



Short communication

# Synthesis, characterization and correlation with the catalytic activity of efficient mesoporous niobia and mesoporous niobia–zirconia mixed oxide catalyst system



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## ABSTRACT

Mesoporous mixed oxide has always remained as a subject of interest due to diffusion relaxation and generation of new surface potential and acidity by mixing of different stoichiometries of metal oxide. To deliver more insight on niobia based catalyst, herein, we have synthesized mesoporous niobia and five different mole ratios of niobia–zirconia mixed oxide. The catalysts were characterized by XRD, N<sub>2</sub>-physorption, FTIR, UV–Vis and NH<sub>3</sub>-TPD techniques. Less distorted NbO<sub>6</sub> octahedra and NbOH or Nb–OH–Zr are found to act as Bronsted center responsible for reaction. The results established the role of Kung model to generate acidic sites in mesoporous mixed oxide.

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## 1. Introduction

The current trend of greener approach towards  $\epsilon$ -caprolactam production through Beckmann rearrangement reaction has changed through the use of mesoporous catalytic materials instead of microporous materials [1,2]. In most of earlier studies sulfated or phosphated microporous/mesoporous or B, Al, Bi, W and Nb supported microporous/mesoporous materials were used [1,2]. Among the supports chiefly alumina, zirconia, titania, silica and mixed supports were used. Although the heterogeneous chemistry of B, Al based catalyst system has been practiced however W and Nb based systems are focussed [3,4] recently. Mesoporous mixed oxide is always a subject of interest due to diffusion relaxation by pores in mesoporous range and generation of new surface potential and acidity by mixing of different stoichiometries of metal oxide. Tanabe et al. proposed that acidity is generated when mixed oxides formed from oxide of different stoichiometries [5]. Further, Kung explored the consequences of balance of stoichiometry [6,7]. To deliver more insight on niobia based catalyst, herein, we have synthesized mesoporous niobia by varying Nb:Zr mole ratios and characterized it by XRD, FESEM, UV, IR and NH<sub>3</sub>-TPD techniques. The activity of the catalyst

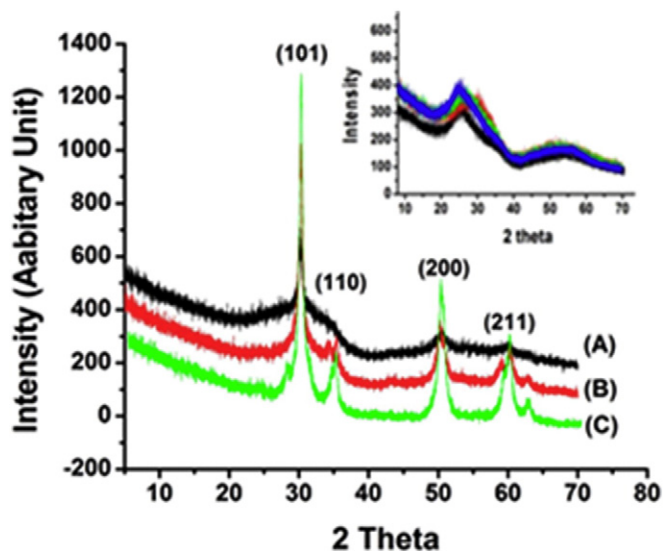
was tested for vapor phase Beckmann rearrangement reaction. The characterization results were correlated with catalytic activity results by Kung model.

## 2. Experimental

### 2.1. Catalyst preparation

Highly ordered mesoporous niobia–zirconia composites with broad Ti/Zr ratios were prepared via an evaporation-induced self assembly (EISA) process [8]. 1.0 g Pluronic P123 was dissolved in 10 ml of ethanol at room temperature. Then quantitative 1.45 g ZrOCl<sub>2</sub>·8H<sub>2</sub>O and 0.270 g NbCl<sub>5</sub> ethanol solutions were added (total amount of Nb plus Zr is 5 mmol) into the above solution with vigorous stirring. The composition of Nb/Zr/P123/EtOH (molar ratio) was varied in the range of (0.5–4.5)/(4.5–0.5)/0.08/170. The mixture was covered with polyethylene film. After stirring for at least 2 h at room temperature, the homogeneous sol was transferred to an oven for solvent evaporation. After two days of aging at 313 K, the gel product was dried in another oven at 373 K for 1 day. Further, calcination was carried out by slowly increasing temperature from room temperature to 673 K (1 K min<sup>-1</sup> ramping rate) and the heating at 673 K was continued for 4 h in air. Finally, high temperature treatment was carried out in air for 1 h with a temperature ramp of 10 K min<sup>-1</sup>.

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**Fig. 1.** XRD of (A)  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 30/70$ ), (B)  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 10/90$ ), (C)  $\text{ZrO}_2$ . Inset shows XRD of  $\text{Nb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 90/10$ ,  $\text{Nb/Zr} = 70/30$ ,  $\text{Nb/Zr} = 50/50$ ).

