

PA4) A new NO oxidation catalyst

Qiang Wang*¹ and Jong-Shik Chung^{1,2}

¹School of Environmental Science and Engineering, POSTECH

²Department of Chemical Engineering, POSTECH

1. Introduction

Due to the increasingly stringent NO_x emission regulations imposed by the EPA [1], several research efforts are ongoing to understand the potential NO_x abatement techniques that are available for lean-burn diesel engines, which include: NO_x storage and reduction (NSR) [2-4], selective catalytic reduction (SCR) [5-6] and continuously regenerating trap (CRT) [7].

In these technologies, the oxidation of NO to NO₂ is an important step for the after treatment reactions. At present, it is mainly achieved by using Pt-based catalyst. However, many problems remain to be solved before its commercial application.

There has been little attempt to search substitute for Pt based catalyst. In present work, we report a new catalyst of Co-ion exchanged K₂Ti₂O₅ as alternatives of Pt based catalysts. The activity comparing with Pt-based catalysts for the NO oxidation was investigated by varying concentration of oxygen and GHSV. The deactivations of the catalyst with SO₂ and NO₂ were also evaluated.

2. Experimental

Reaction tests were performed in flow-reactor equipment, consisting of a packed-bed made of quartz tube (10mm internal diameter). 0.6g catalyst was charged in each run, with various space velocities from 20,000 h⁻¹ to 240,000 h⁻¹. The gas existing the reactor was continuously analyzed by means of a NO_x analyzer (Chemiluminescence NO-NO₂-NO_x analyzer, Model 42C, high level, Thermo environmental instruments INC.). Catalyst deactivation test is another important part in this work, which include the influence of SO₂ and NO₂.

3. Results and discussion

3.1. Influence of GHSV and O₂

Figure 1 shows the oxidation of 700ppm NO at various GHSV as a function of temperature with 10% O₂ in the feed. From the figure we can find that the optimum temperature shifted to higher region (from 282 °C to 320 °C) and the maximum NO con-

version decreases from 84.5 to 72% with increasing GHSV from $20,000\text{h}^{-1}$ to $240,000\text{h}^{-1}$, which is due to the thermodynamic equilibrium ($\text{NO}_2 \rightleftharpoons \text{NO} + \frac{1}{2} \text{O}_2$). When the GHSV is high as $120,000\text{h}^{-1}$, the NO conversion is still over 80%, which means the reaction rate is very high.

The effect of O_2 concentration is shown in Figure 2. The maximum conversions observed at various temperatures are dependent on the O_2 concentration. The peak temperature at which the maximum conversion is shown decreases with an increase in the concentration of O_2 . Above the peak temperature, the conversions decrease with the temperature increase due to the thermodynamic equilibrium. The same phenomenon was also observed for Pt-based catalysts by Joël Després [8].

