

# Comparison of Catalytic Activities both for Selective Oxidation and Decomposition of Ammonia over Fe/HZβ Catalyst

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Abstract: Ammonia is one of the syngas contaminants that must be removed before using the syngas downstream applications. The most promising hot-gas clean-up techniques of ammonia are selective catalytic oxidation (SCO) and catalytic decomposition. In this study, the catalytic activities over Zeolite  $H\beta$ -supported iron catalyst (Fe/HZβ) were compared both for the two catalytic routes. For SCO experiments, temperature (300-550 °C),  $O_2$  (2000-6000 ppmv) and (0-10%)  $H_2$  concentrations were investigated with the presence of 800 ppm of  $NH_3$  in each final gas mixture. In the second route, catalytic ammonia decomposition experiments were carried out with H<sub>2</sub> in balance N<sub>2</sub> (0-30%) containing 800 ppm of NH<sub>3</sub> at 700 °C and 800 °C. In the SCO, NH<sub>3</sub> conversions were increased with increasing reaction temperatures with the absence of  $H_2$ in the reaction mixture. With 10% H<sub>2</sub>, it was shown that NH<sub>3</sub> conversions increased with decreasing the reaction temperature. This was interpreted as the competing  $H_2$  and  $NH_3$ oxidations over the catalyst. On the other hand, in the catalytic decomposition, thermodynamic equilibrium conversion of almost 100% was attained at both 700 and 800 °C. Upon H<sub>2</sub> addition, all conversions decreased. The decrease in conversion seemed to be linear with inlet hydrogen concentration. Hydrogen was seen to inhibit the decomposition of ammonia. It was shown that Fe/HZB catalyst is better to use for catalytic decomposition of  $NH_3$  in syngas rather than SCO of  $NH_3$  in spite of higher reaction temperatures needed in the decomposition reaction.

**Keywords:** Ammonia; decomposition; selective catalytic oxidation (SCO); hot-gas clean-up.

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### INTRODUCTION

Gasification is a thermochemical conversion technology applied for the production of synthetic fuels and chemicals from coal and biomass. A syngas containing H<sub>2</sub> and CO is released as a result of gasification reactions [1]. The integrated gasification combined cycle (IGCC) uses the syngas to meet heat and power demand. Synthetic fuels and chemicals are catalytically produced from this syngas through the Fischer-Tropsch (FT) process as well. Before FT reaction, the syngas should be cleaned to remove all nitrogenous (NH<sub>3</sub>, HCN) and sulfurous (H<sub>2</sub>S, COS) pollutants in ppm level, otherwise they lead to the poisoning of the FT catalysts shortly [2-3]. While NH<sub>3</sub> concentrations can be reached up to 10000 ppmv in syngas as a function of the nitrogen content of the solid fuel [4], its threshold level is below 1 ppmv [5]. NH<sub>3</sub> removal can be achieved via three different ways; scrubbing, thermal incineration, and catalytic routes. In the scrubbing as a wet process, the waste gas is washed with a chemical solution and it is necessary to treat the waste water later. In the thermal incineration, ammonia is thermally burnt and  $NO_x$  is formed. In the catalytic processes;  $NH_3$  is passed through a column packed with a catalyst. In the one way of catalytic routes,  $NH_3$  in the syngas can oxidatively be converted into harmless nitrogen and water in an exothermic manner. This process is called as selective catalytic oxidation (SCO). In the second way of the catalytic route, NH<sub>3</sub> can be decomposed into hydrogen and nitrogen via the non-oxidative endothermic reaction (Reaction 1) [6].

$$2NH_3 \leftrightarrow N_2 + 3H_2 \tag{Eq. 1}$$

Catalytic decomposition of ammonia occurs on a variety of transition metals and natural minerals. Many metals, mainly Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, W, and Cu, have been tested for ammonia decomposition and it was found that ruthenium is the most active among them [7,8]. The cost of ruthenium is a major concern for commercial utilizations. Therefore, iron based catalysts have been investigated for NH<sub>3</sub> decomposition [9-12]. In the review study of Hongrapipat *et al.*, it was stated that ferrous minerals are promising catalysts for NH<sub>3</sub> decomposition [4]. For example iron sinter, iron pellets, and ferrous dolomite all catalyze the decomposition of 2500 ppm NH<sub>3</sub> in product gas from a peat fueled gasifier at 900°C and about 85% conversions were achieved [9]. In a study by Xu *et al.*, pyrolysis chars from low rank coals were tested and found that the inherently present Fe and Ca minerals in the coal chars were responsible for their activities towards ammonia decomposition [11]. Ohtsuka and co-workers demonstrated that low-valued iron ore, namely limonite, rich in goethite (a-FeOOH) can achieve the almost complete decomposition of 2000 ppm NH<sub>3</sub> in inert atmosphere at 500°C. They also discovered that the presence of phosphorous in the carbon-supported Fe catalysts could greatly promote

