

Synthesis, Characterization of Ceria Modified ZSM-5 and Its Performance Towards NO Oxidation

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Abstract

Ce-ZSM-5 catalyst has been successfully synthesized and studied for NO oxidation to NO₂. Ce-ZSM-5 at various Ce % such as 5, 10, 15% were synthesized and characterized using various physiochemical analytical techniques like Diffuse reflectance UV spectroscopy (UV-DRS), Brunauer Emmett Teller (BET) technique, Differential Scanning Calorimetry (DSC), Thermo gravimetric analysis (TGA), powder XRD and scanning electron microscopy (SEM). From the results it was noted the successful inclusion of Cerium oxide over the ZSM-5 used. Among the synthesized Ce-ZSM-5, ZSM-5 with 15% Ce loading was shown better activity towards the conversion of NO-NO₂. Around 50 % of NO was converted into NO₂.

Keywords: Ce-ZSM-5, Characterization, NO-conversion, NO₂

1. Introduction

ENIWARE Washington Inc., has recently developed a NO₂ based power independent sterilizing system for medical equipments sterilization in the uniquely adverse environments during disaster relief, and governments facing emergency response call for innovative solutions. And they claimed their portable NO₂ sterilizer technology is rugged enough to withstand the rigors of use and a variety of severe locations and environments in addition to meeting performance characteristics required in fixed facilities. The Eniware Portable Sterilizer could replace the existing steam sterilizers [1-2]. Further SAIAN Corporation inc, Japan have also introduced a patent technology for sterilization using NO₂. These two studies strongly evidence the need for continuous production of NO₂ during disaster management and emergency situations for sterilization of medical equipments. Catalytic route or fixed catalytic reactor is the best source for the continuous production of NO₂ gas from NO. Further the saturation of NO and NO₂ is considered as the greenhouse gases which can promote the acid rain fall if their concentration is exceed in the environment. Hence there is an immediate need to prevent its emission and utilize the same for other useful purpose.

Various catalytic systems have been adopted for the conversion of NO to NO₂ by various groups. Platinum is the most active catalyst for NO oxidation but in presence of SO₂ it will get severely inactivated further its high cost should make it to avoid for continuous application [3–5]. The transition metals provide the active site to the catalysts have much attracted for this purpose [6-9]. The next choice of catalyst is manganese oxides which also provide active site for NO oxidation and have high catalytic performance. However, Mn-based catalysts also undergo irreversible deactivation easily [10]. Poly acrylonitire based activated carbon fibre was also found application in the conversion of NO-NO₂. But its activity was decreased with increasing the humidity [11]. Barium modified CuOx–CeO₂

catalysts is also having the capability to convert NO to NO₂ [12]. Chromium oxide–support interaction yielded some certain structural characteristics. A highly dispersed Cr–O species on the support surface with Cr⁶⁺ was the dominant oxidation states [13]. CeOx is used as structure promoter and a buffer in redox cycle to enhance catalytic property of catalyst. Some literatures have reported the interactions of ceria and other active sites, such as Ce–Pt [14-16], Ce–Mn [8, 9]. The unique properties of Ce have been confirmed in the catalyst field. NO oxidation on Cr–Ce was also studied by some authors, they found the catalyst with a composition of Cr(1)Ce(0.25)/TiO₂-pillared clay yielded 69% NO to NO₂ conversion at 350 °C (in the condition of GHSV = 35,400 h⁻¹). With the content of ceria increasing, the NO conversion increased significantly while when the Cr/Ce equaled 1:1, the activity decreased.