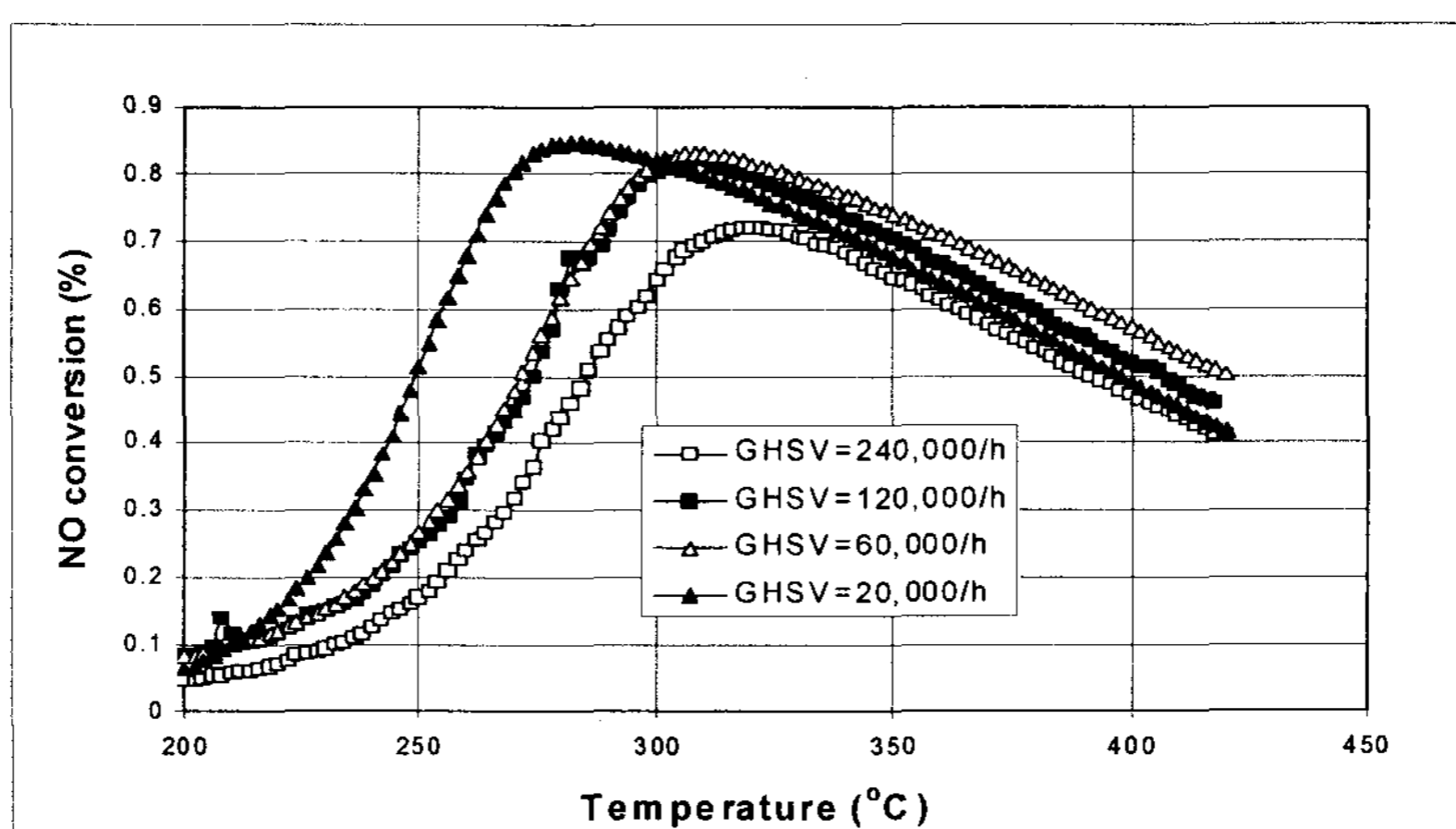


Fig.1. Influence of GHSV on the conversion of NO as a function of temperature. Feed: 700ppm NO, 10% O_2 , T: 200 °C ~ 420 °C, increasing rate: 2 °C/min, GHSV: $20,000\text{h}^{-1}$ ~ $240,000\text{h}^{-1}$, He balances.