catalytic decomposition of ammonia [13-14]. But in these studies, typically temperatures above 850°C were needed when the reaction was run in the presence of fuel gases. The catalytic performance of the catalysts was severely affected by the fuel gases. The requisite of high temperatures is the drawback of decomposition of NH<sub>3</sub>. On the other hand, selective catalytic oxidation (SCO) of ammonia is one of the most efficient technologies for ammonia removal from oxygen-containing waste gases. SCO of ammonia involves the controlled addition of an oxidizer ( $O_2$ , NO, NO/ $O_2$ ) to the gasification gas to quantitatively and selectively transform NH<sub>3</sub> into N<sub>2</sub> and H<sub>2</sub>O. The catalytic oxidation of ammonia usually occurs between 400-600 °C and depending on operating conditions and the type of catalysts used, can proceed in the three principal reactions (Reactions 2-4).

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6 H_2O + 302 \text{ kcal}$$
 (Eq. 2)

$$4NH_3 + 6NO \rightarrow 5N_2 + 6 H_2O$$
 (Eq. 3)

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
 (Eq. 4)

But in the presence of  $O_2$ , undesirable competing reactions with Reaction 2 can occur and NOx emissions can be released (Reactions 5-7) [15-16].

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O + 264$$
 kcal (Eq. 5)

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 216$$
 kcal (Eq. 6)

$$4NH_3 + 7O_2 \to 4NO_2 + 6H_2O$$
 (Eq. 7)

Or alternatively N<sub>2</sub>O emission may be formed through Reaction 8:

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O$$
 (Eq. 8)

When the ammonia removal from gasification gas is needed, it is more convenient to use oxygen as oxidant rather than nitrogen oxides. The oxygen that used as oxidant on SCO of ammonia should not affect the syngas composition which contains combustible gases like CO, H<sub>2</sub>, CH<sub>4</sub>, *etc.* Also it is undesirable to convert ammonia to nitrogen oxides. In the patented study of Y. Shioya *et al.*, it is said that the optimal O<sub>2</sub> amount should be two moles or more O<sub>2</sub> for one mole of ammonia [17]. Catalysts used for SCO of ammonia are classified in three groups: One is metallic catalysts, the other is transition metal catalysts and their oxides (Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> or V<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub> supported Ni, Fe and Mn, CuO/Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> *etc.*), and zeolites. Precious metal catalysts (Pt, Pd, Ir, Ru, Ag, *etc.*) show high activity at temperatures lower than 200 °C. On the other hand, transition metal oxide catalysts are active at higher temperatures (<400 °C) than precious catalysts but show higher selectivity to N<sub>2</sub>. Another potential group is transition metal oxide impregnated zeolite (ZSM5, Y, mordenite, beta, ferrierite, chabazite, *etc.*)

catalysts. Zeolite supported catalysts are active at relatively high temperatures [15]. High acidity ZSM5, Zeolite Beta and Zeolite Y supported iron catalysts were tried at 350, 400 and 450 °C and it was seen that with the increase in temperature NH<sub>3</sub> conversion and N<sub>2</sub> selectivity increased as well. The highest ammonia conversions (95-100%) were achieved at 450 °C. 450 °C is a relatively low temperature when compared with catalytic ammonia decomposition temperatures which are typically 750-850 °C. High iron content of catalysts, low Si/Al ratio of zeolites and low ammonia concentration is advantageous cases in selective catalytic oxidation of ammonia [18]. A detailed PhD study on SCO of ammonia showed that activity of different active metals at 300°C decrease in this order: Pt>Pd>Cu>Ag>Au>Fe>W>Ti. High ammonia conversions and N<sub>2</sub> selectivities can be achieved with copper based catalysts at atmospheric pressure. But at high pressures, the ammonia conversion can decrease under 30% [19]. In this study, the catalytic activities of Zeolite H $\beta$  supported iron catalyst (Fe/HZ $\beta$ ) were compared both for the selective catalytic oxidation and catalytic decomposition of 800 ppmv ammonia.

