

PREPARATION OF CERIUM-IMPREGNATED SODIUM Y AND INVESTIGATION OF ACID-BASE BY CATALYTIC TRANSFORMATION OF METHYLBUTYNOL

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Received: November 28, 2020; Revised: December 15, 2021; Accepted: December 17, 2021

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 NaY, Impregnation, Cerium Oxide, Acid-Base, Methylbutynol

Introduction

There are several reports on the preparation of supported cerium zeolite Y (Ce-NaY) by impregnation (Krishna Reddy *et al.*, 2009; Huang *et al.*, 2010; Saceda *et al.*, 2012; Cheng *et al.*, 2019). This method gives a good dispersion of active species, in this case, cerium oxide (CeO₂). Its surface contains both acid and basic sites (Cutrufello *et al.*, 2002). 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 (Chen *et al.*, 2017).

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. (Wu *et al.*, 2015). Apart from that, catalytic test reaction has been developed as a tool for the differentiation of acid-base properties of materials (Lauron-Pernot, 2006). Herein, methylbutynol (MBOH), the simplest tertiary alkynol, is a suitable diagnostic molecule for catalytic testing because it decomposes into various products when reacts on

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acidic, basic or coordinatively unsaturated (defect) sites as depicted in Figure 1 (Supamathanon *et al.*, 2012).

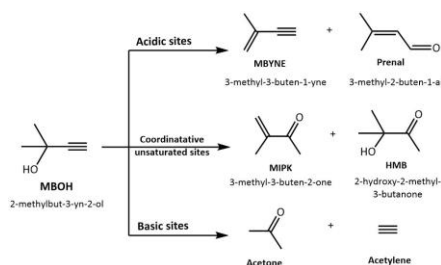


Figure 1. Reaction pathways of MBOH

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.

Methods

Preparation of Cerium-Impregnated NaY

The sample was prepared by the incipient wetness method, modified from the literature (Saceda *et al.*, 2012). 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 a 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%.

Characterization

Phases of impregnated sample and parent zeolite were investigated by X-ray diffraction (XRD, Bruker D8 ADVANCE) with a $\text{Cu K}\alpha$ 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 $1,200\text{--}400 \text{ cm}^{-1}$ 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 $800\text{--}200 \text{ cm}^{-1}$ 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 elemental analysis of the impregnated sample were analyzed by scanning electron microscopy (SEM and SEM-EDX, JEOL JSM-6010 LV). The porosity of the materials was investigated by N_2 sorption analysis (NOVA 2000e Surface Area and Pore Size Analyzer). Prior to the measurement, samples were degassed under vacuum at 300°C for 3 h. The Brunauer-Emmett-Teller equation (BET) equation was used to calculate the surface area while the t-plot method was used to investigate the micropore properties. The basicity of materials was examined by temperature-programmed desorption of carbon dioxide (CO_2 -TPD). The experiment was carried out on a Belcat-B with a thermal conductivity detector (TCD). The sample (50 mg) was packed in a tubular U-shaped quartz cell. The pretreatment was operated at 300°C under a flow of He (50 mL/min) to remove physisorbed species and cooled to 50°C . After that, the mixture of CO_2/He was flowed into the sample for the adsorption process for 30 min. Then the saturated sample was purged by He atmosphere for 15 min. The measurement of CO_2 -TPD was operated in the range of $50\text{--}700^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$ under the flow of He. The basicity of both samples was calculated from the peak areas.

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. Firstly, each sample was ground and sieved into a 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 h 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 N_2 carrier gas. The temperature was maintained at 150°C for the 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 (Kuśtrowski *et al.*, 2004).

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

$$Y_p (\%) = \frac{A_p R_p / M_p}{\sum_K A_K R_K / M_K} \times 100 \quad (2)$$

$$S_p (\%) = \frac{Y_p}{X_{\text{MBOH}}} \times 100 \quad (3)$$

where A_p , R_p , M_p , S_p and Y_p represent the area, response factor, mass, selectivity and yield of product P, respectively. While A_K , R_K and M_K represent the area, response factor and mass of all components.

