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Preparation of Cerium-Impregnated Zeolite NaY and Investigation of Surface Acid-Base by Catalytic Transformation of Methylbutynol

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Abstract. Cerium on zeolite NaY was prepared by incipient wetness impregnation (Ce-NaY-IMP). Upon calcination, CeO₂ species is generated, as confirmed by Raman and DR UV-Vis spectroscopy. The investigation of acid-base properties by the transformation of methylbutynol (MBOH) revealed that Ce-NaY-IMP enhanced only the selectivity of basic pathway products. The impregnation increased Lewis basic sites from oxygen vacancies within CeO₂ lattice. In addition, the basicity of Ce-NaY-IMP suppressed the acidity or charge compensating cations sites of parent NaY.

Keywords: Zeolite Y, Impregnation, Acid-Base, Cerium oxide, Methylbutynol.

1. Introduction

There are several reports on the preparation of supported cerium zeolite Y (Ce-NaY) by impregnation [1-4]. This method gives a good dispersion of active species, in this case, cerium oxide (CeO₂). Its surface contains both acid and basic sites [5]. However, CeO₂ is known as a basicity-dominated catalyst due to oxygen vacancies in the lattice that could contribute two unpaired electrons or called Lewis basic sites [6].

Various techniques have been used to study surface properties of oxides, for instance, infrared (IR) or nuclear magnetic resonance (NMR) spectroscopy, NH₃ or CO₂ thermal desorption and calorimetry, etc. [7]. Apart from that, catalytic test reaction has been developed as a tool for the differentiation of acid-base properties of materials [8]. Herein, methylbutynol (MBOH), the simplest tertiary alkynol, is a suitable diagnostic molecule for catalytic testing because it decomposes into various products when reacts on acidic, basic or coordinatively unsaturated (defect) sites as depicted in figure 1 [9].

The present work aims to prepare Ce impregnated on zeolite Y and characterize by several techniques along with the investigation of the acid-basic properties by transformation of MBOH.

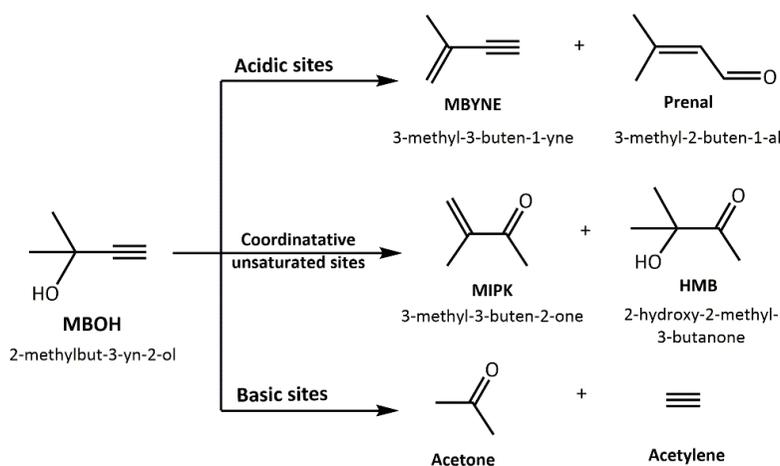


Figure 1. Reaction pathways of MBOH.

2. Experiment

2.1. Preparation of cerium-impregnated NaY

The sample was prepared by the incipient wetness method, modified from the literature [3]. An aqueous solution of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Acros Organics) was dropped slowly to parent zeolite NaY (commercial Y zeolite in sodium form, $\text{SiO}_2:\text{Al}_2\text{O}_3 = 5.1:1$, Alfa Aesar). The mixture was stirred for 10 min and sonicated in an ultrasonic bath for further 10 min. Then, it was air-dried for 24 h, oven-dried at 110 °C for 6 h, and calcined at 550 °C for 2 h. The sample was named “Ce-NaY-IMP”. The Ce loading was 10 wt.%.

2.2. Characterization

Phases of impregnated sample and parent zeolite were investigated by X-ray diffraction (XRD, Bruker D8 ADVANCE) with a Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$ operated at the voltage and current of 40 kV and 40 mA, respectively. Functional groups and vibration bands were studied by Fourier Transform Infrared Spectroscopy (FTIR, Bruker Tensor 27) using Attenuated Total Reflectance (ATR) mode and the spectrum was recorded in the 1200 - 400 cm^{-1} region. Vibration states of the Ce surface species were studied by Raman spectroscopy (FT-Raman, Bruker VERTEX 70, RAM II module). The spectra were recorded in the 800 - 200 cm^{-1} region at a resolution of 4 cm^{-1} for 100 scans. Forms of Ce species were identified by Diffused reflectance UV-Vis spectroscopy (DR UV-Vis) (Agilent Technologies, Cary 300). With double-beam mode, the diffuse reflectance (%R) spectra were recorded in the wavelength range of 200 - 800 nm. Morphology and crystallinity were analyzed by scanning electron microscopy (SEM, JEOL JSM-6010 LV).

