

A commercial V₂O₅-WO₃/TiO₂ catalyst for the reduction of NO by NH₃: Effect of its on-site-use and surface composition modifications on N₂O formation

Moon Hyeon Kim^{1*}, Hyo Sang Lee¹

¹Department of Environmental Engineering, Daegu University, Gyeongsan, Gyeongbuk/Jillyang, Daegudae-ro 201 Korea

*corresponding author: moonkim@daegu.ac.kr

Introduction

Nitrous oxide (N₂O) with a global warming potential of 310 can be produced in the selective catalytic reduction of NO by NH₃ (NH₃-SCR) with V₂O₅/TiO₂-based catalysts [1,2]. The extent of N₂O formation depends strongly on the V₂O₅ loadings, the kind of promoters such as WO₃ and MoO₃, and the feed and operating variables including reaction temperature, NO₂/NO_x ratio, oxygen concentration, etc [1-3]. This study has been focused on N₂O formation levels according to changes in surface compositions in a commercial V₂O₅-WO₃/TiO₂ catalyst after on-site-use for prolong hours at a heavy oils-burning power station.

Materials and Methods

Two types of commercial catalyst were provided: one is a fresh sample of 1.43% V₂O₅-7.56% WO₃/TiO₂, and another is a catalyst sample used for 20,000 h at the power plant. The former was designated to “Com-F” to distinguish it from the latter, hereafter “Com-U”. A sample of “1% V₂O₅/Com-F” was prepared by adding 1% V₂O₅ onto the Com-F so as to have a total V₂O₅ amount very similar to that in the Com-U. The Com-U was ultrasonically treated in a mild acid solution to wash out fly ash deposited on its surface and this sample was designated to “Com-U(AW)”. The physicochemical properties of all these catalysts are listed in Table 1.

An on-line infrared system was employed to directly measure N₂O formation in NH₃-SCR reaction over the catalysts [1]. Typically 0.5 g catalyst was placed above a frit in an I-shaped Pyrex reactor and calcined for 1 h at 500°C. A flowing mixture consisting of 500 ppm NO, 500 ppm NH₃ and 5% O₂ in N₂ at a GHSV value of 76,200 h⁻¹, was passed over the catalyst bed.

Results and Discussion

Com-F after on-site-use for the indicated hours showed decrease in surface area, and a shift of pore size distribution toward larger size, as provided in Table 1. Particularly, vanadium amounts in the Com-U became greater, by 1%, than that measured for the Com-F.

Table 1. Physicochemical properties of commercial V₂O₅/TiO₂-based catalysts.

Catalyst	Amount (wt%)		S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Mean pore size (nm)
	V ₂ O ₅	WO ₃			
Com-F	1.43	7.56	70	83	14.5
Com-U	2.45	7.08	32	70	21.1
V ₂ O ₅ /Com-F	2.42	-	68	75	-
Com-U(AW)	1.29	7.03	-	56	-

The observed changes in the physicochemical properties before and after on-site-use could lead to noticeable difference not only in the extent of N₂O production in the NH₃-SCR reaction at chosen conditions, but also in the dependence of deNO_xing performances on reaction temperature, as shown in Fig. 1. The Com-U gave the formation of N₂O with much larger concentration levels, and this catalyst also exhibited significant drop in NO conversions at > 350°C although the reverse phenomenon at < 350°C occurred.

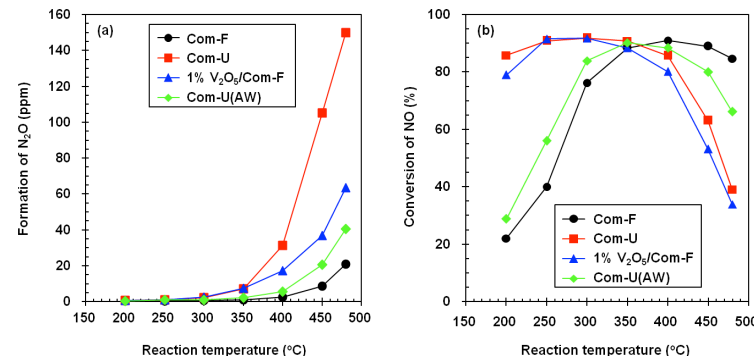


Figure 1. (a) N₂O formation and (b) deNO_xing activity in the reduction of NO by NH₃ with a commercial V₂O₅-WO₃/TiO₂ catalyst after on-site-use and post-modifications.

Samples of 1% V₂O₅/Com-F and Com-U(AW), which had possessed V₂O₅ contents similar to that in the respective Com-U and Com-F catalysts, approached N₂O production and NO conversion of each corresponding sample. It is clear that V₂O₅ nanoparticles deposited on the Com-U facilitated such a N₂O formation, consistent with an earlier report [1,4]. Independent XRD, XRF and ICP measurements indicated the presence of MoO₃ with significant amounts in the Com-U but not in the Com-F. Thus, this metal oxide species might be contributed to the formation of N₂O in the SCR reaction.

Significance

This study clearly represents that the extent of N₂O formation in NH₃-SCR reaction significantly increased after use of a commercial V₂O₅-WO₃/TiO₂ catalyst for prolong hours at a heavy oils-fired power plant, and that alien metal impurities, mainly polycrystalline vanadium and molybdenum oxides, deposited onto the catalyst during on-site operation play a key role in yielding such a huge quantity of N₂O production.

References

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