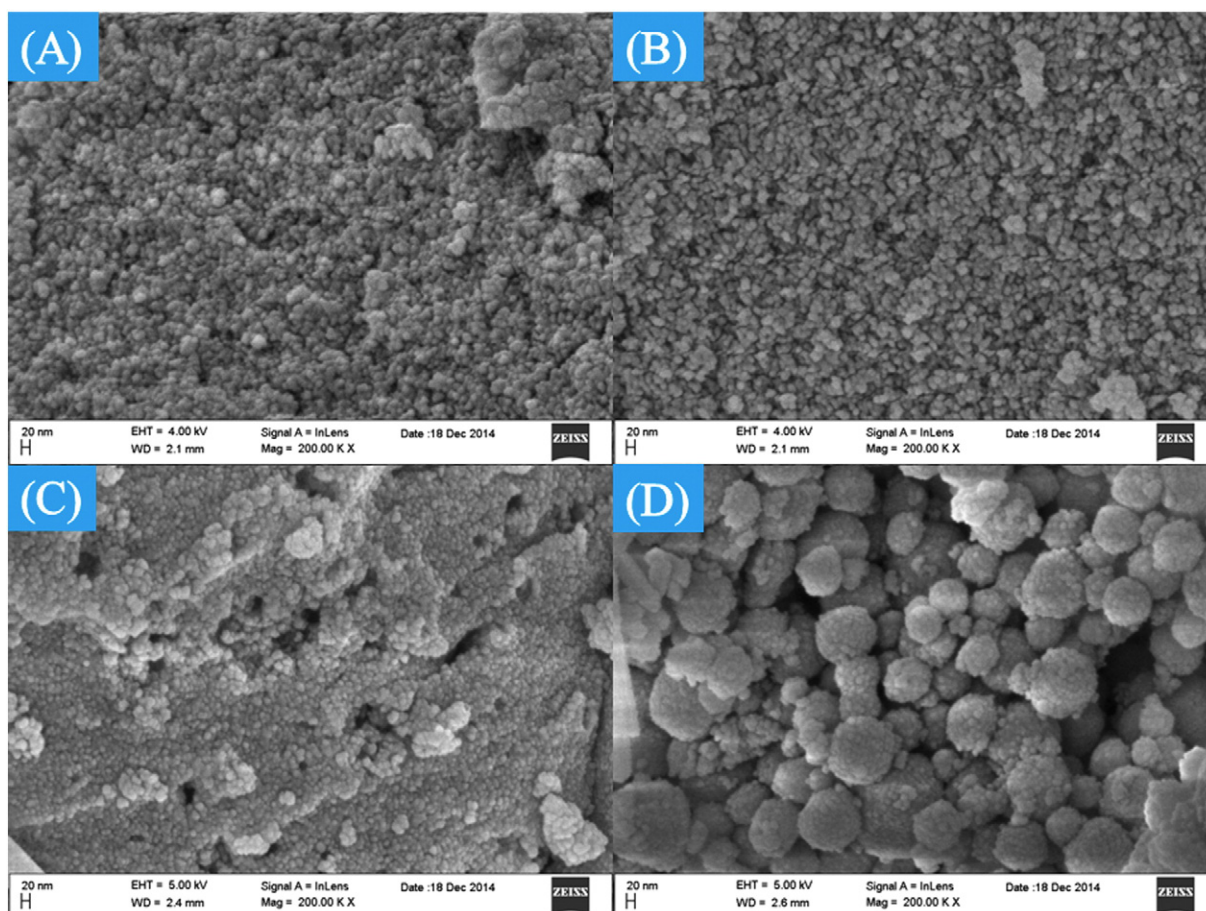
## 2.2. Characterizations

X-ray powder diffraction (XRD) was performed with Rigaku Ultima 4 diffractometer using  $\text{Cu K}\alpha$  radiation having wavelength,  $k = 1.54056 \text{ \AA}$ . The average crystallite sizes were estimated by considering

most intense diffraction peak (101) located at  $2\theta = 30.23^\circ$  through Scherrer's formula  $D = 0.94 k / (\beta \cos\theta)$ , where  $D$  was the average crystallite size,  $k$  was the X-ray wavelength,  $\beta$  was the peak width at half height, and  $\theta$  Bragg's angle. Small angle X-ray diffraction analysis was carried out by using a Bruker AXS D-8 advance diffractometer. Field emission scanning electron microscopy (FESEM) was done using supra 55 (Zeiss, Germany) microscope equipped with oxford instrument X-max detector and Gemini beam line attachment. The BET surface area and pore size analysis of the samples were carried out with liquid nitrogen at 77 K temperature with a Quantachrome Nova 3200e instrument. The sample pretreatment was done at 573 K for 5 h under high vacuum. Surface area and pore size distribution were calculated through Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) pore size distribution respectively. UV visible measurement was carried out in Varian Cary 500 (Shimadzu) spectrophotometer. Ammonia temperature programmed desorption ( $\text{NH}_3\text{-TPD}$ ) of the sample was done by using a thermal conductivity detector (TCD) in a Micromeritics Chemisorb 2750 (USA) instrument. For the experiment, the samples were first degassed in Helium flow at a flow rate of 30 ml/min for 2 h at 473 K temperature. Then the sample was saturated with 10%  $\text{NH}_3$  in Helium at room temperature for 30 min. Afterwards the excess  $\text{NH}_3$  was flushed out in 30 ml/min He flow for 45 min. Then desorption of ammonia (carrier gas He) in various temperature was obtained by heating the catalyst to 773 K at a temperature ramp of 10 K/min.

## 2.3. Vapor phase Beckmann rearrangement of cyclohexanone oxime

The catalytic reaction was carried out in fixed bed quartz catalytic reactor (inner diameter 1.5 cm). 0.5 g catalyst was packed into the reactor



**Fig. 2.** FESEM image of (A)  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 90/10$ ), (B)  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 70/30$ ),  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 30/70$ ),  $\text{Nb}_2\text{O}_5\text{-ZrO}_2$  ( $\text{Nb/Zr} = 10/90$ ).

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