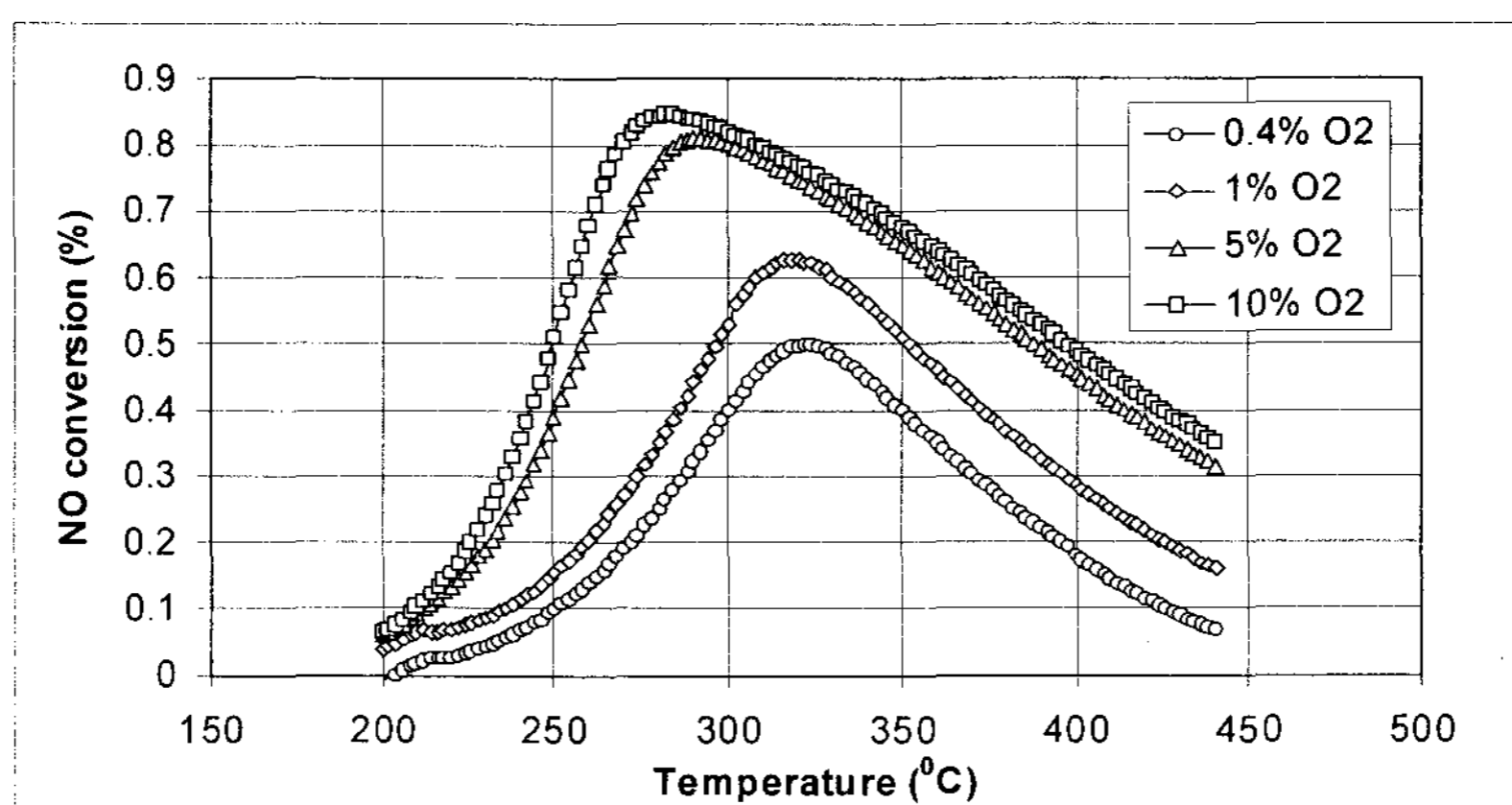


Fig. 2. Influence of the O_2 concentration on NO conversion as a function of temperature. Feed: 700ppm NO, 0.4~10% O_2 , Temperature 200 °C ~ 440 °C, increasing rate: 2 °C/min; GHSV: $20,000\text{h}^{-1}$, He balances.

3.2. Deactivation by SO₂ and NO₂

SO₂ poisoning is one of the key problems for Pt-based catalysts. In order to check accelerated deactivation, more than one order of magnitude higher than the typical value present in gasoline engine emission were used. The results of the test are shown in Figure 3. When the SO₂ concentration is kept within 10ppm, there is only a slight decrease in the NO conversion, which indicates that Co-ion exchanged K₂Ti₂O₅ is resistant to the SO₂ poisoning.

