Selective Catalytic Reduction of NO with Ammonia over Nanostructure H-ZSM-5 Supported Transition Metal Oxide Catalysts

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Abstract

A series of transition metal oxides (Co, Cr, Mn, Fe and Cu) promoted H-ZSM-5 catalysts were prepared by wet impregnation method using dilute soltions of metal nitrate precursors. These were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD and SEM images approved that the formed metal species are in the nanometer size range and well dispersed. The catalytic activity of these materials was evaluated for the selective catalytic reduction (SCR) of NO with NH_3 as reductant in the presence of excess oxygen (5 vol.%). The results revealed that the catalytic activity of Cu-ZSM-5 for NO removal was about 80% at 300 °C, which was the best among various promoted oxides. Then effect of catalyst preparation parameters for Cu-ZSM-5 optimum catalyst was studied.

Keywords: ZSM-5, transition metal oxides, nitric oxide (NO), selective catalytic reduction (SCR)

1. Introduction

Nitrogen oxides (NOx) remain a major source of air pollution. They contribute to photochemical smog, acid rain, ozone depletion, and greenhouse effects. Nearly all NOx (95%) derives from transportation (49%) and power plants (46%) [1]. Due to the increasing threat of NOx to our survival, many approaches have been developed to reduce its emission, among which selective catalytic reduction technique (SCR) is proven to be an effective way compared with other NOx abatement technologies, such as nonselective catalytic reduction technique, storage, and thermal decomposition. The most common reductants for SCR are ammonia, urea, CO, H_2 and hydrocarbons like methane, ethane and propylene but ammonia is still found to be a suitable reductant for NO in the presence of oxygen, in spite of being difficult to handle, because ammonia reacts selectively with NOx to produce N_2 without consuming an excess O_2 [2].

In the past few decades, the backbone of SCR technology is the development of SCR catalysts such as noble metals, supported metal oxides, zeolites and others [3, 4]. The conversion efficiencies of NOx in the catalytic reactions depend mostly on the supports and the nature of active sites. Therefore, the choices of supports and catalysts are especially important [5]. Zeolite-based SCR catalysts have received a great deal of attention because of their high activity for the reduction of

NOx. Some of the extensively studied metal cations exchanged into zeolites to prepare lean NOx catalysts include Co, Pt, Pd, Fe, Ni, and Cu [6].

In the present study we have screened a number of transition metal oxides (Co, Cr, Mn, Fe and Cu) supported on H-ZSM-5 for SCR of NO with NH_3. The objectives of this work are to compare the activity of various metals (Cu, Mn, Fe, Co,...) loaded on H-ZSM-5 and carry out the reaction selectively in a wide temperature range. The prepared catalysts were thoroughly characterized by various physicochemical techniques. Among various catalysts, the Cu-ZSM-5 catalyst showed very promising catalytic activity for SCR of NO with NH_3 by exhibiting high conversions over a wide temperature window and the reaction was highly selective in the presence of oxygen.

2. Experimental

2.1. Catalysts Preparation

H-ZSM-5 obtained from Zeochem Int with $SiO_2/Al_2O_3 = 50$ was used for preparation of the catalysts. The properties of H-ZSM-5 are listed in Table 1. All catalysts were prepared through incipient wetness impregnation method. The aim of this procedure is to deposit metal oxide on the zeolite surface, whereas a proton exchange is not explicitly intended and with this technique an accurate load of metal is adjusted. The precursors of different metals were $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2$, $Cr(NO_3)_2$, $Fe(NO_3)_2$, and $Mn(NO_3)_2$, and the total metal content was kept at 5 wt%. The prepared catalysts were dried in an oven at 100°C overnight and then calcined at 500°C for 4 h in the air; under these conditions complete decomposition of metal nitrate into metal oxide occurs.

