Ag/Al₂O₃ 촉매하의 HC-SCR에서 환원제로서 수소 풍부 바이오디젤의 반응 특성 연구

김진걸*, 이민주**, 이혜민***, 전지용*, 김성수****, 유승준*****†

*순천향대학교 나노화공과, **아신기술 주식회사, ***(주)씨아이티
****한국에너지연구소 폐기물 연구실, *****서남대학교 환경·화공학부

Study of Efficiency of Hydrogen Rich Biodiesel as Reductant for HC-SCR over Al₂O₃ Supported Ag Catalyst

JINGUL KIM*, MINJU LEE**, HEMIN LEE***, JIYONG JEON*, SEONGSOO KIM****, SEUNGJOON YOO*****†

*Dept. of Chemical Eng., Soonchunhyang Univ., Asan 337-745
**ANT Corporation, Sangdaewon-Dong, Seongnam, 462-729
***Creative Imaging Technology, Inc., Shiwa Industrial Base, Siheung
****Wastes Energy Research Center, Korea Institute of Energy Research, Yusongku, Daejon.
*****Dept. of Env. and Chem. Eng., Seonam Univ., Namwon, 590-711

ABSTRACT

Ag/Al₂O₃ 촉매하에 디젤 엔진에서 배출되는 NOx를 정화하기 위하여, 수소가 풍부한 바이오디젤을 환원제로 사용하였다. Ag 전구체 함침과정에서 촉매기공이 부분적으로 폐쇄되는 것을 BET 실험을 통하여 관찰하였다. 2% Ag/Al₂O₃ 촉매의 형상과 조성은 산처리 과정을 거치더라도 변화하지 않는 것을 SEM과 EDXS 분석으로부터 확인하였다. Ag/Al₂O₃ 촉매 표면에서 생성되는 -NCO와 -CN을 in-Situ DRIFT 방법을 사용하여 관찰하여 HC-SCR에서의 NOx 제거 반응구조를 확인하였다.

KEY WORDS : Hydrogen rich biodiesel (수소 풍부 바이오디젤), Reduction (환원), HC-SCR, Ag/Al₂O₃, NOx removal (질소 산화물 제거)

1. 서 론

NO$_x$ has been known to be a cause of air pollution such as smog or acid rain. In order to reduce the amount of NO$_x$ exhaust, research of either restraining the NO$_x$ production or cleaning up the exhausted NO$_x$ has been continued. However, it was widely accepted that the former method exhibited the lower reduction efficiency than the latter method did. Therefore, most of SCR research was based on the latter method, which converted NO$_x$ in an oxygen-rich exhausts into N$_2$ and O$_2$ by hydrogen rich reduction method[1,2].

Traditional ammonia SCR has revealed many problems in ammonia storage, since NH$_3$ slip has created a serious environmental problem such as

† Corresponding author : sjyoo@tiger.seonam.ac.kr

toxicity and explosiveness. Moreover, SO$_2$ was reported to be oxidized into SO$_3$ which reacted with ammonia, resulting in ammonium sulfate to be known as cause of shortening engine durability[3,4].

HC-SCR research has continued in order to overcome those problems of NH$_3$-SCR method since 1990[1,2]. Hydrogen rich light hydrocarbon such as methane, ethane, propene and butene has been used as reductant for HC-SCR[5]. Hydrogen rich biodiesel would be a possible promising reductant for HC-SCR but never been applied for use as reductant for HC-SCR until today. To convert the NO$_x$ exhaust into N$_2$ and O$_2$, this study was aimed to investigate the efficiency of hydrogen rich biodiesel as reductant for HC-SCR.

2. Experimental

2.1 Catalyst Preparation

AgNO$_3$ (Hangyul Gold Co.) solution was dissolved into a deionized water and impregnated into honeycomb (200 cpsi) coated with γ-Al$_2$O$_3$ and calcined at 600℃ for 6 hours. Catalyst was impregnated using 0.7% H$_2$SO$_4$ solution and dried at 120℃ for 3 hours and calcined at 400℃ for 3 hours.