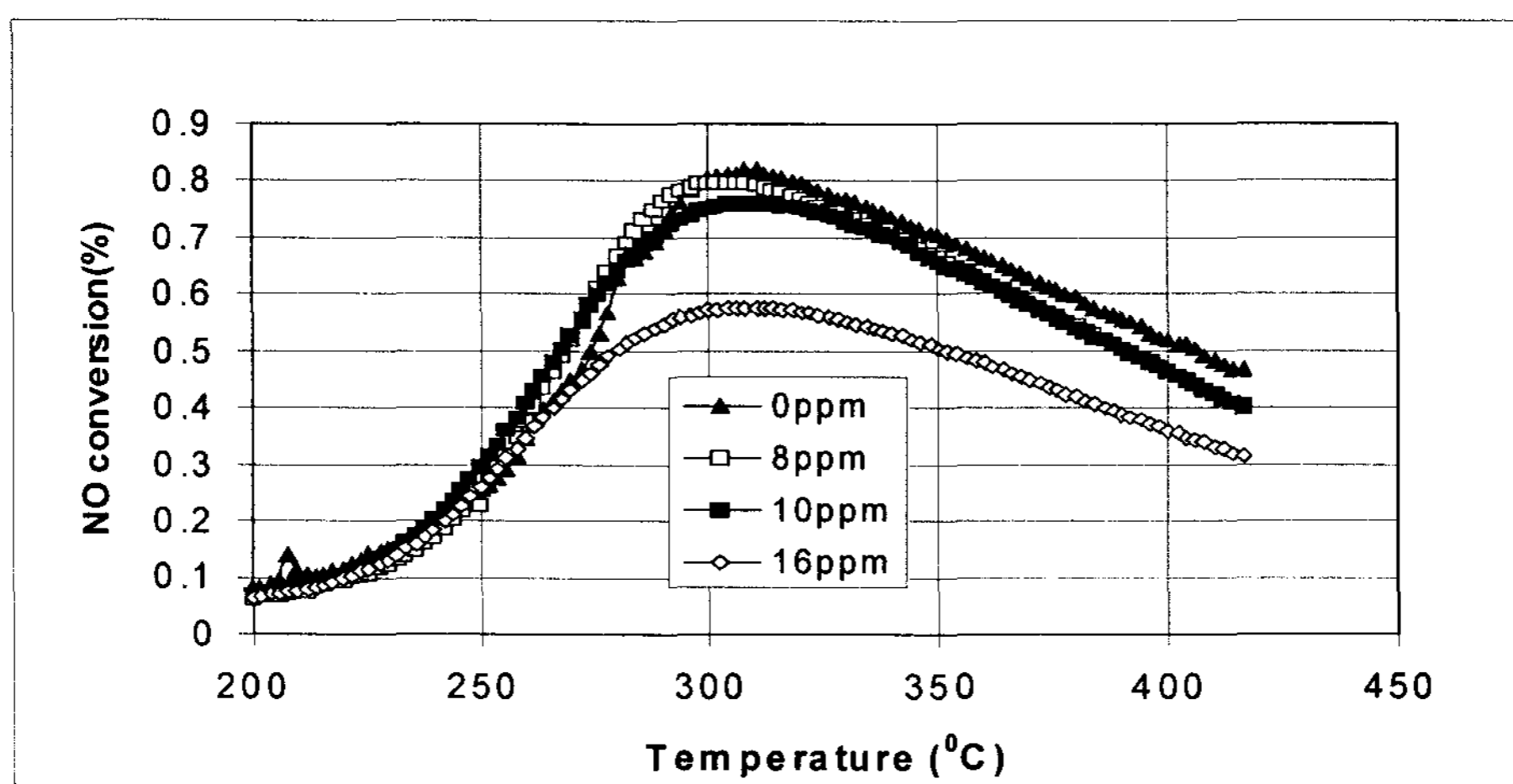


Fig. 3. Influence of SO₂ on NO conversion as a function of temperature.
Feed: 700ppm NO, 10% O₂, Temperature 200 °C ~ 420 °C, increasing rate: 2 °C/min;
GHSV: 120,000h⁻¹, He balances.

