

The study of a synergetic effect over a H-ZSM-5/V₂O₅ hybrid catalyst on SCR reaction

Seong Moon Jung^{*,1}, Olivier Demoulin, Paul Grange[✕]

Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

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Abstract

The synergetic effect over a H-ZSM-5/V₂O₅ hybrid catalyst on selective catalytic reduction (SCR) reaction has been studied by steady state reaction (SSR), temperature programmed reaction (TPR) and NH₃-temperature programmed desorption (TPD). The improved NO conversion is observed on the layered hybrid catalyst with V₂O₅ as the first layer. TPR experiment suggested that V₂O₅ plays a role as a supplier of oxygen source through N₂O formation, while H-ZSM-5 decomposes N₂O into N₂ and α-oxygen. α-Oxygen may contribute to the increase in NO₂ species on H-ZSM-5 and improves the apparent SCR activity. NH₃-TPD by NO experiments shows the possibility of the contribution of spillover oxygen in the improvement of SCR activity.

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1. Introduction

The elimination of nitrogen oxides emitted from the combustion process is particularly important in the reduction of the environmental problems caused by the formation of acid rain and ozone through secondary reactions in the atmosphere [1]. Several processes have been proposed for the elimination of NO_x through the widespread application of available methods and/or via the development of new technologies [2]. Among the flue gas treatment methods, selective catalytic reduction (SCR) is well developed and used worldwide due to its efficiency, selectivity and economy. The SCR process is based on the reaction between NO_x and a reducing agent such as CO, H₂ and ammonia, injected into the flue gas stream, to produce innocuous water and nitrogen [1]. Especially, NO_x

elimination with ammonia as a reducing agent has been extensively studied as a non-catalytic technology (SNCR) and a catalytic technology (SCR) for stationary sources [1–6].

The SCR mechanisms can be classified into two categories: (i) Eley–Rideal, and (ii) Langmuir–Hinshelwood [7–16]. The former mechanism has been emphasized at low temperature over reducible materials including catalysts like V₂O₅ based catalyst, which enables the adsorbed ammonia to activate, whereas the Langmuir–Hinshelwood mechanism has been used to explain the activity of highly acidic catalysts with negligible reducibility such as zeolites and sulfate types, at high temperature.

In the Eley–Rideal mechanism, the ammonia adsorbed on the catalyst surface should be activated to react with NO from the gas phase. Ramis et al. [7] have suggested that the amide or amide radical forms through the dissociation of ammonia adsorbed on Lewis acid sites, while Topsøe et al. [8] have concluded that the NH₃⁺ formed by the dissociation of ammonia adsorbed on Brønsted acid sites is the main species. Although the adsorption site of ammonia for the formation of active species is still under debate, the agreement point between both authors is that one H atom of ammonia

* Corresponding author at: Corporated Research & Development, LG Chem, Ltd./Research Park, 104-1, Moonji-dong, Yuseong-gu, Daejeon 305-380, Korea Tel.: +82 42 866 2892; fax: +82 42 863 7466.

E-mail address: jungsm@lgchem.com (S.M. Jung).

¹ Tel.: +32 10 47 35 80; Fax: +32 10 47 36 49.

✕ Deceased.

should be dissociated by the reducible site located near the ammonia.

The mechanism involving the dissociation of ammonia was already known in SNCR [4]. The NH_2 radical formed by the reaction of OH radical with ammonia at 800°C is known as the main species, which prefers the reaction with NO to N_2 . Besides, in the SNCR mechanism, further dissociation ammonia generates NH and this material prefers the reaction with O_2 to NO. The decrease in NO conversion is usually identified over all SCR catalysts. As far as the SNCR mechanism is concerned, it can be imagined that the excess hydrogen dissociation of ammonia to NH_x species due to the highly reducible site would occur at high temperature and is the main step to accelerate the ammonia oxidation.

In a previous paper [17], we reported that the hybrid catalyst between TiO_2 sulfate and V_2O_5 showed a high activity due to the synergetic effect, which is attributed to the increased amount of nitrate and NH_2 species. In this hybrid system, the effect of oxygen transfer was supposed to be the main synergy in the mechanism.