#### **MATERIALS AND METHODS**

Zeolite support, namely Zeolite Hβ, was supplied by Zeolyst International Incorporation. The silica-to-alumina ratio of the zeolite was 38. Wet impregnation method was used to prepare the catalyst. Zeolite  $H\beta$  was in ammonium form prior to impregnation. For preparation of the catalyst, iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, Alfa Aesar) was dissolved in a minimum volume of water and the zeolite was added to the solution so as to achieve a nominal iron content of 10% by weight. The slurry was subsequently dried at 90 °C overnight. Zeolite-supported iron catalyst was labeled as  $Fe/HZ\beta$  through the article. Chemical analysis of the catalyst was performed using inductively coupled plasma spectroscopy (Perkin Elmer Optima 2100 ICP-OES). Iron content of the synthesized catalyst was analyzed to be 12.96%. Fe/HZ $\beta$  catalyst was milled and sieved under 500  $\mu$ m before the catalytic experiments. A 5 cc (~3 g) sample of the dry catalyst powder was placed in a vertical stainless steel reactor with 310 grade (17 mm i.d.), calcined in dry air at 420°C for 5 hours and reduced under pure hydrogen flow at the same temperature for 10-12 hours as previously explained in detail [20]. After the reduction of the catalyst, different gas mixtures composed of 800 ppmv ammonia were prepared. For selective catalytic oxidation experiments, 2000-6000 ppmv  $O_2$  and 0-10%  $H_2$ concentrations were prepared in balance with  $N_2$  at the temperatures of 300-550 °C. For decomposition experiments; 0-10-20-30% H<sub>2</sub> and balance N<sub>2</sub> were flown over the catalyst bed for 5h at the temperatures of 700 °C and 800 °C and a GHSV of 60 000 h<sup>-1</sup>. Reaction products were analyzed in line using a UV-Vis NH<sub>3</sub> Analyzer and a Mass

Spectrometer. NH<sub>3</sub> conversion to hydrogen was calculated from the measured NH<sub>3</sub> in the product stream, reaction stoichiometry, and the differential reactor assumption, as  $P_{NH3 to} H_2/P_{NH3, inlet.}$  NO<sub>x</sub> concentrations were measured with off-line Analytic Jena multi EA<sup>®</sup> 5000 Total Nitrogen (TN) measuring device equipped with Nitrogen Chemiluminescence Dedector (NCD).

#### **RESULTS AND DISCUSSION**

#### **Comparison of Catalytic Activities Under N2 Atmosphere**

Approximately 3 g (~5 cc) of Fe/HZ $\beta$  catalyst was charged to the reactor and calcined with air at 420°C for 5 h. Then the reduction procedure was started by shifting to pure H<sub>2</sub> flow at the same temperature and the catalyst was reduced for 10 h. In the first set of experiments (selective catalytic reduction labelled as SCO), a gas mixture consisting of 800 ppm NH<sub>3</sub>, 2000 and 4000 ppm O<sub>2</sub> and balance N<sub>2</sub> was flown over the catalyst with a gas flow rate of 5 L/min (GHSV=60,000 h<sup>-1</sup>). SCO reaction tests were conducted at 300, 350, 400, 450 and 500 °C. In the second set of experiments (catalytic decomposition), a gas mixture of 800 ppm NH<sub>3</sub> and balance N<sub>2</sub> was flown over the reduced catalyst with the same gas flow rate and catalytic decomposition of NH<sub>3</sub> was carried out at 700 °C and 800 °C in the absence of O<sub>2</sub>. In the last set, blank reactor tests were conducted with the same gas mixture used for catalytic decomposition of NH<sub>3</sub>. Reaction products were analyzed in line using a UV-Vis NH<sub>3</sub> analyzer and a mass spectrometer. Calculated NH<sub>3</sub> conversions versus reaction temperature were plotted in Figure 1.

