metals on physical properties. As low quantity the prepared mixed oxides are cost effective, reusable as bimetallic catalysts due to remarkable improvement in crystallinity, surface area and Ni particles are in nano sizes. In carbon dioxide dry reforming of methane to produce synthesis gas over modified Ni/Al<sub>2</sub>O<sub>3</sub> with La<sub>2</sub>O<sub>3</sub>, MgO and CaO, Roh and Jun<sup>[30]</sup> found that La<sub>2</sub>O<sub>3</sub> increased better the activity and stability compared to MgO or CaO. It was suggested that carbon deposition was suppressed when Ni was supported on a metal oxide with a strong Lewis basicity<sup>[31]</sup>. The nature of the support was reported to significantly influence the performance of the catalyst due to a metal-support interaction and acid-base properties of the catalyst<sup>[32-34]</sup>. The cobalt catalyst when combined with other oxides, showed different activities. The Co–Mn mixed oxides were found to be the most active and stable catalysts for N<sub>2</sub>O

decomposition on alumina support by changing their acid–base function of the surface and metal dispersion<sup>[35]</sup>. Juan-Juan<sup>[36]</sup> studied the effect of potassium as a promoter on the catalytic activity and structural properties of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst used for the CO<sub>2</sub> reforming.

Morphological characteristics of the NCoZ mixed oxide was examined by HRTEM analysis in an attempt to find further evidence to support the existence of Ni metal in nano sizes and ZrO<sub>2</sub> as shown in Fig. 2. The morphology of the NCoZ mixed oxide shows aggregation Ni nano particles are well dispersed over ZrO<sub>2</sub> crystals with particle size of 3.6 nm. The NCoZ mixed oxide is made of fairly uniform spherical particles with much smaller sizes. The particle size distributions obtained by random counting from the HRTEM micrographs showed that more than 75% of the particles were below 10 nm. The particles sizes from XRD and HRTEM are shows a good agreement. It is observed that the white spots as the desired element mapping exhibit good distributions on the catalyst granule without any serious segregation. It is known that the nano size of active metals is important to catalytical applications like reforming reactions to maintain high surface area, stability and decoking of catalyst<sup>[37,38]</sup>.



**Fig. 2.** HRTEM image of NCoZ mixed oxide

#### 4. Conclusion

Highly crystalline nanoporous Ni loaded ZrO<sub>2</sub> crystals mixed oxide are developed by cost effective co-precipitation method. Low fractions of promoters are added to in synthesis to enhance the physical properties. All the mixed oxides are retain the crystallinity and well improved textural properties and these mixed oxides can be used as a catalyst in different reactions as Ni particles are in nano sizes. In nutshell promoters do assist the formation of smaller and more reduced metal particles on ZrO<sub>2</sub> support to increase the number of active sites.

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