In addition, the hybrid system consisting of H-ZSM-5 and V_2O_5 also showed the modified SCR activity. Based on the SCR mechanism of H-ZSM-5 [18–21], this promotional effect can be explained by the enhanced formation rate of NH_2 and NO_2 species. As a result, it is postulated that the oxygen from V_2O_5 can transfer to the surface of strongly acidic materials (TiO_2 sulfate and H-ZSM-5) and that this oxygen contributes to the increase in the rate of NH_2 and nitrate formation. The oxygen transfer in the hybrid system may be explained by hypotheses such as (i) transfer of oxygen by NO_2 formation over V_2O_5 , (ii) α -oxygen due to the decomposition of N_2O over H-ZSM-5 catalyst and (iii) spillover of oxygen.

In this communication, we focus on the identification of the oxygen source in the hybrid catalytic system with V_2O_5 and H-ZSM-5. Firstly, in order to verify the synergy, the SCR reaction was performed using hybrid catalysts consisting in V_2O_5 and H-ZSM-5 arranged in the reactor in different ways, namely, disposed in separate beds with either V_2O_5 or H-ZSM-5 in the top layer. Additionally, the various reaction techniques were employed over pure and hybrid materials.

2. Experimental

H-ZSM-5 (PQ Co.) has a surface area of about $400\text{ m}^2/\text{g}$ and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30. used in this experiment is a commercial oxide (Aldrich Co.). The specific surface area of V_2O_5 (Aldrich Co.) is $2.5\text{ m}^2/\text{g}$. Hybrid H-ZSM-5/ V_2O_5 catalysts are prepared through the superposition of H-ZSM-5 and V_2O_5 with an equal weight (0.075 g).

Temperature programmed reaction (TPR) and steady state reaction (SSR) were carried out in a continuous flow fixed bed reactor operating at atmospheric pressure. The catalyst weight was 0.075 g in the case of a pure sample. The total flow rate was 100 ml/min and the feed composition (volume) was:

nitric oxide 0.1%; ammonia 0.105%; 2.5% oxygen in helium. The reactor was vertical and made of quartz. The ramping rate of temperature in TPR was $10^\circ\text{C}/\text{min}$. The inlet and outlet gas compositions were measured using a QMC 311 Balzers quadrupole mass spectrometer coupled to the reactor.

NO oxidation was also carried out in a continuous flow fixed bed reactor operating at atmospheric pressure. The total flow rate was 100 ml/min and the feed composition was: nitric oxide 0.1%; oxygen 2.5%. The inlet and outlet NO_2 compositions were measured using a detector with a chemical sensor (TX2000, Oldham).

An NH_3 -TPD (temperature programmed desorption) spectrum was obtained by monitoring the desorbed species, after ammonia adsorption (0.5 vol.% in helium) on the catalyst at room temperature, under 50 ml/min of diluted nitric oxide flow (0.5 vol.% in helium) while increasing the temperature at a constant rate ($10^\circ\text{C}/\text{min}$). Outlet gas compositions of NO and N_2 were measured using a Balzers QMC 311 quadrupole mass spectrometer coupled to the reactor.

3. Results and discussion

Using the hybrid catalysts prepared by superposition of the two solids, SCR reaction was carried out and the result are compared with those obtained with pure V_2O_5 and H-ZSM-5, as shown in Fig. 1. Pure V_2O_5 shows a considerable activity at temperatures lower than 350°C . But the NO conversion decreased due to the ammonia oxidation after 350°C . It is reported that over pure V_2O_5 , the decrease in NO conversion at high temperature is attributed to the direct oxidation of ammonia to NO since the reduced vanadium surface is fully reoxidized. On pure H-ZSM-5, the SCR activity appeared at 400°C , while ammonia oxidation was negligible.