2.3. Catalytic transformation of methylbutynol (MBOH)

The reaction was conducted in a fixed bed reactor controlled by an automated bench unit at Carl von Ossietzky Universität Oldenburg, Germany [10]. Firstly, each sample was ground and sieved into 200-315 μm size range. The 0.200 grams of sample was activated by heating to 350 °C and kept at this temperature for 4 hours under N_2 flow. Then the temperature was lowered to 150 °C. A reactant or MBOH (95 vol%) was mixed with toluene (5 vol% as an internal standard) and cooled to 13 °C (MBOH and toluene with a purity of 99% were obtained from Fluka and used without further purification). Afterward, the mixture was vaporized and

flowed over the sample by N₂ carrier gas. The temperature was maintained at 150 °C for catalytic activity test. The gas products were analyzed on-line by a gas chromatograph (Hewlett Packard, HP 5890 Series II with FID detector type). The data analysis was obtained from a calculation of MBOH conversion (X_{MBOH}), yield (Y) and selectivity (S) of each product from the transformation of MBOH by Equations 1-3, respectively.

$$X_{\text{MBOH}} (\%) = \frac{n_{\text{MBOH, in}} - n_{\text{MBOH, out}}}{n_{\text{MBOH, in}}} \times 100 \quad (1)$$

$$Y_{\text{P}} (\%) = \frac{A_{\text{P}} R_{\text{P}} / M_{\text{P}}}{\sum_{\text{K}} A_{\text{K}} R_{\text{K}} / M_{\text{K}}} \times 100 \quad (2)$$

$$S_{\text{P}} (\%) = \frac{Y_{\text{P}}}{X_{\text{MBOH}}} \times 100 \quad (3)$$

3. Results and Discussion

3.1. Phase analysis, functional groups and Ce forms

Figure 2(a) exhibits XRD patterns of the parent zeolite Y (NaY) and sample from impregnation method (Ce-NaY-IMP). The characteristic peaks at 2 θ around 6.19, 10.11 and 11.86 degree of faujasite framework [11] are observed from both diffractograms. The relative zeolite peaks intensities of Ce-NaY-IMP are lower than that of NaY indicating the loss of crystallinity after calcination. Moreover, the decrease could be from X-ray absorption of Ce species [12]. However, peaks corresponding to cerium oxide (2 θ = 28 °, 33 ° and 48 °) are not observed in Ce-NaY-IMP, implying a good dispersion or CeO₂ peaks might overlap with the similar peak positions of the zeolite [3].

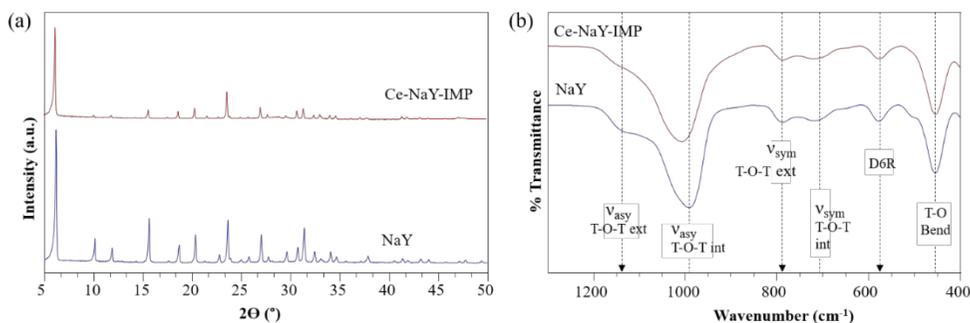


Figure 2. XRD patterns (a) and FT-IR spectra (b) of NaY and Ce-NaY-IMP.