2.2. Catalysts characterization

2.2.1. X-ray diffraction (XRD)

The structure of the catalysts were analysed by powder XRD at room temperature with a D500 Siemens diffract meter using CuK_α radiation (λ= 1.54050 Å). The X-ray tube was operated at 35 kV and 30 mA and the X-ray pattern was scanned with a step size of crystallites sizes of 0.016° (2θ) from 5 to 50° (2θ) and counting time of 1 s per step.

2.2.2. Scanning electron microscopy (SEM)

SEM images for H-ZSM-5 and M-ZSM-5 (M= Co, Cr, Mn, Fe and Cu) were obtained using SEM model EQ-CL 1 instrument to observe particle size and surface homogeneity.

2.3. Catalytic activity measurement

Catalysts activities in NOx reduction were studied at atmospheric pressure in a fixed bed reactor. The reactor consisted of a 0.9 cm i.d. glass tube was located inside in a furnace which was electrically heated. The reactant gas feed, consisting of NO (1000 ppm), NH_3 (1000 ppm), O_2 (5 vol%) and Ar as balanced gas, was mixed in a mixing chamber and introduced to the reactor at a total flow rate of 200 ml/min. In each run, 0.2 g of the catalyst powder was dispread between quartz wool plugs, yielding a gas hourly space velocity (GHSV) of 12000 h^{-1}. Before starting each run,

zeolites were pretreated with Ar at 150°C in order to eliminate possible compounds adsorbed on the zeolite surface. After this pretreatment, the reactor was cooled to 100°C and activity tests were performed from 100 to 400°C with a step of 100°C. The concentration of N_2 (as selective product) in the outlet of the reactor was measured by a gas chromatograph (shimadzu) equipped with a thermal conductivity detector (TCD) with Molecular sieve column to separate N_2 and N_2O.

3. Results and Discussion

3.1. Characterization of catalysts

Figure 1 shows the XRD patterns of the series H-ZSM-5 and M-ZSM-5 (M = Cu, Mn, Fe, Co,...). XRD patterns of the prepared samples M-ZSM-5 are similar to that of H-ZSM-5 which suggests that the original structure of H-ZSM-5 is not destroyed during the process of impregnation and calcination. All The characteristic peaks of HZSM-5 were observed in impregnated ZSM-5 samples. XRD peaks remain sharp and intense for M-ZSM-5, but a slight decrease in intensity of main peaks can be observed. This reveals a decrease in crystallinity of catalysts compared to H-ZSM-5. Decreases of peaks intensity imply the entrance of metal species into the channels. Also there is not any other peak in XRD patterns of M-ZSM-5 catalysts compared to XRD pattern of H-ZSM-5 indicating that metal species (i.e. oxide, cations,…) are well dispersed through the zeolites structure.

Figure 2 shows SEM micrographs of H-ZSM-5 and M-ZSM-5 (M = Cu, Mn, Fe, Co,...) catalysts. This figures indicates the formation small size of metal particles, the high dispersion on support and the uniform size distributionin in M-ZSM-5 catalysts that increase activity. Also SEM images approved the nanostructure of catalysts (<100 nm).