When H-ZSM-5 was placed in the first layer, the feature of NO consumption in the SCR reaction was almost

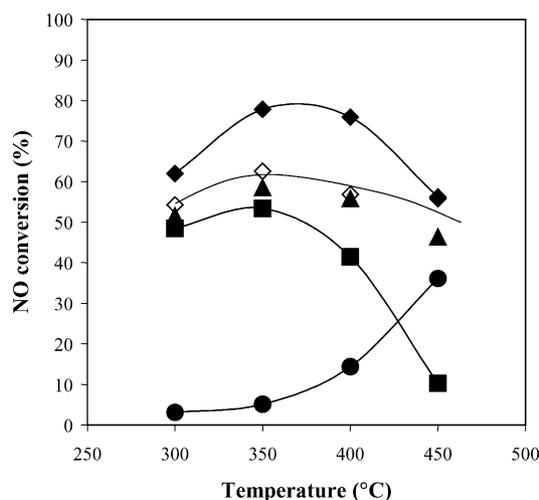


Fig. 1. SCR activity of V_2O_5 (■), H-ZSM-5 (●), H-ZSM-5 (F)- V_2O_5 (◇) (◇), and V_2O_5 (F)-H-ZSM-5 (S) (▲). Theoretical value (▲).

the same as the sum of activities observed on pure V_2O_5 and H-ZSM-5. However, when V_2O_5 was placed in the first layer, the NO conversion at all temperature ranges was higher than the sum of activities of pure V_2O_5 and pure H-ZSM-5.

In the SCR mechanism over H-ZSM-5 [18–21], it is known that the NO to NO_2 oxidation is the rate-determining step. Considering this suggestion, it could be imagined that the role of V_2O_5 can be attributed to the increase in the oxidation rate of NO_2 . It is also conceivable that two different pathways exist by which V_2O_5 can increase the oxidation rate of NO to NO_2 : (1) direct oxidation of NO by V_2O_5 ($V_2O_5 + NO \rightarrow V_2O_4 + NO_2$) and (2) indirect oxidation via oxygen transfer ($V_2O_5 \rightarrow V_2O_4 + O^*$; O^* migrates to H-ZSM-5 so as to oxidise NO).

3.1. The direct formation of NO_2 over V_2O_5

Misono proposed a bifunctional mechanism in SCR by propylene over a physical mixture of Mn_2O_3 and Ce-ZSM-5 [22]. In this system, the role of each component was explained as follows: Mn_2O_3 oxidizes NO to NO_2 and Ce-ZSM-5 is responsible for the reaction between NO_2 and propylene and the decomposition of intermediates to N_2 . Considering this synergetic scheme, the direct formation of NO_2 over V_2O_5 can be postulated over the hybrid system of V_2O_5 and H-ZSM-5 in the SCR reaction. To identify the contribution of V_2O_5 on NO_2 formation, the direct NO oxidation was carried out over pure H-ZSM-5 and pure V_2O_5 in the presence of oxygen. The NO_2 concentrations observed are shown in Fig. 2. H-ZSM-5 catalysts showed a higher NO_2 concentration at room temperature, while no NO_2 formation was detected on V_2O_5 . When temperature increased up to 200 °C, the NO_2 formation over H-ZSM-5 rapidly decreased. But when temperature further increased, NO_2 formation gradually increased. In the case of V_2O_5 , only 8 ppm NO_2 was detected at 450 °C. This result suggests that the direct oxidation of NO to NO_2 over V_2O_5 is not sufficient to explain the synergetic effect observed in a layered hybrid system.

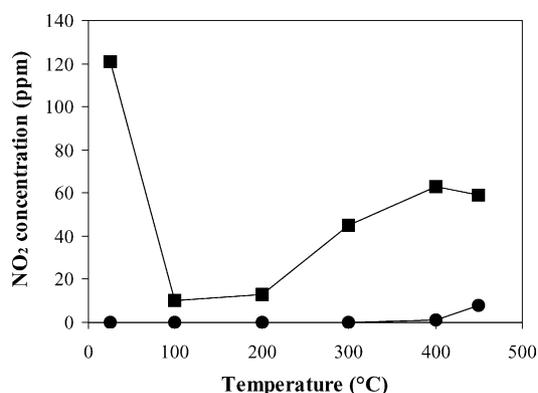


Fig. 2. NO_2 concentration (ppm) formed according to the temperature over H-ZSM-5 (\blacksquare), and V_2O_5 (\bullet), under a flow of NO (1000 ppm) and O_2 (2.5%) in He.