Figure 2(b) illustrates FTIR spectra in 1200 to 400 cm⁻¹, the range of the zeolite vibrations. Both spectra are similar in shape but different in frequency and intensity. Comparing with the dash lines position of NaY, the spectrum of Ce-NaY-IMP show vibrational bands around 453, 712 and 992 cm⁻¹ corresponding to TO₄ (T = Si, Al) bending, symmetrical and asymmetrical stretching of internal tetrahedron linkages [13]. These vibrations are observed for all aluminosilicates. While the peaks (dash lines with arrow) around 578, 789 and the shoulder at 1145 cm⁻¹ are attributed to the double 6-membered ring (D6R), symmetrical and asymmetrical stretching of external linkages between TO₄ tetrahedra of faujasite framework, respectively [13]. However, differences among Ce-NaY-IMP with parent NaY are clearly seen at the band and shoulder in the region of 900-1200 cm⁻¹. The frequencies shifts are sensitive from the framework Si/Al ratio [14]. The shifts might be attributed to acidic impregnated solution of cerium nitrate hexahydrate step that lead to partial dealumination of parent zeolite [15].

Figure 3 shows SEM images with different magnitudes. The parent NaY has various shape and size of crystals (figure 3a - c). The images from the larger magnification show agglomeration of polycrystalline (figure 3b) and mix morphologies (figure 3c). For Ce-NaY-IMP, the micrographs reveal similar appearance to NaY. The crystallinity with clear faces and edges of zeolite are preserved after Ce introduction by incipient wetness impregnation. However, the CeO₂ particles are not observed in these images. The presence of Ce forms is explained by the next techniques.

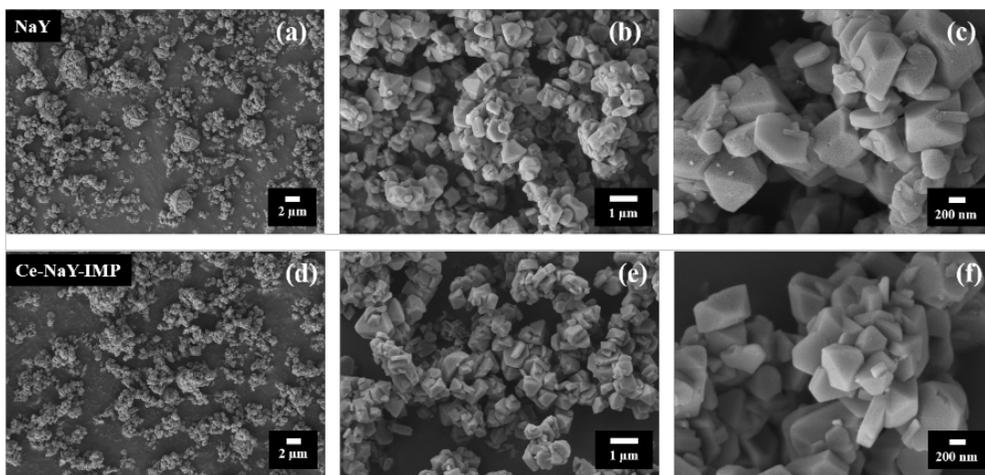


Figure 3. SEM images of NaY (a-c) and Ce-NaY-IMP (d-f).

Figure 4a presents Raman spectra in the range of 800 to 200 cm⁻¹. The band corresponding to Ce species is observed at 464 cm⁻¹ in Ce-NaY-IMP which locates at the same wavenumber compared with pure CeO₂ (inset figure). This peak is assigned to symmetric vibration mode of oxygen at neighboring positions of the Ce⁴⁺ ions (O – Ce – O). It is characteristic F_{2g} vibration of CeO₂ or ceria fluorite-type lattice [17]. Another Raman band at ~500 cm⁻¹ in both spectra is attributed to T–O–T bending of zeolite 4-membered rings. This band is correlated to the ring size, average T–O–T angle and the Si/Al ratio in the crystalline framework [17].

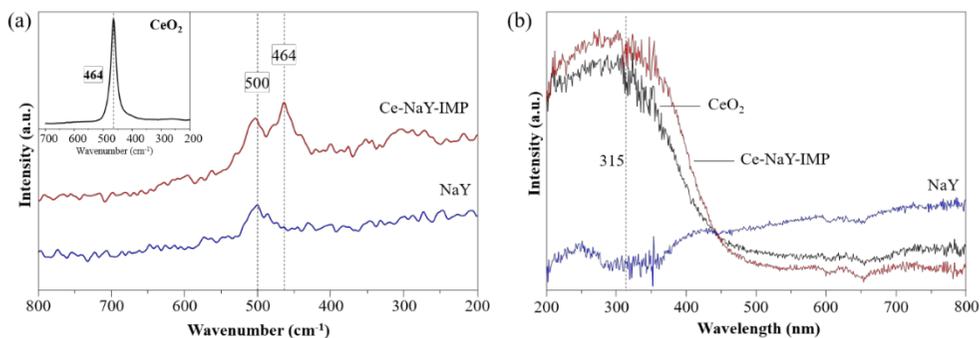


Figure 4. Raman spectra (a) and DR UV-Vis spectra (b) of NaY, Ce-NaY-IMP and CeO₂.