Results and Discussions

Phase analysis, functional groups and Ce forms Figure 2(a) exhibits XRD patterns of the parent zeolite Y (NaY) and sample from impregnation preparation (Ce-NaY-IMP). The characteristic peaks at 2θ around 6.19° , 10.11° and 11.86° of faujasite framework (Mintova and Barrier, 2016) 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 (Garcia *et al.*, 2011). However, peaks corresponding to cerium oxide ($2\theta = 28^\circ$, 33° and 48°) are not observed in Ce-NaY-IMP, implying a good dispersion or CeO_2 peaks might overlap with the similar peak positions of the zeolite (Saceda *et al.*, 2012). Figure 2(b) illustrates FTIR spectra in $1,200$ to 400 cm^{-1} , the range of the zeolite vibrations. Both spectra are similar in shape but different in frequency and intensity. Compared 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 TO_4 ($\text{T} = \text{Si}, \text{Al}$) bending, symmetrical and asymmetrical stretching of internal tetrahedron linkages (Flanigen, 1976). These vibrations are observed for all aluminosilicates. While the dash lines with arrow of peaks existed around 578 , 789 and the shoulder at $1,145 \text{ cm}^{-1}$ are attributed to the double 6-membered ring (D6R), symmetrical and asymmetrical stretching of external linkages between TO_4 tetrahedra of faujasite framework, respectively (Flanigen, 1976). However, differences among Ce-NaY-IMP with parent NaY are clearly seen at the band and shoulder in the region of 900 - $1,200 \text{ cm}^{-1}$. The frequencies shifts are sensitive from the framework Si/Al ratio (Miecznikowski and Hanuza, 1985). The shifts might be attributed to an acidic impregnated solution of cerium nitrate hexahydrate step that

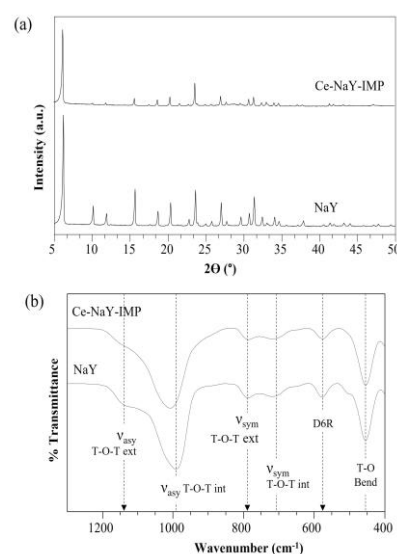


Figure 2. XRD patterns (a) and FT-IR spectra (b) of NaY and Ce-NaY-IMP

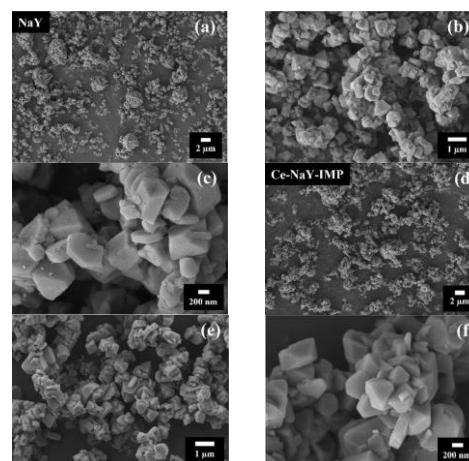


Figure 3. SEM images of NaY (a-c) and Ce-NaY-IMP (d-f)

leads to partial dealumination of parent zeolite (Beyer, 2002).