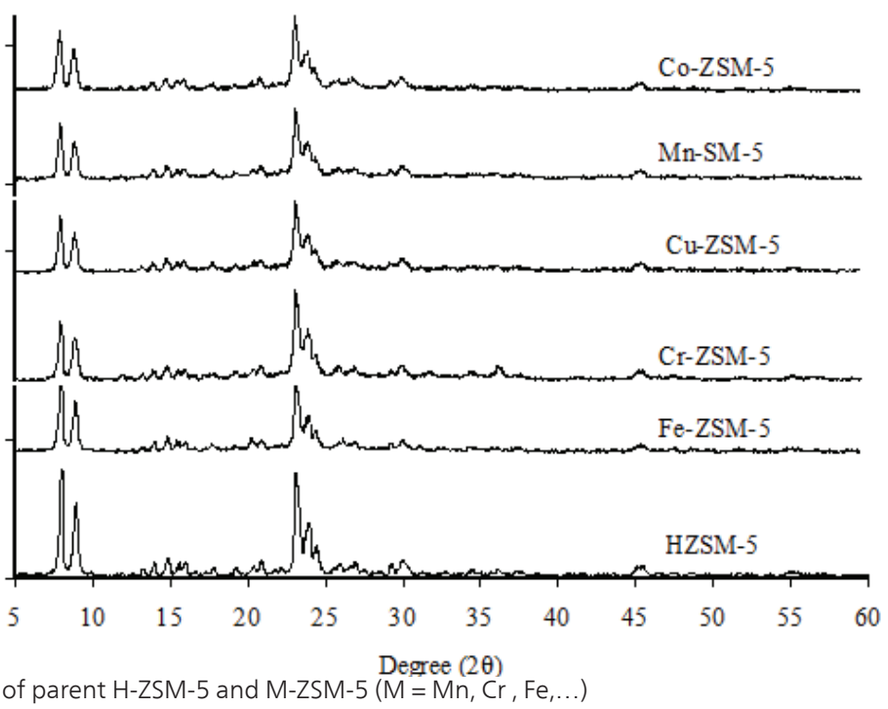

Figure 1. XRD of parent H-ZSM-5 and M-ZSM-5 (M = Mn, Cr , Fe,…)