2.2. Evaluation of catalyst kinetics

After fixing the catalyst honeycomb on the plate in the center of the reactor, MFC (Brooks, model 5850E) was used to control the gas flow rate into the reactor. Feed rate of biodiesel was set at 0.003 sccm through preheating equipment using HPLC pump. To study the reaction kinetics, FTIR (JASCO 6100) and NOx analyzer (Siemens, Ultramat 23) were dedicated to analyze the ppm of NO$_x$, N$_2$O and CO. In-situ DRIFT analyzer was employed to investigate the adsorbed reaction intermediates over catalyst surface with the heating

Table 1 Experimental condition

Parameter		Application
Catalyst		Ag/Al$_2$O$_3$
Reducing Agent		bio-diesel 0.003ml/min
Temperature Range		200℃ - 500℃
Ag Loading(%)		2.0/5.0
Gas Flow Rate(cc/min)		36
Space Velocity(hr^{-1})		20,000
Feed Composition	NO(ppm)	800
	O$_2$ (%)	10.5

Table 2 BET result

| Catalyst	Surface area (m^3/g)	Average pore diameter(a)	Pore volume (cm^3/g)
Pure γ-Al$_2$O$_3$	298.33	60.21	0.382
2wt% Ag/γ-Al$_2$O$_3$	271.71	56.54	0.372

cell (PIKE) at resolution of 4cm^{-1}. The detailed experimental condition was described in Table 1.

2.3. Catalyst Characterization

BET apparatus (Micrometrics, model 2010) was dedicated to measure the surface area, pore diameter and pore volume. SEM (JEOL, 5600) and EDXS (Oxford, ISIS 300) were used to investigate morphology and composition of catalyst.

3. Results and Discussion

Table 2 demonstrated the BET result such as specific surface area, pore diameter and pore volume. With higher Ag loading, specific surface area of the catalyst was decreased by 9.1% while pore diameter was decreased by 6.1% and pore volume was decreased by 2.7%. According to this result, catalyst pore was thought to be partly blocked during impregnation step with Ag precursor, so that a large portion of Ag precursor would be impregnated over the external surface of catalyst

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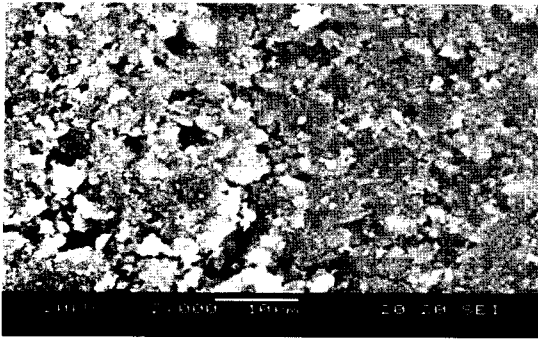
(a) 2%Ag/ɣ-Al₂O₃ - No treatment
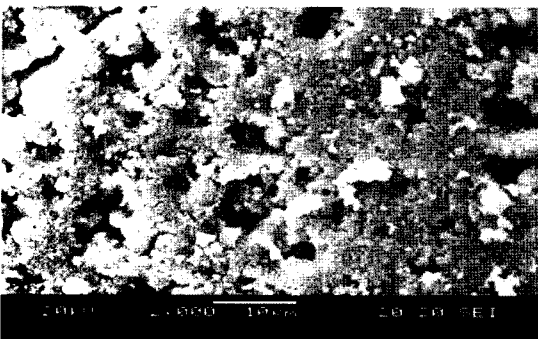
(b) 2%Ag/ɣ-Al₂O₃ - Acid (1% H₂SO₄) treatment

Fig. 1 SEM result of 2% Ag/ɣ-Al₂O₃.

Table 3 EDXS result of 2% Ag/Al₂O₃

Species	O	Al	Ag
No treatment	47.1	51.2	1.67
Acid treatment	47.9	50.4	1.6

rather than into the internal volume of the pore.

Figure 1 was taken with SEM to see the effect of acid treatment on the morphological change of catalyst surface. It showed that the surface morphology of 2.0% Ag/ɣ-Al₂O₃ was almost same before and after acid treatment.

Table 3 showed EDXS results to investigate the effect of acid treatment on catalyst composition. The pretreatment with sulfuric acid over 2% Ag/ɣ-Al₂O₃ did not affect catalyst composition since analyzed composition of both catalysts was almost same.
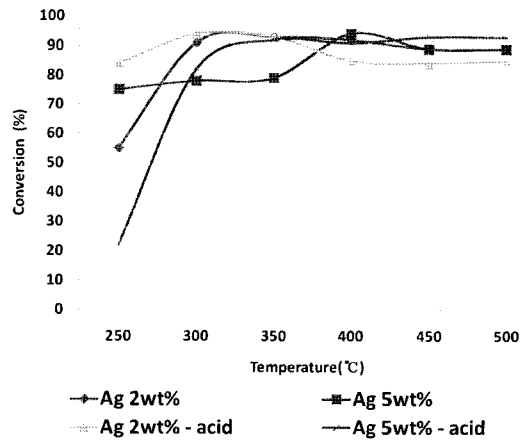

Fig. 2 Effect of Ag loading and acid treatment on De-NOx conversion over 2% Ag/ɣ-Al₂O₃.