For the first set of SCO experiment, 4% of ammonia conversion (based on UV-Vis measurements) was achieved at 300 °C in the presence of 2000 ppm O<sub>2</sub>. When the reaction temperature was increased stepwise to 500°C, NH<sub>3</sub> conversions were steadily increased. 100% ammonia conversion was reached at 500 °C under SCO conditions. SCO tests were conducted at 350 and 400 °C by increasing the oxygen concentration from 2000 ppm to 4000 ppm to see the effect of O<sub>2</sub> on NH<sub>3</sub> conversion. At 350 °C, ammonia conversions of 12.5% and 8.8% at the reactor exit were obtained with the presence of 2000 and 4000 ppm O<sub>2</sub>, respectively. When the reaction temperature was increased to 400 °C, while NH<sub>3</sub> conversion was reached to 31.2% in the presence of 2000 ppm O<sub>2</sub>, it was 41.2% for 4000 ppm O<sub>2</sub>. It was shown that higher NH<sub>3</sub> conversions could be achieved with increasing O<sub>2</sub> concentrations.



**Figure 1:** The change of NH<sub>3</sub> conversion with temperature in N<sub>2</sub> atmosphere at atmospheric pressure and 800 ppm inlet NH<sub>3</sub> concentration •Selective Catalytic Oxidation (SCO) over Fe/HZ $\beta$  at 2000 ppm O<sub>2</sub>  $\Delta$ SCO over Fe/HZ $\beta$  at 4000 ppm O<sub>2</sub>  $\triangle$  catalytic decomposition over Fe/HZ $\beta$   $\Box$  blank reactor test without O<sub>2</sub>.

During the tests, NO<sub>x</sub> and H<sub>2</sub>O concentrations in the reactor exit were followed by mass spectrometer as well. Figure 2 shows the m/z peak intensities of these components (m/z=30 for NO/NO<sub>2</sub>, m/z=18 for H<sub>2</sub>O, m/z=46 for the fragment of NO<sub>2</sub>, m/z=44 for N<sub>2</sub>O and m/z=18 for H<sub>2</sub>O). It must be pointed out here that measuring the NO<sub>x</sub> components with mass spectrometer have some difficulties because of the overlapping m/z values at m/z=30 for NO and NO<sub>2</sub>. On the other, these measurements give an idea on the formation of NO<sub>x</sub> components. As seen from the Figure 2, NO<sub>x</sub> formation was apparent for all reaction temperature. As expected, water vapor was also formed upon Reactions 2-7. The rate of water vapor formation was started decreasing at 500°C where 100% NH<sub>3</sub> conversion was achieved. This was attributed to a possible secondary reaction between NO<sub>2</sub> and H<sub>2</sub>O in the stoichiometric excess of O<sub>2</sub> according to Reaction 9. On the other hand, further verifications are needed to make sure on the occurrence of this reaction.

$$4 \text{ NO}_2(g) + O_2(g) + 2 \text{ H}_2O(\text{vapor}) \rightarrow 4 \text{ HNO}_3(\text{vapor})$$
 (Eq. 9)



Figure 2: Effects of temperature and  $O_2$  amount on SCO of ammonia on Fe/HZ $\beta$  catalyst: MS data of H<sub>2</sub>O and NO<sub>x</sub> in the reactor exit.

Unfortunately, mass spectrometric measurements did not let the selectivity and yield calculations due to the qualitative monitoring of  $NO_x$  components and excess  $N_2$  in the reaction atmosphere.

In the second set of catalytic decomposition of NH<sub>3</sub> experiments, the reaction was intentionally carried out at high temperatures, namely at 700 and 800 °C, due to the endothermic nature of the ammonia decomposition. Quite close conversions were achieved for 700 and 800 °C under nitrogen atmosphere by giving H<sub>2</sub> and N<sub>2</sub> as the decomposition products according to Reaction 1. Thermodynamic equilibrium conversion of almost 100% was attained over both at 700 and 800 °C under nitrogen atmosphere.

In the last set of experiments, blank reactor tests were carried out under  $NH_3$  decomposition reaction conditions in the absence of  $O_2$ .  $NH_3$  decomposition reaction started at 500 °C with a conversion of 4.1%. The rate of  $NH_3$  decomposition reaction was seen to be increased after 700 °C. While  $NH_3$  conversion was 14% at 700°C, it was peaked to 63% at 800 °C where it was still below the value obtained over the catalyst.

It was shown that under N<sub>2</sub> atmosphere, 100% of NH<sub>3</sub> conversion was achieved over Fe/HZ $\beta$  catalyst through selective catalytic oxidation reaction at 500 °C while 94% of conversion was obtained over the same catalyst through the catalytic decomposition at 800°C. These results indicated that while selective catalytic oxidation was promoted below 500 °C, catalytic decomposition of NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> was favored above 600 °C.