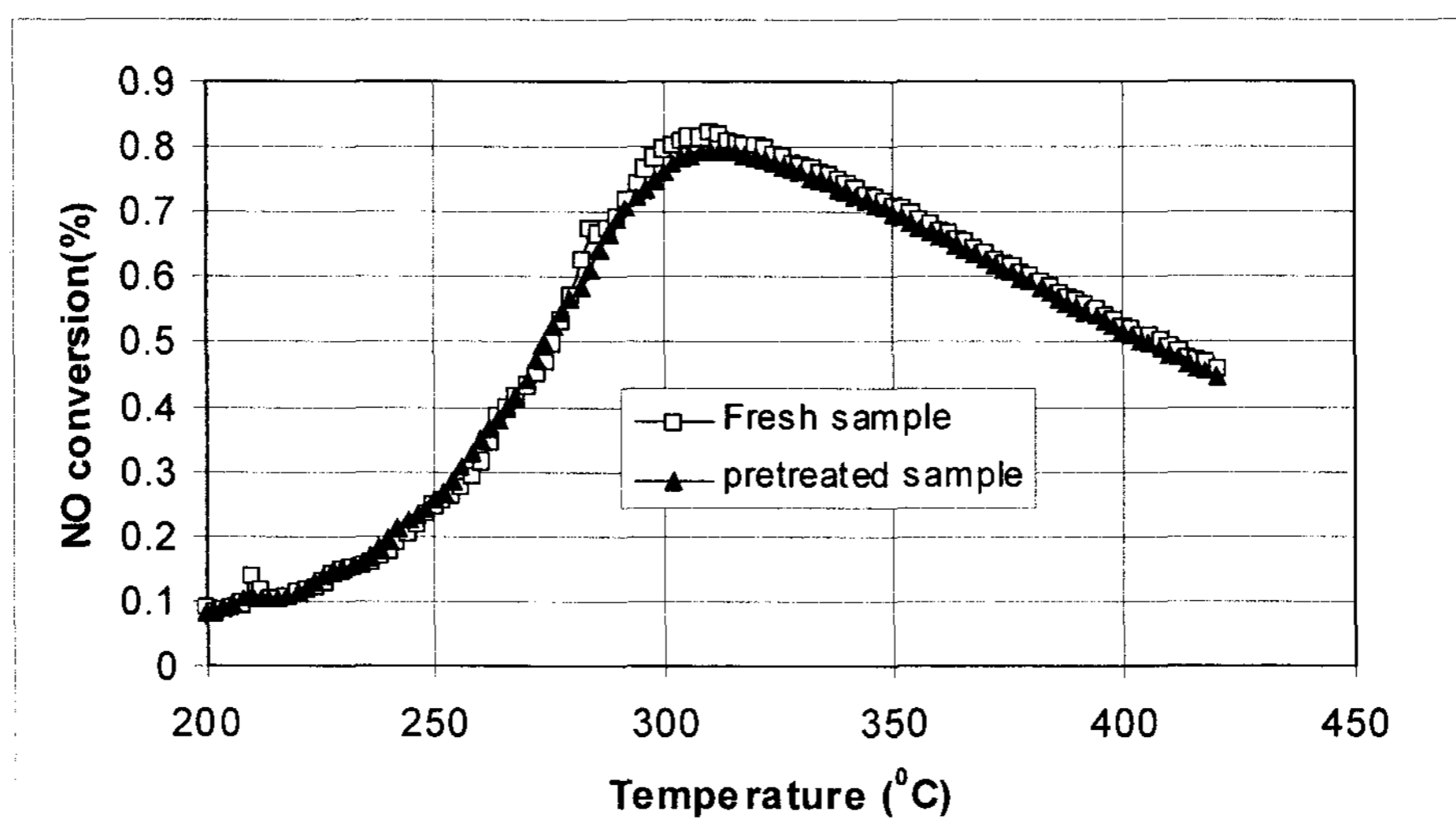


Fig. 4. Oxidation of NO over fresh and pretreated catalysts.
Feed: 700ppm NO, 10% O₂, Temperature 200 °C ~ 420 °C, increasing rate: 2 °C/min,
GHSV: 120,000h⁻¹, He balances.

Figure 4 shows the oxidation of 700ppm NO over fresh and pretreated catalyst in 550ppm NO₂ and 10% O₂ at 250 °C for 2h as a function of temperature. The pretreated catalyst shows the same activity as the fresh one, which means NO₂ has neglectable effect on Co-ion exchanged K₂Ti₂O₅.

4. Conclusion

The influence of GHSV and O₂ concentration were studied. It is found that the reaction rate of NO oxidation on Co-ion exchanged K₂Ti₂O₅ catalyst is very high. The peak temperature is as low as that of Pt-based catalyst.

Deactivation tests have shown that Co-ion exchanged K₂Ti₂O₅ catalyst is more resistant to SO₂ and NO₂. Comparing to Pt-based catalyst, the high NO oxidation activity and high resistance to NO₂ and SO₂ of the new Co-ion exchanged K₂Ti₂O₅ catalyst make it a promising candidate catalyst for commercial application.

Reference

1. F. Basile, G. Fornasari, A. Grimandi, M. Livi, A. Vaccari, 2006. Applied Catalysis B: Environmental 69, 5965.
2. H. Shinjoh, N. Takahashi, K. Yokota, M. Sugiura 1999. Applied Catalysis B: Environmental 15, 189-201.
3. N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, 1996. Catal. Today 27, 63.
4. S. Matsumoto, 1996. Catal. Today 29, 43.
5. R. Burch, J.A. Sullivan, T.C. Watling, 1998. Catalysis Today 42, 13-23.
6. Hideaki Hamada, Yoshiaki Kintaichi, Megumu Inaba, Mitsunori Tabata, Tomohiro Yoshinari, Hiroshi Tsuchida, 1996. Catalysis Today 29, 53-57.
7. Cooper B. J., Jung H. J., Thoss J. E., 1990. US Patent 4,902,487.
8. Joël Després, Martin Elsener, Manfred Koebel, Oliver Kröcher, Bernhard Schnyder, Alexander Wokaun, 2004. Applied Catalysis B: Environmental 50, 7382.