Among metal oxides CeO₂ has proved its potentiality in the oxidation of soot [17]. For example, if we add cerium compound as fuel additive first they decrease the engine-out particulate [18]. The second effect of the cerium additive is that it enhances the reactivity of the soot formed [19-21]. If it combine with traces of precious metals such as platinum catalyst may showed synergetic effect in the oxidation of soot with NO and O₂ [22]. The reaction mechanism of conversion NO to NO₂ by CeOx catalyst is unclear but possible mechanism proposed by earlier work is at low temperature ceria will adsorb NO from the soot and converted in to cerium nitrate and high temperature it will release the NO₂ and come back to its original CeO₂ phase [23]. But yet now none of the study has proposed the ceria impregnated ZSM-5 for the catalytic conversion of NO to NO₂. Being microporous materials the ZSM-5 is expected to adsorb more amount of NO in the first step. Further in our past report on ceria impregnated ZSM-5, we indentified the potentiality of the catalyst to adsorbing CO₂ gas. Here in our present study we reported a method to convert NO to NO₂ using a ceria impregnated ZSM-5 catalyst on fixed bed continuous flow reactor.

2. Experimental

2.1. Catalyst Preparation

The Amonium form ZSM-5 catalyst (Zeolyst International Company) was calcined in air at 500 °C for 3 hours to get HZSM-5. The Ceria impregnated HZSM-5's with varying Ceria loadings were prepared by wet impregnation of 5 g of HZSM-5 with ethanolic solution of cerium nitrate hexahydrate (Aldrich 99%). The mixture was stirred and dried in oven at 90 °C to remove the ethanol. The obtained material is finally calcined in air at 550 °C for 10 hours and designated as Ce (x)/ZSM-5 where X = 5, 10 and 15 wt% of Ceria loading.

2.2. Catalyst Characterization

Powder X-ray diffraction pattern (XRD) were recorded on Rigaku Miniflex diffractometer using a Cu K α radiation ($\lambda = 0.154$ nm). The diffraction data were recorded in the 2θ range 5–40° with a step size of 0.02° and a step time of 1 s. The nitrogen adsorption–desorption isotherms were measured at –196 °C on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 100 °C under vacuum ($p < 10^{-5}$ mbar) in the degas port. The surface area was determined from the linear part of the Brunauer–Emmett–Teller (BET) equation. The pore volume was calculated using the BET plot from the amount of nitrogen gas adsorbed at the last adsorption point ($p/p_0 = 0.95$). The thermogravimetric analysis (TGA) was carried out in a N₂ atmosphere at a flow rate of 40 ml/min on a SCINCO N-1000 thermo gravimetric analyzer, by heating *ca.* 10 mg of the sample from

25 to 800 °C in steps of 10 °C/min. The morphologies of the samples were studied using a JEOL JSM 5600 scanning electron microscope (SEM) with an energy dispersive X-ray analysis (EDS) detector. Ultraviolet–visible diffuse reflectance (DRS-UV–vis) spectra of the samples were recorded on SCINCO Neosys 2000 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Multilab 2000 using monochrome Al K α as the excitation source.

2.3. NO conversion

NO conversion measurements using in-house fixed bed reactor (Figure 1) using NO (10.01%) and air mixture gas (1000ppm) as feed gas. The reaction was studied up to a maximum temperature 600 °C with space velocity 13000 hr⁻¹, about 0.3203 g of sample was loaded and the gas flow rate kept at 400 cc/min. The effluent gas was analyzed by NO_x analyzer.