Figure 4b exhibits the UV-DR spectra. The spectrum of NaY displays no significant absorption. The bare ceria shows a large absorption band around 315 nm (dash line) originates from a charge transfer transition from O 2p to Ce 4f [18]. The Ce-NaY-IMP spectrum exhibits a small difference in the peak shape compared to CeO₂. That probably caused by some interaction between the oxide species and zeolite [1].

3.2. Catalytic transformation of MBOH

The acid-bas properties of NaY and Ce-NaY-IMP were investigated by the transformation of MBOH at 150 °C with the sample amount of 0.200 g. The catalytic activity in term of conversion and selectivity versus time on stream are presented in figure 5. From figure 5a, the MBOH conversion of NaY is around 9% in the first 25 min. After that, it swings and slightly decreases to 4% after 90 min. Comparing to the similar work [9], they obtained low conversion with a steady value of around 4%. This difference is mainly from the lower reaction temperature and less catalyst amount, namely, 120 °C and 0.020 g, respectively. In the case of Ce-NaY-IMP, it shows higher conversion and steady numbers between 16 - 18%. It was noticeable that the modification of zeolite Y by cerium impregnation changes the catalytic activity of the materials, which are discussed in more detail together with the results of product selectivity.

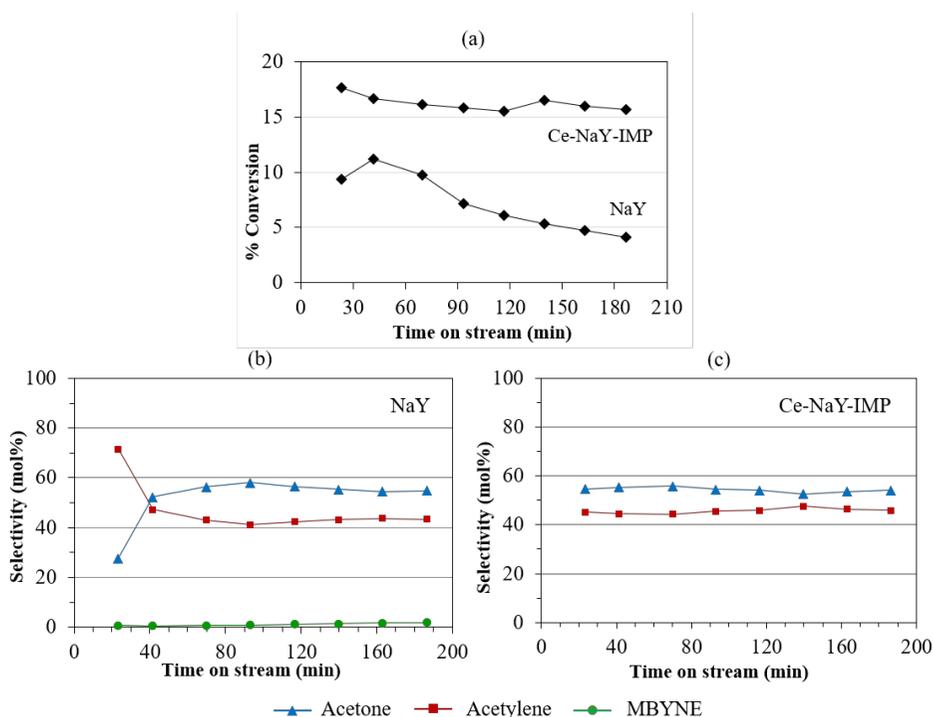


Figure 5. MBOH conversion (a) of NaY and Ce-NaY-IMP and product selectivity of (b) NaY, and (c) Ce-NaY-IMP.

Figures 5b and 5c present the selectivity versus time on stream. The NaY contains acetone and acetylene as major products with a small amount of MBOH as depicted in figure 5(a). So, the surface of the NaY zeolite contains predominantly basic sites and a very small number of acidic sites. The basic reactivity of zeolites is contributed from intrinsic oxygen atoms in the framework, defined as Lewis basic sites that form acid-base pairs with the charge compensating cations [19]. Apart from that, the selectivity distribution of NaY reveals the molar ratio between acetone and acetylene higher than the theoretical value. The possible ratio is 1.00 as acetone and acetylene generated from the cleavage of MBOH molecule. In addition, the ratio could be less than 1.00 since acetone might further condense producing products that adsorbed strongly on the surface [20]. However, the obtained converse result in this work still could not be explained.