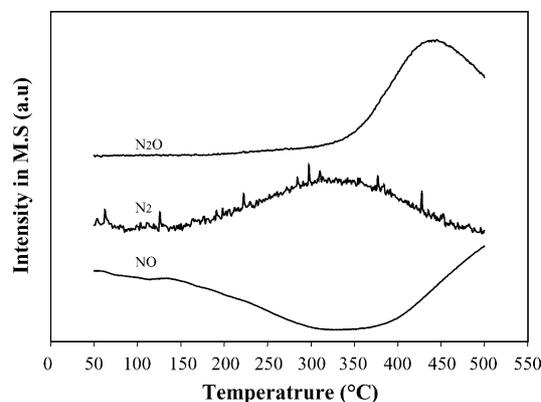


Fig. 3. TPR result obtained over pure V_2O_5 under a flow over NO (1000 ppm), NH_3 (1000 ppm) and O_2 (2.5%) in He.

3.2. The indirect formation of NO_2 via oxygen transfer

TPR experiment were performed in order to elucidate the possibility that V_2O_5 acts more like an O reservoir, increasing the oxidation rate of NO to NO_2 considered as the rate determining step of the SCR reaction over H-ZSM-5.

The distribution of the products over V_2O_5 in the $NO + NH_3 + O_2$ reaction was investigated firstly. The change of composition according to temperature increase is shown in Fig. 3. The behavior of NO is similar to that observed in the steady state SCR reaction, shown in Fig. 1. It was shown that the increase in the NO concentration above 350 °C is accompanied by either the increase in the N_2O concentration or by the decrease in N_2 concentration. The N_2 concentration curve in TPR above 350 °C is almost symmetrical with that below 350 °C, whereas the increasing slope of NO above 350 °C was steeper than the decreasing slope of NO below 300 °C. The different behavior in the NO concentration change below and above 350 °C suggested the contribution of ammonia oxidation reaction. In other words, 1 mole of NO and 1 mole of NH_3 react to be converted to 1 mole of N_2 below 350 °C, whereas above 350 °C, NH_3 gradually reacts with O_2 to form NO preferentially. Thus, the total NO concentration above 350 °C is attributed to the sum of the NO produced due to ammonia oxidation and the unreacted NO.

The N_2O formation began between 300 and 350 °C and is maximized at 450 °C. Above 450 °C, the N_2O concentration decreased, whereas NO formation still increased. In this experiment, NO_2 is not detected. Thus, it was shown that the ammonia oxidation began around 300–350 °C and N_2O is the only by-product, not included in reactant.

To find the contribution of N_2O on the promoted SCR activity over the layered hybrid sample, a TPR experiment was also performed over the layered hybrid catalyst with V_2O_5 and H-ZSM-5 as the first and the second layers, respectively. The results are depicted in Fig. 4. Below 350 °C, the distribution of product is similar to that observed for pure V_2O_5 as shown in Fig. 2. Above 350 °C, the high consumption rate of NO is maintained up to 480 °C. Especially, the consumption rate of NO between 350 and 480 °C led to the increase

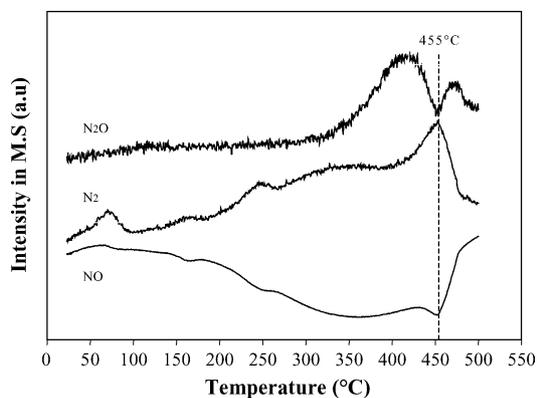
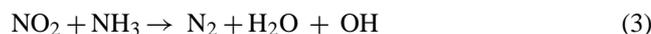


Fig. 4. TPR result obtained over layered hybrid sample composed of V_2O_5 (F)-H-ZSM-5 (S) under a flow of NO (1000 ppm), NH_3 (1000 ppm) and O_2 (2.5%).