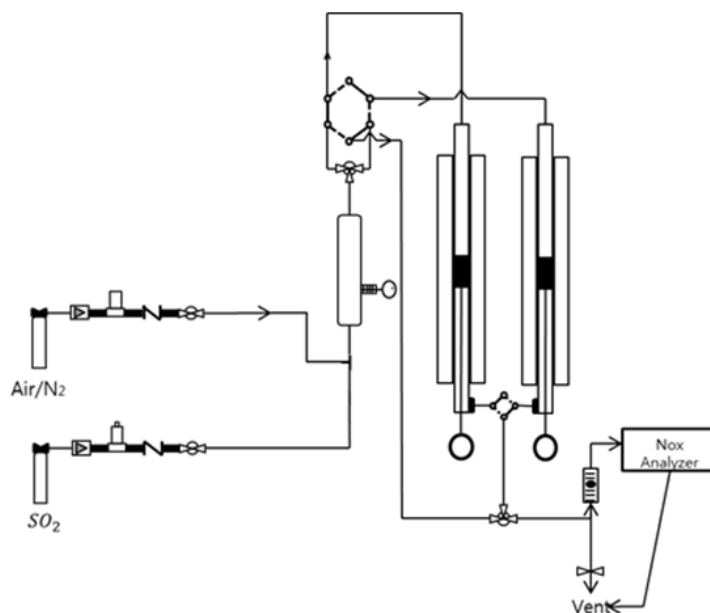


Figure 1. Reactor and Instrument for NO conversion

3. Results and Discussion

The powder diffraction patterns of the HZSM-5 and the Ce-ZSM-5 (5, 10, and 15%) are presented in Figure 2. The spectra carry the characteristic patterns of ZSM-5. For lower loading of ceria (5 %) the characteristic XRD patterns for ceria was not obtained indicates the insufficient dimension of ceria particles to yield XRD patterns. But for 15% loading the patterns shows the presence of ceria phase this proves the formation of ceria particle with large dimension. This was confirmed by broadening of the XRD pattern close to 28° (2 θ). From the JCPDS files for ceria (JCPDS 34-394), the intensive diffraction peak located at 2 θ = 28.66° is due to the (111) lattice plane of fcc CeO₂.

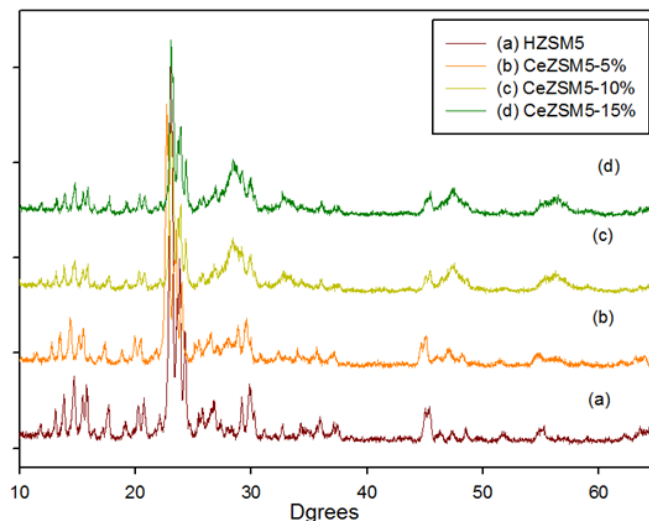
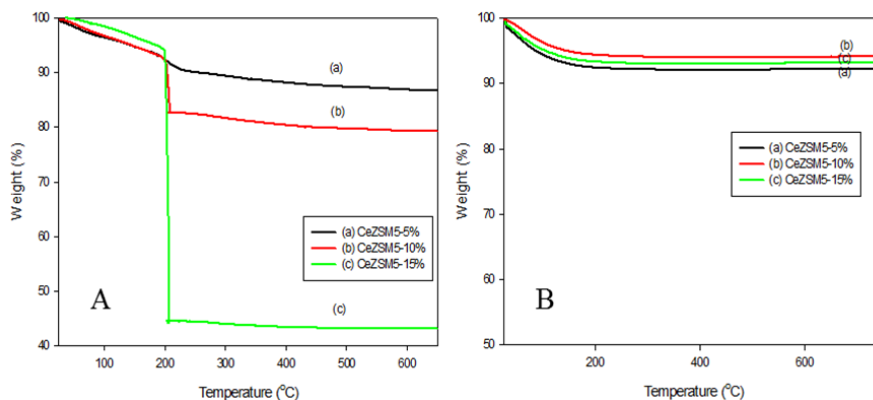


Figure 2. XRD patterns of (a) HZSM5, (b) CeZSM5-5%, (c) CeZSM5-10%, (d) EZSM5-15%

The thermograms of as-synthesized CeZSM-5(5, 10 and 15%) are illustrated in Figure 3. The sharp weight loss which followed this was due to decomposition of template. In the Ce/ZSM-5 (5, 10 and 15%) (Figure 3) the initial weight loss from 25 to 200 °C is due to loss of H₂O from zeolite and the sharp weight loss at 200 °C corresponding to the decomposition of the nitrate.