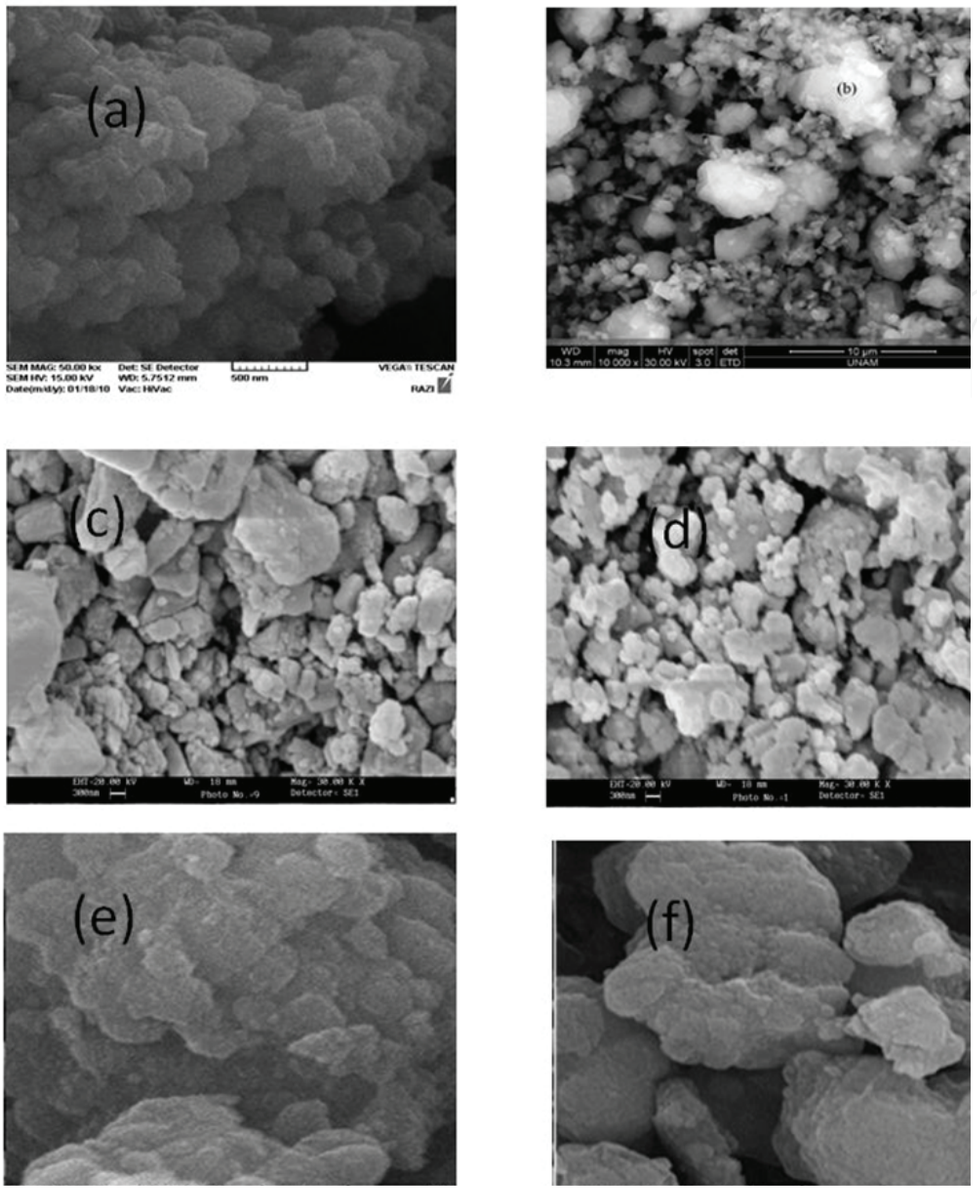

Figure 2. SEM images of (a): parent H-ZSM-5 and (b): Fe-ZSM-5 (c): Mn-ZSM-5 (d): Cr-ZSM-5 (e)Cu-ZSM-5 (f): Co-ZSM-5

3.2. Effects of different metals for NH_3 – SCR activity

Catalytic activity results for NO conversion to N_2 of NH_3 – SCR reaction over H-ZSM-5 and various transition metal oxides supported on H-ZSM-5 are presented in Figure 3. No obvious NO conversion was observed over pure H-ZSM-5 support up to 300ºC. When the transition metal oxide phases were introduced, the catalytic activities were enhanced significantly over the whole range of temperature investigated. For all catalysts, NO conversion increased with increasing temperature and all catalysts were highly selective. Under identical operating conditions Cu-ZSM-5 showed excellent performance giving 80% NO conversion at 300°C, which was the best among catalysts. High activity for Cu-ZSM-5 also were shown by sultana et al. [7], who reported high selective and activity for Cu/NaZSM-5 and Cu/HZSM-5 in NOx reduction by NH_3.

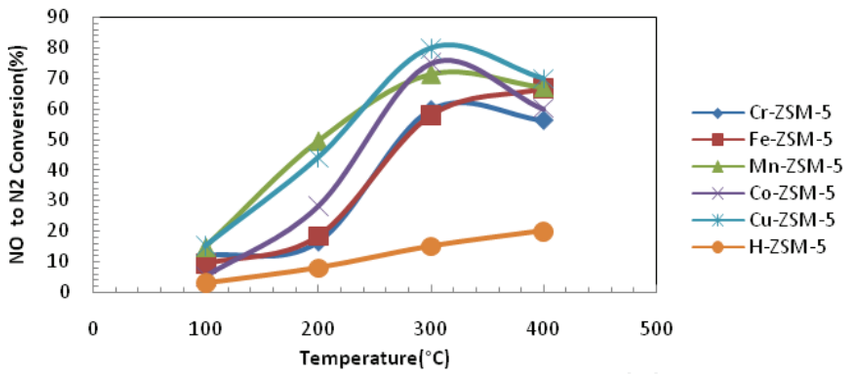

Figure 3. NO to N2 conversion as a function of temperature on M-ZSM-5 (M= Fe, Cr, Co, Mn and Cu) catalysts.

3.3. Catalytic activity of Cu-ZSM-5 catalysts with various Cu-loadings

Cu-ZSM-5 showed more activity than other catalysts thus we focus additional studies on Cu-ZSM-5. To further improve the performance of the Cu-ZSM-5 catalyst, the composition of the catalyst was optimized by varying Cu loading and calcinations temperature. Figure 4 compares the NO conversion to N_2 as a function of temperature over Cu-ZSM-5 catalysts with different loading (1, 3, 5, 7, 9 wt.%). The result indicates that below 5wt.%, increasing Cu content in Cu-ZSM-5 resulted in an increase in conversion but Further increase in Cu content was found to weaken the NO conversion to N_2, therefore Cu loading of 5 wt.% was found to be the optimum loading in this study. The low activity in Cu-ZSM-5 with loading of 1 and 3 wt.% can be attributed to low quantity copper oxide species. A decrease in conversion with an increase in Cu content after that was attributed to excessive metal agglomeration leading to the formation of larger metal particle also further loading of copper causes to block the pores and active sites of zeolite, leading to decrease the catalytic activity of catalyst [8].