To investigate the effect of  $O_2$  on SCO activity of Fe/HZ $\beta$  catalyst in detail, additional tests were conducted at both 400 and 500 °C. SCO tests were carried out at changing  $O_2$  concentrations with an inlet gas composition of 800 ppmv NH<sub>3</sub> in balance N<sub>2</sub>. O<sub>2</sub>

233

concentrations were changed between 2000 ppm and 6000 ppm. Obtained results are given in Figure 3. As it was seen in the Figure, conversions at 500 °C were slightly increased from ~94% to ~98% at increasing O<sub>2</sub> concentrations. On the other hand, the highest ammonia conversion (41%) at 400 °C was achieved with 4000 ppm O<sub>2</sub>. Relatively lower conversion values were observed with 2000 and 6000 ppm O<sub>2</sub>. This indicates that there seemed to be an optimal O<sub>2</sub> concentration at 400°C for an acceptable surface adsorption and NH<sub>3</sub> oxidation. K. Duan *et al.* reported the similar case over Cu-Mn/TiO<sub>2</sub> catalyst for 0.5%, 3% and 5% O<sub>2</sub> concentrations. In their study, the highest NH<sub>3</sub> conversion (~%85) was achieved in the presence of 3% O<sub>2</sub> at 250 °C [21]. This study supported the finding that there is an optimum O<sub>2</sub> concentration related with temperature.



Figure 3: Effect of O<sub>2</sub> concentration on ammonia conversion at 400 and 500 °C.

To get the main picture of the catalytic decomposition and selective catalytic oxidation of ammonia results over Fe/HZ $\beta$  and in blank reactor, ammonia conversion values were also given in Table 1.

**Table 1:** The change of NH3 conversion with temperature and O2 amount without H2 atatmospheric pressure and 800 ppm inlet NH3 concentration: Selective Catalytic Oxidation(SCO) and catalytic decomposition over Fe/HZ $\beta$ 

		Ammonia Conversion, %							
		Ammonia Decomposition	Blank Reactor Test	Selective Catalytic Oxidation of Ammonia		lytic monia			
O <sub>2</sub> amount		0	0	2000	4000	6000			
(ppm)	300	-	-	4	-	_			
	350	-	-	13	9	-			
	400	-	0	31	41	23			
Temperature	450	-	-	77	-	-			
(°C)	500	-	4	100	98	99			
	600	-	5	-	-	-			
	700	97	14	-	-	-			
	800	99	63	-	-	-			

In order to evaluate the selectivity of the reaction, gas samples were collected into the Tedlar bags after each test conducted at 500 °C and 2000, 4000 and 6000 ppm O<sub>2</sub>. Collected gas samples were analyzed with Analytic Jena multi EA<sup>®</sup> 5000 Total Nitrogen (TN) measuring device equipped with Nitrogen Chemiluminescence Detector (NCD). NO<sub>x</sub> concentrations of the samples were measured and results were drawn in Figure 4. As seen from the Figure, NO<sub>x</sub> concentration is linearly decreasing with increasing oxygen concentration. This might be due to the further oxidation of NO species according to Reaction 4 or N<sub>2</sub>O formation through Reaction 8 under excess oxygen atmosphere. Therefore, excess O<sub>2</sub> might lead to the undesired N<sub>2</sub>O emissions.





## **Comparison of Catalytic Activities Under H2 Atmosphere**

Fe/HZ $\beta$  catalyst was pretreated in the way of the experimental work conducted under N<sub>2</sub> atmosphere. Similarly, three sets of experiments were carried out, namely selective catalytic oxidation, catalytic decomposition and blank reactor test for decomposition. Selective catalytic oxidation (SCO) experiment was conducted with a gas mixture consisting of 4000 ppm O<sub>2</sub>, 800 ppm NH<sub>3</sub>, 10% H<sub>2</sub> and balance N<sub>2</sub>. The effect of reaction temperature on NH<sub>3</sub> conversion was screened between 400 and 550°C. The same gas mixture in the absence of O<sub>2</sub> was flown over the reactor to carry out the catalytic decomposition of NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> with or without catalyst. Decomposition reaction was tested at 700 and 800 °C. Conversion results were plotted in Figure 5 and also given in Table 2. Contrary to the observation for SCO reaction under N<sub>2</sub> atmosphere, NH<sub>3</sub> conversions decreased with increasing reaction temperatures.