**Figure 3. A – Thermograms of before calcined (a) CeZSM5-5%, (b) CeZSM5-10%, (c) EZSM5-15%
B – Thermograms of after calcined (a) CeZSM5-5%, (b) CeZSM5-10%, (c) EZSM5-15%**

The N₂ adsorption–desorption isotherms are depicted in Table 1. The isotherms are of type I confirming the characteristic microporous nature of ZSM-5 with hysteresis. Hence the presence of hysteresis in all of them prove slight enlargement of pores to mesopore range. The BET surface area (S_{BET}) and the pore volume are tabulated in Table 1. The surface area decreased with increase in ceria loading. The pore volume of HZSM-5 was decreased gradually while increasing the ceria loading.

Table1. BET result of HZSM5 and CeZSM5 (5, 10 and 15%)

Sample name	S_{BET} [$m^2 g^{-1}$]	Pore volume ($p/p_0=0.965$) [$cm^3 g^{-1}$]	Pore diameter [nm]
HZSM5	387.89	0.2324	2.397
CeZSM5-5%	324.83	0.2017	3.2749
CeZSM5-10%	267.57	0.1902	2.5614
CeZSM5-15%	246.38	0.1713	2.342

The SEM pictures of the synthesized samples are shown in Figure 4. The ZSM-5 crystals assemble to form small cuboid particles. The SEM picture of the ceria impregnated sample (Fig. 4b) did not show any evidence for separate crystals for cerium. The presence of cerium is evidenced by EDX analysis (figure not shown).

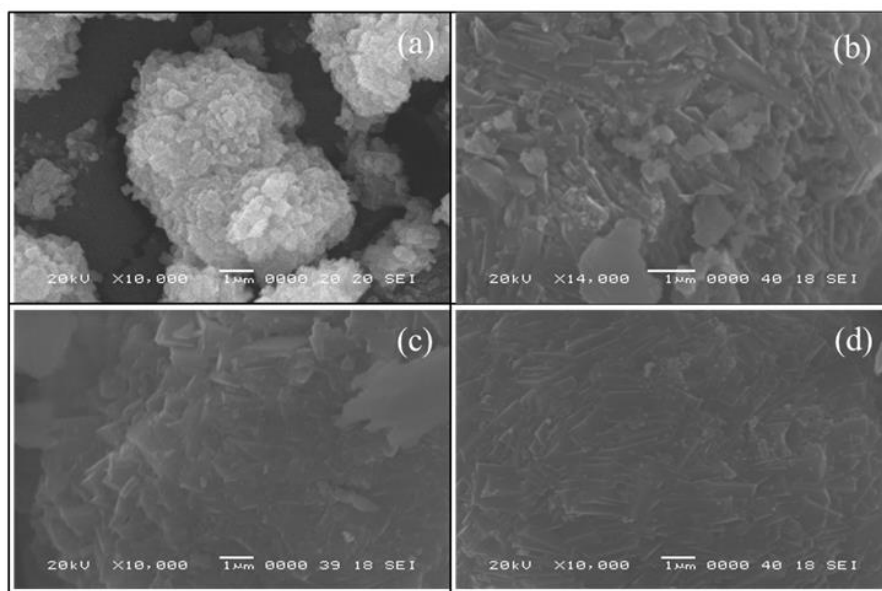


Figure 4. SEM image of (a) HZSM5, (b) CeZSM5-5%, (c) CeZSM5-10%, (d) CeZSM5-15%

The DRS-UV-vis spectrum of CeZSM-5 showed two absorption maxima (Figure 5). The peak at 370 nm was due to band gap excitation in ceria and the peak near 250 nm was due to its O^{2-} to Ce^{4+} charge transfer. The results were similar with that of our previous report.