The product selectivity of Ce-NaY-IMP in figure 4a only shows acetone and acetylene. Hence, the sample contains basic-catalyzed property. The conversion improvement is attributed from an enhancement of Lewis basic sites resulted from oxygen vacancies of CeO₂ phase [21] containing in Ce-NaY-IMP. The catalytic activity of ceria supports the existence of Ce⁴⁺ species with above Raman and DR UV-Vis results. Nevertheless, the selectivity of acid-catalyzed products like parent NaY are not observed. This result indicates that impregnation with cerium suppressed the acidic sites of NaY. As [9] reported the absence of acidic products from the potassium-impregnated on zeolite Y.

4. Conclusion

CeO₂ on zeolite Y (Ce-NaY-IMP) is prepared by the impregnation method. The structure of zeolite is preserved after Ce loading. The catalytic testing of Ce-NaY-IMP, comparing to parent NaY, promoted MBOH transformation by oxygen vacancies - containing in CeO₂ that act as Lewis basic sites. In addition, the impregnated CeO₂ suppressed the acidity of NaY and provided only basic-catalyzed property.

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6. References

- [1] Krishna Reddy J, Suresh G, Hymavathi C H, Durga Kumari V, and Subrahmanyam M 2009 *Catal. Today* 141(1) 89
- [2] Huang Q, Xue X, and Zhou R 2010 *J. Hazard. Mater.* 183(1) 694
- [3] Saceda J J F, Rintramee K, Khabuanchalad S, Prayoonpokarach S, de Leon R L and Wittayakun J 2012 *J. Ind. Eng. Chem.* 18(1) 420
- [4] Cheng X, Huang L, Yang X, Elzatahry A A, Alghamdi A and Deng Y 2019 *J. Colloid Interf. Sci.* 535 425
- [5] Cutrufello M G, Ferino I, Monaci R, Rombi E, and Solinas V 2002 *Top. Catal.* 19(3) 225
- [6] Chen W, Ran R, Weng D, Wu X, Zhong J and Han S 2017 *J. Rare Earth.* 35(10) 970
- [7] Wu Z, Mann A, Li M, and Overbury S 2015 *J. Phys. Chem. C* 119(13) 7340
- [8] Lauron-Pernot H. 2006 *Catal. Rev.* 48(3) 315
- [9] Supamathanon N, Supronowicz W, Roessner F, Wittayakun J and Prayoonpokarach S 2012 *Quim. Nova* 35(9) 1719
- [10] Kuśtrowski P, Chmielarz L, Bożek E, Sawalha M and Roessner F 2004 *Mater. Res. Bull.* 39 263
- [11] Mintova S (Editor) and Barrier N (XRD Patterns) 2016 *Verified syntheses of zeolitic materials, 3rd revised edition* (Amsterdam: Elsevier)

- [12] Fillipe A C G, Araújo D R, Silva J C M, Macedo J L D, Ghesti G F, Dias S C L, Dias A J and R Filho G N 2011 *J. Braz. Chem. Soc.* 22 1894
- [13] Flanigen E M 1976 *ACS Monograph* 171 80
- [14] Miecznikowski A and Hanuza J 1985 *Zeolites* 5 188
- [15] Beyer H K 2002 *Dealumination Techniques for Zeolites. In Post-Synthesis Modification I* (Berlin, Heidelberg: Springer Berlin Heidelberg)
- [16] Schmitt R, Nenning A, Kraynis O, Korobko R, Frenkel A I, Lubomirsky I, Haile S M and Rupp J L M 2020 *Chem. Soc. Rev.* 49(2) 554
- [17] Wang N N, Wang Y, Cheng H F, Tao Z, Wang J and Wu W Z 2013 *RSC Adv.* 3(43) 20237
- [18] Sahu P, Eniyarppu S, Ahmed M, Sharma D, and Sakthivel A 2018 *J. Porous Mater.* 25(4), 999
- [19] Barthomeuf D 1996 *Catal. Rev.* 38(4) 521
- [20] Aramendía M A, Boráu V, García I M, Jiménez C, Marinas A, Marinas J M, Porras A and Urbano F J 1999 *Appl. Catal. A-Gen* 184(1) 115
- [21] Chen W, Ran R, Weng D, Wu X, Zhong J and Han S 2017 *J. Rare Earth.* 35(10) 970