Figure 3 shows SEM images with different magnitudes. The parent NaY has various shapes and sizes of crystals Figure 3(a-c). The images from the larger magnification show agglomeration of polycrystalline Figure 3(b) and mix morphologies Figure 3(c). For Ce-NaY-IMP, the micrographs reveal a similar appearance to NaY. The crystallinity with clear faces and edges of zeolite are preserved after Ce introduction by incipient wetness impregnation. SEM-EDX analysis of Ce-NaY-IMP is displayed in Figure 4. Three different positions on the impregnated sample are studied and revealed in

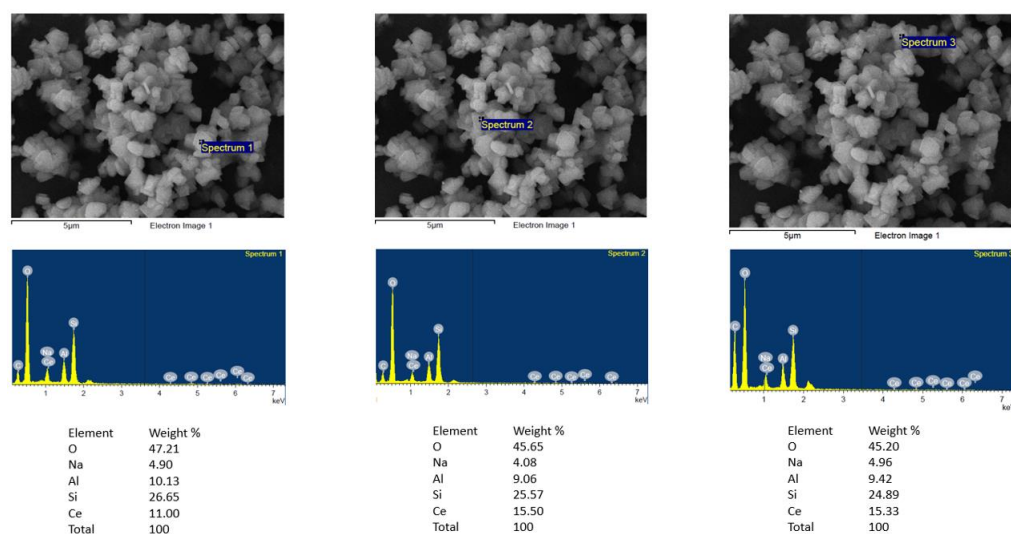


Figure 4. SEM-EDX analysis of Ce-NaY-IMP (re-calculated by neglecting the signal of carbon tape)

spectrum no. 1-3. All spectra provided the signals of O, Na, Si, and Al which are the components of NaY. All samples also show the signal of Ce with 11.0-15.5 wt%. The amount is higher than the added amount (10 wt%), suggesting that Ce covers the zeolite surface. However, the CeO_2 particles are not distinguishable in these images. The presence of Ce forms is explained by the next techniques.

Figure 5(a) 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 CeO_2 (inset Figure). This peak is assigned to the symmetric vibration mode of oxygen at neighboring positions of the Ce^{4+} ions (O-Ce-O). It is a characteristic F_{2g} vibration of CeO_2 or ceria fluorite-type lattice (Schmitt *et al.*, 2020). Another Raman band at $\sim 500 \text{ cm}^{-1}$ 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 (Wang *et al.*, 2013).

Figure 5(b) 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 (Sahu *et al.*, 2018). The Ce-NaY-IMP spectrum exhibits a small difference in the peak shape compared to CeO_2 . That is probably caused by some interaction between the oxide species and zeolite (Krishna Reddy *et al.*, 2009).

The textural properties of NaY and Ce-NaY-IMP were measured by N_2 sorption analysis. Both isotherms in Figure 6 exhibited type-I isotherms

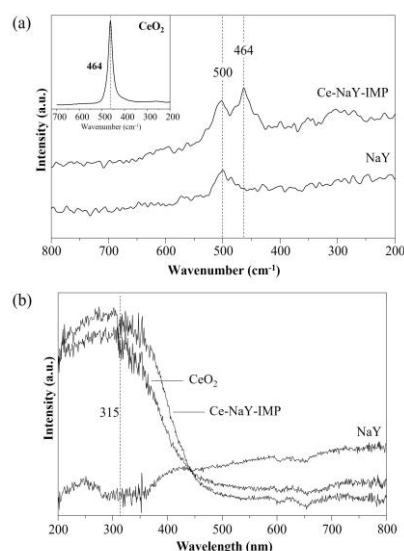


Figure 5. Raman spectra (a) and DR UV-Vis spectra (b) of NaY, Ce-NaY-IMP and CeO_2