Figure 6 shows the trends for  $H_2O$  formation and  $O_2$  consumption through the mass spectrometer. It is apparent that the main reaction product,  $H_2O$ , was formed at all reaction temperatures. On the other hand, its concentration decreased with concomitant increase in  $O_2$  concentration when the reaction temperature was decreased from 450 °C to 400 °C. Although a decrease in reaction temperature and water vapor and an increase in  $O_2$  concentration, NH<sub>3</sub> conversion was increased from 35% to 41%. This is the clear indication of unselective oxidation of  $H_2$  at increasing temperatures. To clear the situation,  $H_2$  flow was cut from the mixture at 400 °C and it was shown that  $H_2O$ concentration continued decreasing but the NH<sub>3</sub> conversion remained the same. Therefore it was believed that  $H_2$  oxidation reaction competes with selective catalytic oxidation reaction of ammonia to  $N_2$  and  $H_2O$ .

$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O+302$$
 kcal (Eq. 10)

$$4H_2+2O_2 \rightarrow 4H_2O+231$$
 kcal (Eq. 11)



**Figure 5.** The change of NH<sub>3</sub> conversion with temperature in <u>10% H<sub>2</sub></u> balance N<sub>2</sub> atmosphere at atmospheric pressure and 800 ppm inlet NH<sub>3</sub> concentration. •Selective Catalytic Oxidation over Fe/HZ $\beta$   $\Delta$ Catalytic Decomposition over Fe/HZ $\beta$   $\Box$ Blank reactor test without O<sub>2</sub>.



Figure 6: H<sub>2</sub> effect on SCO of ammonia at different temperatures with 4000 ppm O<sub>2</sub>.

In the second case, catalytic decomposition of NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> was tested under 10% H<sub>2</sub> concentration. Although high NH<sub>3</sub> conversions over 90% were achieved upon H<sub>2</sub> addition, these conversions under N<sub>2</sub> atmosphere were close to 100%. For the third case, where catalytic decomposition of NH<sub>3</sub> was tested without catalyst, it was seen that while NH<sub>3</sub> conversion was 63% at 800°C, it was decreased to 54% with H<sub>2</sub> addition. On both

#### Durak-Çetin, Sarıoğlan and Okutan, JOTCSA. 2017; 4(1): 227-242. RESEARCH ARTICLE

cases, loss of activity upon H<sub>2</sub> addition was apparent. Therefore, a new set of experiments were conducted to investigate the effect of H<sub>2</sub> concentration on the activity of Fe/HZ $\beta$  catalyst for NH<sub>3</sub> decomposition. To do this, H<sub>2</sub> concentration was changed between 10% and 30% for the same inlet NH<sub>3</sub> concentration (800 ppm). Reactions were conducted at 700 °C and 800 °C. The change of conversions with H<sub>2</sub> concentration was plotted in Figure 7 and the corresponding conversion values were given in Table 2. It was shown that all conversions decreased. The decrease in conversion seemed to be linear with inlet hydrogen concentration. Hydrogen was seen to inhibit ammonia decomposition reaction. Conversion loss in the presence of hydrogen is reasonable for the dehydrogenation reactions regarding unfavorable thermodynamic conditions. On the other hand, competing kinetically relevant steps, namely N-H bond breaking and atomic nitrogen association might also be responsible for this inhibition. Rate determining step might be NH<sub>3</sub> dissociation due to hydrogen surrounding the active site [22]. Therefore, restricted N–H bond breaking might limit the number of active sites to be occupied by N-N pairs.



Figure 7:  $NH_3$  decomposition conversions changing with inlet  $H_2$  concentration at 700 and 800 °C.

		Ammonia Conversion, %							
		Ammonia Decomposition			on	Blank Reactor Test	Selective Catalytic Oxidation of Ammonia		
O <sub>2</sub> amount (ppm)				0		0	4000		
H <sub>2</sub> amount (%)		0	10	20	30	10	10		
	400	-	-	-	-	-	41		
Temperature (°C)	500	_	-	-	_	-	17		
	550	-	-	-	-	-	0		
	700	97	92	80	68	19	-		
	800	99	97	91	82	54	-		

**Table 2:** The change of NH<sub>3</sub> conversion with temperature, O<sub>2</sub> and <u>H<sub>2</sub> amounts</u> at atmospheric pressure and 800 ppm inlet NH<sub>3</sub> concentration: Selective Catalytic Oxidation (SCO) and catalytic decomposition over Fe/HZ $\beta$ .