Other groups reported that 2.0 ~ 2.4% Ag/ɣ-Al₂O₃ exhibited the highest conversion between 200℃ and 500℃ and de-NOx yield was relatively high at space velocity of 38000 hr⁻¹ with HC/NOx ratio of over 1.25[6]. Based on this study, experimental condition of this biodiesel-SCR kinetics study was performed in the condition of Table 1.

Figure 2 demonstrated the de-NOx conversion between 250℃ and 500℃. Regardless of Ag content and acid pretreatment, de-NOx conversion reached almost 90% over 300℃. This result indicated that condition of Ag amount and acid pretreatment did not affect the reaction yield. Instead of these effects, the feed ratio of HC/NO would be the dominating factor to control the de-NOx conversion, since all the catalysts demonstrated the maximum yield about 90%[5].

Figure 3 showed the amount of N₂O formed at reaction temperature between 250℃ and 500℃. Regardless of condition of catalyst preparation, all the catalyst showed the highest N₂O yield between 300℃ and 400℃. Since maximum N₂O yield of 2% Ag/Al₂O₃ catalyst was higher than maximum N₂O yield of 5% Ag/Al₂O₃, higher loading of Ag amount was supposed to play a role
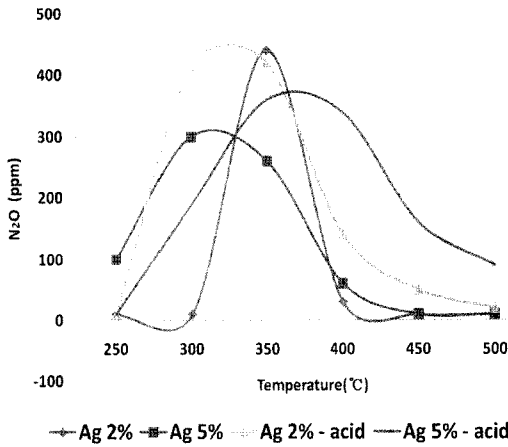
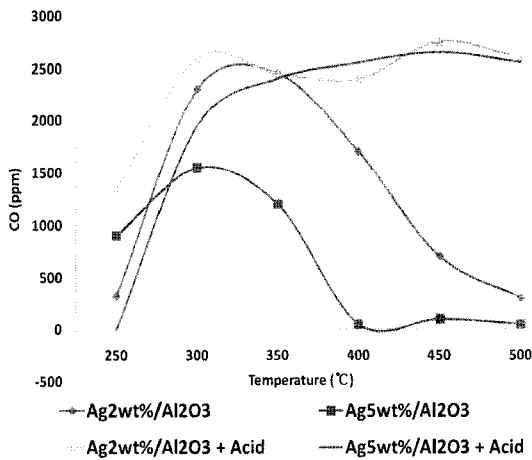Fig. 3 Effect of Ag loading and acid treatment on N_2O yield over 2% Ag/γ-Al₂O₃.

Fig. 4 Effect of Ag Loading and acid treatment on CO yield over 2% Ag/γ-Al₂O₃.

for the higher selectivity into N_2 and O_2 during de-NOx reaction.

Figure 4 showed the amount CO formed at reaction temperature between 250℃ and 500℃. Regardless of condition of catalyst preparation, all the catalyst showed the highest CO yield between 300℃ and 400℃, while non-treated Ag/Al₂O₃ demonstrated lower CO yield than acid-treated Ag/Al₂O₃ over 450℃. This indicated that
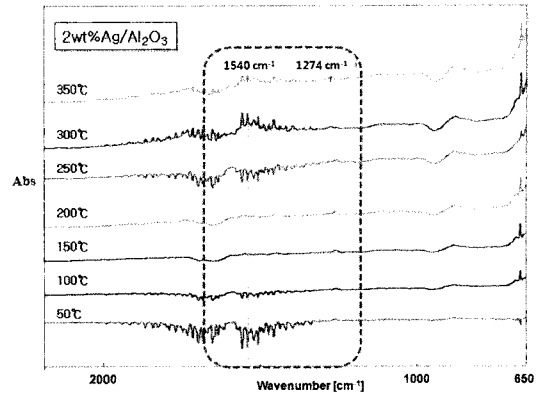

Fig. 5 Temperature Programmed NO adsorption over 2wt% Ag/Al₂O₃.

acidic sites created by acid treatment would be related with higher CO formation over 400℃.

Temperature programmed NO adsorption over 2% Ag/Al₂O₃ was studied using in-situ DRIFT analyzer, as temperature was increased from 50℃ to 350℃.

Intensity of NO adsorption band at $1274cm^{-1}$ and $1540cm^{-1}$ stays high between 250℃ and 350℃ as shown in Figure 5, while de-NOx yield became higher from 250℃ to 500℃ as shown in Figure 2. This proportional increase of adsorped NO and de-NOx yield suggested that NO adsorption step would be slow reaction rate step.