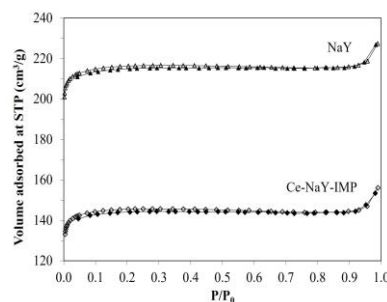


Figure 6. N_2 adsorption-desorption isotherms of NaY and Ce-NaY-IMP

which are characteristic of microporous materials. All porosity parameters of Ce-NaY IMP are lower than that of parent NaY (Table 1). The smaller micropore and external surface areas of Ce-NaY IMP suggest that the Ce species could exist on both the inner micropore and external surface area of zeolite (Saceda *et al.*, 2012).

The CO₂-TPD profiles of NaY and Ce-NaY-IMP are exhibited in Figure 7. The parent NaY displayed only one broad peak in the temperature range of 200-420°C, corresponding to weak basicity, similar to the work by (Rakmae *et al.*, 2016). While the profile of Ce-NaY-IMP displayed the desorption in three ranges. Two small peaks in the range of 50-180°C and 180-320°C contributed to weak basicity. A broadband with two overlapping peaks in the range 300-700°C corresponds to medium and strong basic sites. These results confirm that the presence of cerium on zeolite NaY generates medium and strong basic sites. The basicity of Ce-NaY-IMP was 0.123 mmol CO₂/g, higher than that of the parent NaY which was 0.036 mmol CO₂/g.

Catalytic transformation of MBOH

The acid-base 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 terms of conversion and selectivity versus time on stream are presented in Figure 8. From Figure 8(a), 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. Compared to the similar work by Supamathanon *et al.* (2012), they obtained low conversion with a steady conversion 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 improve MBOH conversion due to higher basicity as mentioned in CO₂-TPD section. Moreover, the addition of Ce changes the catalytic activity of the materials, which are discussed in more detail along with the results of product selectivity.

Figures 8(b) and 8(c) present the selectivity versus time on stream. The NaY contains acetone and acetylene as major products with a small amount of MBYNE 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

Table 1. Textural properties of NaY and Ce-NaY-IMP

Parameter	NaY	Ce-NaY-IMP
Surface area (m ² g ⁻¹) ^a	645	435
Micropore area (m ² g ⁻¹) ^b	635	427
External area (m ² g ⁻¹) ^b	9.99	7.85
Micropore volume (cm ³ g ⁻¹) ^b	0.32	0.22

^a Determined by BET method.

^b Determined by t-plot method.