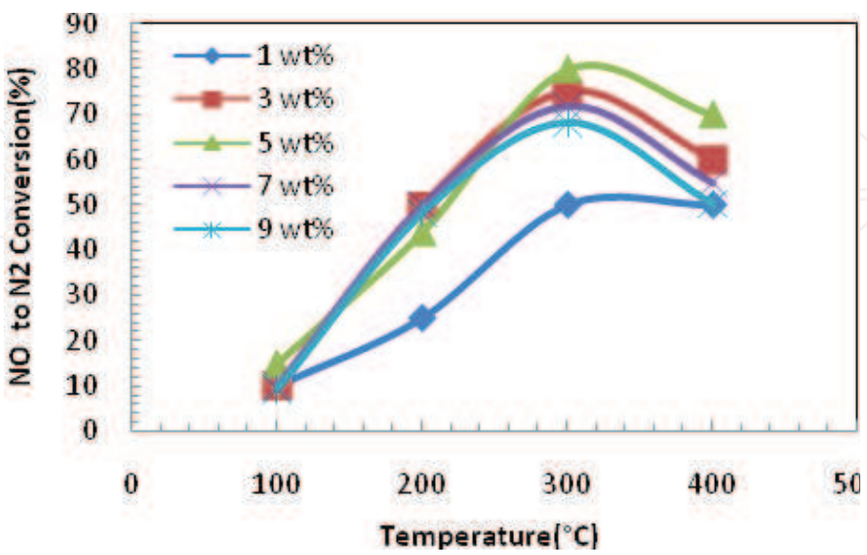

Figure 4. NO to N2 conversion as a function of temperature on Cu-ZSM-5 with different Cu loadings.

3.4. Effect of calcination temperature on the catalytic activity Cu-ZSM-5

Figure 5 shows the NO conversion to N_2 as a function of temperature over 5 wt.% Cu-ZSM-5 at different calcination temperatures. The result indicates that the calcination temperature influenced the SCR activity. From figure 6 we can see that the catalyst calcinated at 550°C had the highest activity. The NO conversion over Cu-ZSM-5 catalysts decreased in the order of Cu-ZSM-5 (550)> Cu-ZSM-5 (500)> Cu-ZSM-5 (600)> Cu-ZSM-5 (650) Cu-ZSM-5 (450)> Cu-ZSM-5 (400). Different calcination temperatures result in different oxidation states of copper, so the calcination temperature affects the activity and selectivity of SCR of NO by NH_3. Further increase in calcination temperature above 600°C caused decreasing NOx conversion. This can be due to the sintering to some extent at high calcinations temperature [9].