in the N_2 concentration as well as the consumption of N_2O . From this result, it is suggested that N_2O may participate in the reaction of NO with ammonia. Kapteijn et al. [23], extensively studied the behaviour of the N_2O over solid catalysts, including the transition metal exchanged zeolites. They reported that the nitrous oxide began to decompose into N_2 and activated oxygen at $350^\circ C$, according to Eq. (1):



In the above equation, the activated oxygen (O^*) is supposed to be a strong oxidant. Thus, the contribution of N_2O on SCR reaction over H-ZSM-5 can be depicted as follows:



To verify the reaction of N_2O over H-ZSM-5, the N_2O decomposition was performed. Fig. 5 shows the dependency of N_2O concentration on temperature as well as the product distributions due to the decomposition of N_2O . Up to $300^\circ C$, there was no change in the N_2O concentration. The evolution of the water adsorbed on the surface was only detected below $300^\circ C$. The first consumption of N_2O occurred between 350 and $470^\circ C$, with the appearance of N_2 and H_2O , although the N_2O concentration gradually recovered from $450^\circ C$ to reach 500 ppm. The second consumption of N_2O appeared at $470^\circ C$ and continued up to $600^\circ C$. In the second consumption of N_2O , O_2 instead of H_2O was detected with N_2 . This result clearly indicates that pure H-ZSM-5 itself can show an activity for the N_2O decomposition.

In order to explain the pathways of N_2O decomposition based on the conventional mechanism, the in-depth zeolite structure should be considered. It is known that the dehydration of the H form zeolite at high temperature creates a coordinatively unsaturated site and excess negative charge in the structure, as shown in Scheme 1 [24]. As mentioned above, the active site for the N_2O decomposition should be followed by dehydration. Actually, as shown in Fig. 5, H_2O appeared in the first consumption of N_2O . Thus, in the first

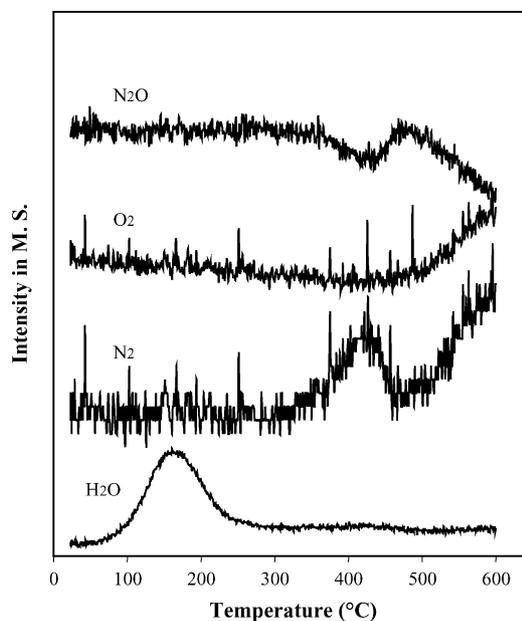
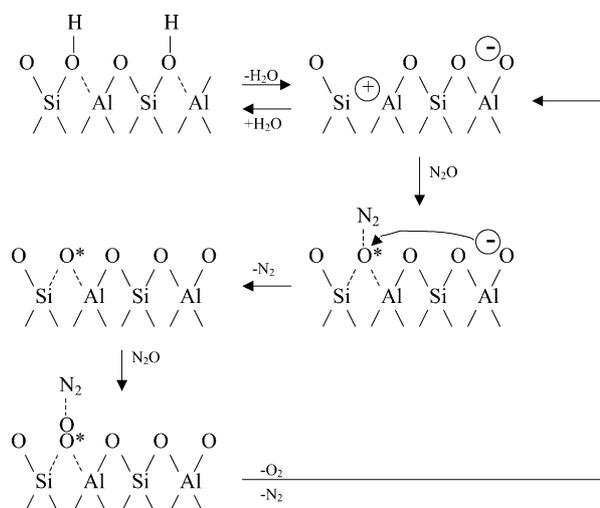


Fig. 5. N_2O decomposition over H-ZSM-5.