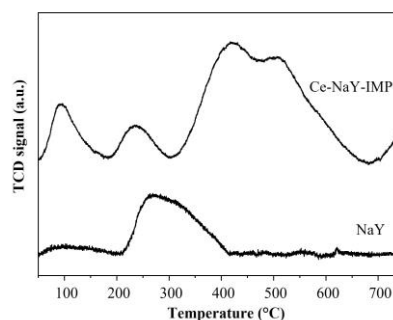


Figure 7. CO₂-TPD profiles of NaY and Ce-NaY-IMP

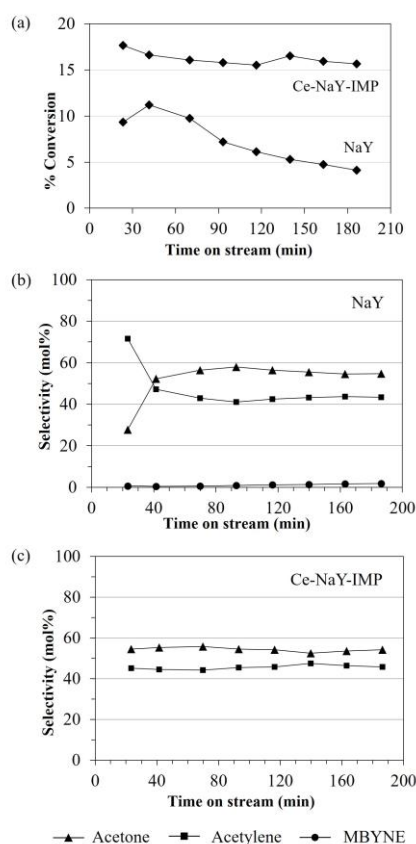


Figure 8. MBOH conversion of NaY and Ce-NaY-IMP (a), product selectivity of NaY (b) and Ce-NaY-IMP (c)

cations (Barthomeuf, 1996). 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 are 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 (Aramendía *et al.*, 1999). However, the ratio from this work was more than 1, suggesting that acetylene might also change to other compounds or adsorb on NaY.

The product selectivity of Ce-NaY-IMP in Figure 8(c) only shows acetone and acetylene. Hence, the sample contains basic-catalyzed properties. The conversion improvement is attributed to an enhancement of Lewis basic sites from oxygen vacancies of CeO₂ phase (Chen *et al.*, 2017) containing in Ce-NaY-IMP. The catalytic activity of ceria on NaY supports the existence of Ce⁴⁺ species with above Raman and DR UV-V is results. Nevertheless, the selectivity of acid-catalyzed products as parent NaY was not observed. This result indicates that impregnation with cerium suppressed the acidic sites of NaY. (Supamathanon *et al.*, 2012) also reported the absence of acidic products from the potassium-impregnated on zeolite Y.

Conclusions

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.

Acknowledgments

W. Rattanawongsa is supported by the Development and Promotion of Science and Technology Talents Project (DPST) and Suranaree University of Technology. S. Kosawatthanakun is supported by the Royal Golden Jubilee Ph.D. program (Grant No. PHD/0142/2557) from the Thailand Research Fund (TRF) and Thai German S&T Cooperation 3rd Researcher Mobility Scheme. Full-Time Doctoral Researcher Grants for N. Osakoo is supported by (i) Suranaree University of Technology, (ii) Thailand Science Research and Innovation (TSRI), and (iii)

National Science, Research and Innovation Fund (NSRF) (90464/project code 90464).