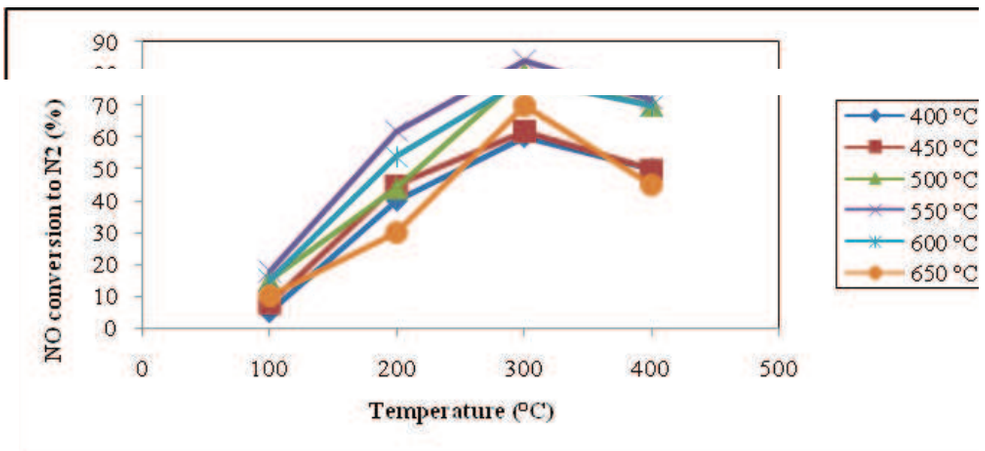

Figure 5. I) to N2 conversion as a function of temperature on Cu-ZSM-5 with different calcination temperatures.

4. Summary and conclusion

This study confirmed higher catalytic activity of M-ZSM-5 (M = Co, Cr, Mn, Fe and Cu) for the selective catalytic reduction (SCR) of NO with NH3 as reductant and revealed that introduction of metal ions onto ZSM-5 caused improvement in catalytic activity of M-ZSM-5 catalysts compared to parent HZSM-5, which confirms catalytic role of metal ions for selective catalytic reduction. Under identical operating conditions Cu-ZSM-5 showed excellent performance giving 80% NO conversion at 300°C, which was the best among catalysts. Also, It was concluded that Cu loading of 5 wt.% be the optimum loading and catalyst calcinated at 550°C had the highest activity in this study.

5. References

[1] Gongshin Qi, Ralph T. Yang, Ramsay Chang. 2004. MnOx-CeO2 mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH3 at low temperatures. Applied Catalysis B: Environmental (51) : p. 93–106.

[2] Min Kang a, Eun Duck Park b, Ji Man Kim c, Jae Eui Yie. 2007. Manganese oxide catalysts for NOx reduction with NH_3 at low temperatures. Applied Catalysis A: General (327) : p. 261–269.

[3] javad amanpour .2011. Catalytic reduction of NOx over active carbon coated with Cupper and Vanadium. MSc Thesis, Faculty of chemistry, Tabriz University, Tabriz, Iran.

[4] masood samandari.2011. Optimization of properation condition of some transition metal nanocatalyst based on active carbon in NOx catalytical reduction. MSc Thesis, Faculty of chemistry, Tabriz University, Tabriz, Iran.

[5] Kui-Hao Chuang , Zhen-Shu Liu , Yu-Hao Chang , Chi-Yuan Lu , Ming-Yen Wey. 2010. Study of SBA-15 supported catalysts for toluene and NO removal: the effect of promoters (Co, Ni, Mn, Ce). Reac Kinet Mech Cat (99) : p. 409–420.

[6] M. Mečárová N.A. Miller, N.C. Clark, K.C. Ott, T. Pietraß. 2005. Selective catalytic reduction of NOx with ammonia on gallium-exchanged ferrierites. Applied Catalysis A: General. (282) : P. 267–272.

[7] Asima Sultana, Tetsuya Nanba, Masaaki Haneda, Hideaki Hamad. 2009. SCR of NOx with NH3 over Cu/NaZSM-5 and Cu/HZSM-5 in the presence of decane. Catalysis Communications (10) :p. 1859–1863.

[8] Niaei Aligholi, Salari Dariush, Hosseini Seyed Ali, Khatamian Masumeh, Jodaei Azadeh. 2009. Catalytic Combustion of Ethyl Acetate Over Nanostructure Cobalt Supported ZSM-5 Zeolite Catalysts. Chinese Journal of Chemistry, (27): p.1—10.

[9] Azadeh Jodaei, Aligholi Niaei†, and Darush Salari. 2011. Performance of nanostructure Fe-Ag-ZSM-5 catalysts for the catalytic oxidation of volatile organic compounds: Process optimization using response surface methodology. Korean J. Chem. Eng.