#### CONCLUSIONS

In this study, the catalytic activities over Zeolite H $\beta$  supported iron catalyst (Fe/HZ $\beta$ ) were compared both for the two catalytic routes, namely SCO and Catalytic Decomposition. It was shown that SCO of ammonia reaction is directly related with temperature and O<sub>2</sub> amount. Although comparably higher conversions can be achieved under N<sub>2</sub> atmosphere through SCO reaction, the presence of a fuel gas like H<sub>2</sub> inhibits the selective oxidation of NH<sub>3</sub> and leads to the poor conversions. The loss of SCO activity under H<sub>2</sub> atmosphere was interpreted as the competing H<sub>2</sub> and NH<sub>3</sub> oxidations over the catalyst. On the other hand, although decomposition reaction of NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> requires higher reaction temperatures, it was seen to be less sensitive to the presence of hydrogen. Activity loss with H<sub>2</sub> addition in the case of decomposition reaction was considered to be due to both unfavorable thermodynamic conditions for dehydrogenation and restricted N–H bond breaking due to the hydrogen surrounding the active sites.

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Durak-Çetin, Sarıoğlan and Okutan, JOTCSA. 2017; 4(1): 227-242. RESEARCH ARTICLE

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## Türkçe Öz ve Anahtar Kelimeler

## Fe/HZβ Katalizörü Üzerinde Amonyağın Seçici Katalitik Yükseltgenme ve Bozunma Aktivitelerinin Karşılaştırılması

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Öz: Amonyak, sentez gazı kullanılmadan önce giderilmesi gereken sentez gazı kirleticilerinden biridir. Amonyağın en umut vaat eden sıcak gaz temizleme yöntemi seçici katalitik yükseltgeme (SCO) ve katalitik bozunmadır. Bu çalışmada; Zeolit Hβ-destekli demir katalizör (Fe/HZB) üzerindeki amonyak giderim aktiviteleri iki katalitik yol icin de karşılaştırılmıştır. SCO deneyleri için, sıcaklık (300-550 °C), O<sub>2</sub> (2000-6000 ppmv) ve H<sub>2</sub> (%0-10) konsantrasyonlarının etkisi her gaz karışımında 800 ppm NH<sub>3</sub> olacak şekilde incelenmistir. İkinci yolda ise, katalitik amonyak bozunma denemeleri N<sub>2</sub> icinde H<sub>2</sub> (%0-30) varlığında 800 ppm NH<sub>3</sub> içeren gaz karışımı ile 700 ve 800 °C'de gerçekleştirilmiştir. SCO'da, NH<sub>3</sub> dönüşümlerinin reaksiyon ortamında H<sub>2</sub> olmadığı durumda artan reaksiyon sıcaklığı ile arttığı görülmüştür. %10 H<sub>2</sub> varlığında ise, azalan reaksiyon sıcaklığı ile NH<sub>3</sub> dönüşümlerinin arttığı tespit edilmiştir. Bu durum katalizör üzerinde H<sub>2</sub> ve NH<sub>3</sub> yükseltgenmesinin yarışmalı olarak gerçekleştiği şeklinde yorumlanmıştır. Diğer taraftan, katalitik bozunma reaksiyonunda, hem 700 ve hem de 800 °C'de termodinamik denge dönüşümüne yakın, yaklaşık %100, amonyak dönüşümleri elde edilmiştir. Ortama H<sub>2</sub> ilavesi ile bütün dönüşümlerde azalma görülmüştür. Dönüşümlerdeki azalma giriş hidrojen konsantrasyonu ile doğrusal bir iliski göstermiştir. Hidrojenin, amonyağın bozunma reaksiyonunu engellediği görülmüştür. Fe/HZß katalizörünün, sentez gazındaki NH<sub>3</sub>'ün giderilmesinde NH<sub>3</sub>'ün seçici katalitik yükseltgenmesinden ziyade, daha yüksek sıcaklıklara ihtiyac duyulmasına rağmen (700-800 °C), amonyak bozunma reaksiyonunda kullanılmasının daha etkili olacağı gösterilmiştir.

**Anahtar kelimeler:** Amonyak; bozunma; seçici katalitik yükseltgeme (SCO); sıcak gaz temizleme.

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