In-Situ DRIFT investigation have been acknowledged as useful method for the elucidation of reaction mechanism. The reported reaction mechanism is as follows[7].

$$NO + O_2 + C_xH_y \rightarrow NO_3 + C_xH_yO_z$$

$$R-NO_2 + R-ONO \rightarrow NCO + CN \rightarrow N_2$$
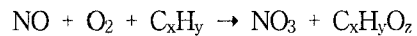
Species of -NCO and -CN were acknowledged to be known reaction intermediates formed during HC-SCR kinetics[7-10]. Based on this, in-situ DRIFT study was performed in the condition of NO 400
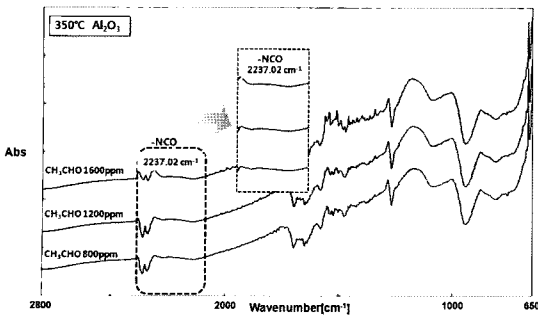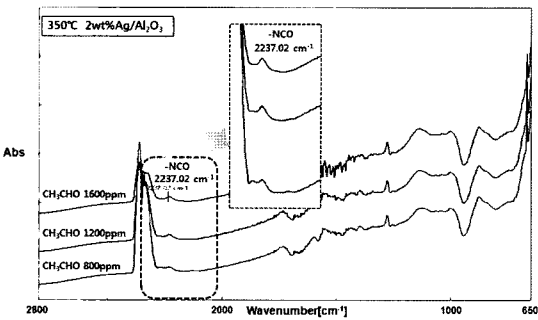
Fig. 6 -NCO production during de-NO$_x$ reaction over γ-Al$_2$O$_3$.

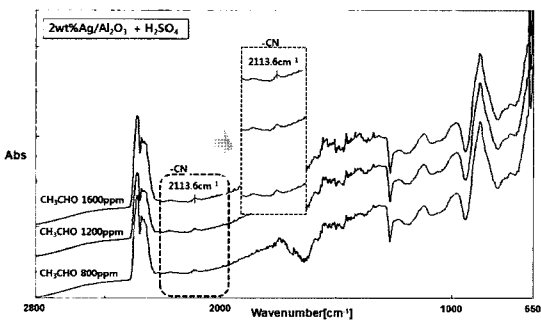Fig. 7 -NCO production during de-NO$_x$ reaction over 2% Ag/γ -Al$_2$O$_3$.

Fig. 8 -CN production during de-NO$_x$ reaction over 2% Ag/γ -Al$_2$O$_3$.

ppm, O$_2$ =10%, CH$_3$CHO/NO = 1, 2 and 3, to investigate reaction intermediates. The results were shown in Figure 6, 7 and 8, where other experimental condition was explained in Table 1. Intensity of -NCO band at 2237cm^{-1} and the -CN

band at 2113cm^{-1} over supported 2% Ag/γ-Al$_2$O$_3$ was increased as CH$_3$CHO concentration became higher[7-10], while -NCO band at 2237cm^{-1} over supported 2% Ag/γ-Al$_2$O$_3$ did not appear. This implied that -NCO species was significant reaction intermdiates as suggested by other group[7-10].

As concentration of CH$_3$CHO increased, NCO at 2237cm^{-1} and CN at 2113cm^{-1} were not observed over the pure Al$_2$O$_3$ as shown in Figure 6.

As concentration of CH$_3$CHO increased, NCO at 2237cm^{-1} and CN at 2113cm^{-1} were not ob- served over the pure Al$_2$O$_3$ as shown in Figure 6. In contrast to this, Figure 7 showed the formation of NCO species at 2237cm^{-1} and Figure 8 exhibited the formation of CN species at 2113cm^{-1}. Based on this result, one of the elementary step was thought to concur with the reported reaction step (-NCO + -CN + NO + O$_2$ other group)[7-10].

4. Conclusion

1) High ratio of hydrogen rich biodiesel/NO re-- sulted in a constant de-NOx yield over 250℃.
2) De-NOx yield was not affected by the amount of Ag loading and acid treatment but was pro- portionally affected by amount of NO adsorption.
3) By-products of N$_2$O and CO showed the maxi- mum amount between 300℃ and 350℃.
4) The reaction intermediates such as -NCO and -CN were supposed to play a role in an increased NO$_x$ removal rate.

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