step, the behavior of N_2O can also be interpreted as shown in Scheme 1: N_2O adsorbed on coordinatively unsaturated Al and Si, after dehydration, and then scission of N_2O takes place by the neighbor negative charge. The dehydrated site of the surface is replenished by the surface oxygen (O^*), which is produced by the decomposition of N_2O . Up to $470^\circ C$, since the surface oxygen combined with the structure may be stable, the conversion of N_2O was decreased. This result suggests the following: the N_2O conversion below $470^\circ C$ may not be detected in steady state reaction, since the replacement of surface oxygen into the dehydrated site re-stabilizes the surface structure and makes the surface inactive for N_2O decomposition. Above $470^\circ C$, however, the surface oxygen captured in the structure is emitted as O_2 , as shown in Fig. 5.



Scheme 1. Pathways of N_2O decomposition over pure H-ZSM-5.

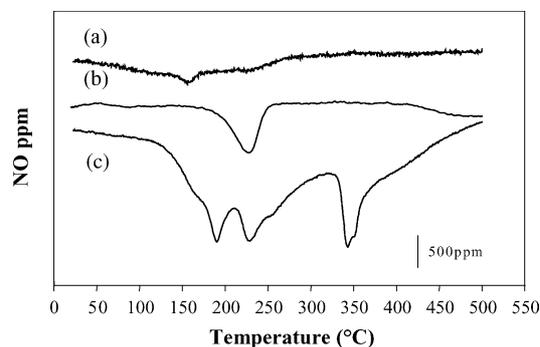
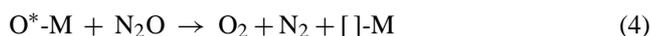


Fig. 6. NH_3 -TPD under NO flow (5000 ppm/He) observed over: V_2O_5 (a), H-ZSM-5 (b), and layered hybrid sample composed of V_2O_5 (F) H-ZSM-5 (S) (c).

This reaction path can be described as follows:



In order to investigate another hypothesis concerning the spillover oxygen from the V_2O_5 layer, NH_3 -TPD by NO in the absence of O_2 was performed in pure V_2O_5 , pure H-ZSM-5 and a layered hybrid sample with V_2O_5 as the first layer, after the preadsorption of ammonia at room temperature. Fig. 6 shows the variation of NO concentrations during a temperature increase by $10^\circ\text{C}/\text{min}$. The variation of N_2 formation completely corresponded to that of the NO consumption, as was shown in [17]. In the case of V_2O_5 , the NO consumption was only detected up to 300°C . Above 300°C , no change is observed. This result shows that the amount of ammonia adsorbed on V_2O_5 is negligible above 300°C . for H-ZSM-5, although a small consumption of NO was detected at 250°C , it can be considered negligible. Considering that H-ZSM-5 showed the highest amount of the adsorbed ammonia at high temperature, it is confirmed that the reaction of NO with ammonia over H-ZSM-5 is activated by the presence of an oxygen intermediate. Over the hybrid samples, the NO consumption showed quite a different behavior from the expectations based on the results of two pure samples. Especially, around 350°C , a high consumption of NO was observed with a high formation of N_2 . Based on SCR mechanism over H-ZSM-5, the concentration of an oxygen intermediate is surely increased due to the superposition of V_2O_5 over H-ZSM-5. This result suggests that the hypothesis of spillover oxygen cannot be totally excluded to explain increased SCR activity on the hybrid catalyst composed of V_2O_5 and H-ZSM-5.

4. Conclusion

Hybrid V_2O_5 and H-ZSM-5 catalysts used in the selective catalytic reduction reaction of NO with NH_3 have been stud-

ied. Vanadium oxide disposed in the first layer upon the zeolite in a reactor shows an improved activity, as compared with the sum of the individual activities of the pure phases. TPR and NH_3 -TPD show that the improved reactivity is closely related to the enhanced formation of oxidation intermediates by V_2O_5 : (i) N_2O , which is the source of α -oxygen, and (ii) spillover oxygen. As a result, it can be suggested that the oxidation rate of NO into NO_2 increased by the transferred oxygen from V_2O_5 , contributing to the increase in the SCR reaction rate over the hybrid catalysts.

Acknowledgements

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