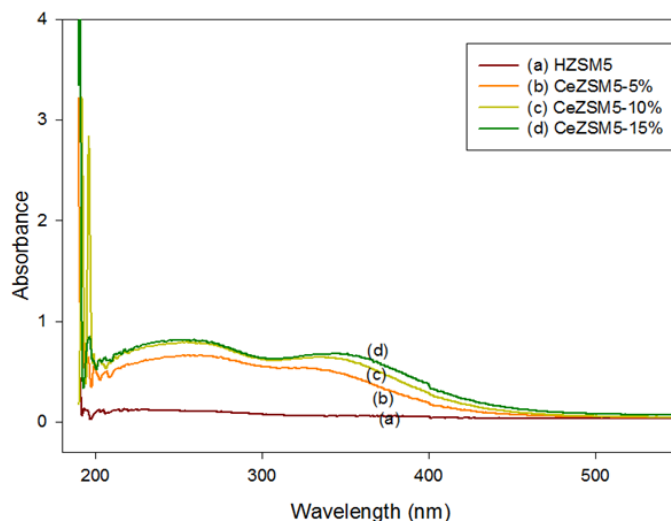


Figure 5. DRS-UV-vis spectra of CeZSM-5 (a) HZSM-5, (b) CeZSM5-5%, (c) CeZSM5-10%, (d) EZSM5-15%

NO-conversion

NO conversion profiles of CeZSM-5 (5, 10, and 15%) were given in Figure 6. The figure for the in house fixed bed reactors was illustrated in Figure 6. From the figure for NO conversion it is clearly evident that the NO conversion was very low in case of catalyst with low ceria content. With respect to mechanism given in the introduction section, the catalyst needs high ceria sites to adsorb NO and covered itself into ceria nitrate, here in the ZSM-5 with 5 and 10% shows very less activity towards conversion it might be due to low content of ceria. But in case of catalyst with 15% ceria loading show a marked increase in conversion. But it need a very high temperature to desorb NO₂ from the site at the temperature of 800 °C the catalyst can desorb all the NO₂ formed over the ceria site. The catalyst converted about 50% of the NO in NO₂ (498 ppm of NO₂ is detected in the NO_x analyzer).

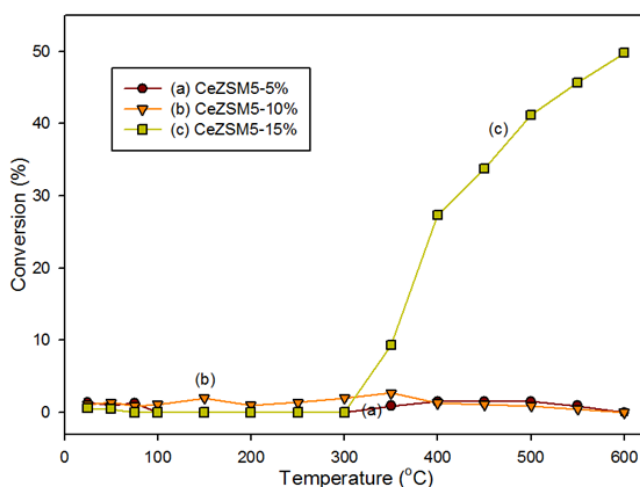


Figure 6. NO₂ conversion percent of (a) CeZSM5-5%, (b) CeZSM5-10%, (c) EZSM5-15% according to Temperature

4. Conclusions

Ceria loaded HZSM-5 catalyst was synthesized successfully and effectively utilized for the production of NO₂ sterilizer. Formation of ceria over the catalyst was proved by the XRD patterns obtained and complete removal NO₂ from the catalyst was evidenced from the TGA. The NO adsorption was found more at temperature and its conversion was favored at the temperature of 600 °C. From this study it is concluded that the ceria impregnated HZSM-5 can be used as a better choice of catalyst for the conversion of NO-NO₂. A study on further improvement on the process and purification of formed NO₂ to be used as sterilizers is underway.

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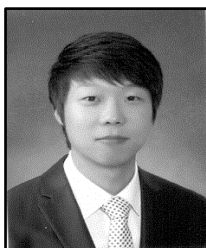
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