References

- Aramendía, M.A., Boráu, V., García, I.M., Jiménez, C., Marinas, A., Marinas, J.M., Porras, A., and Urbano, F.J. (1999). Comparison of different organic test reactions over acid-base catalysts. *Appl. Catal. A-Gen.*, 184(1):115.
- Barthomeuf, D. (1996). Basic zeolites: characterization and uses in adsorption and catalysis. *Catal. Rev.*, 38(4):521.
- Beyer, H.K. (2002). Dealumination techniques for zeolites molecular sieve science and technology. In: *Post-Synthesis Modification I*. Karge, H. G. and Weitkamp, J. (eds). Springer-Verlag Berlin Heidelberg, Heidelberg., p. 203-255.
- Chen, W., Ran, R., Weng, D., Wu, X., Zhong, J., and Han, S. (2017). Influence of morphology on basicity of CeO₂ and its use in 2-chloroethyl ethyl sulfide degradation. *J. Rare Earth.*, 35(10):970.
- Cheng, X., Huang, L., Yang, X., Elzatahry, A.A., Alghamdi, A., and Deng, Y. (2019). Rational design of a stable peroxidase mimic for colorimetric detection of H₂O₂ and glucose: a synergistic CeO₂/Zeolite Y nanocomposite. *J. Colloid Interf. Sci.*, 535:425.
- Cutrufello, M.G., Ferino, L., Monaci, R., Rombi, E., and Solinas, V. (2002). Acid-base properties of zirconium, cerium and lanthanum oxides by calorimetric and catalytic investigation. *Top. Catal.*, 19(3):225.
- Flanigen, E.M. (1976). Structural analysis by infrared spectroscopy. *ACS Monograph.*, 171:80.
- Garcia, F.A.C., Araújo, D.R., Silva, J.C.M., de Macedo, J.L., Ghesti, G.F., Dias, S.C.L., Dias, J.A., and Filho, G.N.R. (2011). Effect of cerium loading on structure and morphology of modified Ce-USY zeolites. *J. Braz. Chem. Soc.*, 22(10):1,894.
- Huang, Q., Xue, X., and Zhou, R. (2010). Decomposition of 1,2-dichloroethane over CeO₂ modified USY zeolite catalysts: effect of acidity and redox property on the catalytic behavior. *J. Hazard. Mater.*, 183(1):694.
- Krishna Redd, J., Suresh, G., Hymavathi, C.H., Durga Kumari V., and Subrahmanyam, M. (2009). Ce (III) species supported zeolites as novel photocatalysts for hydrogen production from water. *Catal. Today.*, 141(1):89.
- Kuśtrowski, P., Chmielarz, L., Božek, E., Sawalha, M., and Roessner, F. (2004). Acidity and basicity of hydrotalcite derived mixed Mg-Al oxides studied by test reaction of MBOH conversion and temperature programmed desorption of NH₃ and CO₂. *Mater. Res. Bull.*, 39:263.
- Lauron-Pernot, H. (2006). Evaluation of surface acido-basic properties of inorganic-based solids by model catalytic alcohol reaction networks. *Catal. Rev.*, 48(3):315.
- Miecznikowski, A. and Hanuza, J. (1985). Application of the long chain approach to the structure and vibrational spectra of X and Y zeolites. *Zeolites.*, 5:188.
- Mintova, S. (ed) and Barrier, N. (XRD Patterns). (2016). *Verified syntheses of zeolitic materials*. 3rd ed. Elsevier, Amsterdam, 405p.
- Rakmae, S., Keawkumay, C., Osakoo, N., Montalbo, K.D., de Leon, R.L., Kidkhunthod, P., Chanlek, N., Roessner, F., Prayoonpokarach, S. and Wittayakun, J. (2016). Realization of active species in potassium catalysts on zeolite NaY prepared by ultrasound-assisted impregnation with acetate buffer and improved performance in transesterification of palm oil. *Fuel.*, 184:512.
- Saceda, J.J.F., Rintramee, K., Khabuanchalad, S., Prayoonpokarach, S., de Leon, R. L., and Wittayakun, J. (2012). Properties

- of zeolite Y in various forms and utilization as catalysts or supports for cerium oxide in ethanol oxidation. *J. Ind. Eng. Chem.*, 18(1):420.
- Sahu, P., Eniyarppu, S., Ahmed, M., Sharma, D., and Sakthivel, A. (2018). Cerium ion-exchanged layered MCM-22: preparation, characterization and its application for esterification of fatty acids. *J. Porous Mater.*, 25(4):999.
- Schmitt, R., Nenning, A., Kraynis, O., Korobko, R., Frenkel, A. I., Lubomirsky, I., Haile, S. M. and Rupp, J.L.M. (2020). A review of defect structure and chemistry in ceria and its solid solutions. *Chem. Soc. Rev.*, 49(2):554.
- Supamathanon, N., Supronowicz, W., Roessner, F., Wittayakun, J., and Prayoonpokarach, S. (2012). Basic properties of potassium oxide supported on zeolite Y studied by pyrrole-TPD and catalytic conversion of methylbutynol. *Quim. Nova.*, 35(9):1,719.
- Wang, N.N., Wang, Y., Cheng, H.F., Tao, Z., Wang, J., and Wu, W.Z. (2013). Impact of cationic lanthanum species on zeolite Y: an infrared, excess infrared and raman spectroscopic study. *RSC Adv.*, 3(43):20,237.
- Wu. Z., Mann, A., Li, M., and Overbury, S. (2015). Spectroscopic investigation of surface-dependent acid-base property of ceria nanoshapes. *J. Phys. Chem. C.*, 119(13):7,340.