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Co/$K_xTi_2O_5$ catalysts prepared by ion exchange method for NO oxidation to NO_2

Qiang Wang [a], So Ye Park [b], Jin Seong Choi [b], Jong Shik Chung [a,b,*]

[a] *School of Environmental Science and Engineering, POSTECH, Pohang 790-784, Republic of Korea*
[b] *Department of Chemical Engineering, POSTECH, Pohang 790-784, Republic of Korea*

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Abstract

Co/$K_xTi_2O_5$ catalysts prepared by ion exchange method were tested for NO oxidation to NO_2. Their catalytic activities are similar to Pt-based catalysts and much higher than Co impregnated on TiO_2 with or without doped K. The conversion pattern shows a typical kinetic control at low temperatures and thermodynamic control at higher temperatures, exhibiting a peak temperature at which the conversion becomes a maximum. Conversion decreases sharply as oxygen concentration decreases below 1.0%. NO concentration shows a positive effect on the conversion. The presence of Co_3O_4 and K ion remaining in $K_xTi_2O_5$ after the ion exchange is responsible for the observed catalytic activity. Thus, Co/$K_xTi_2O_5$ having a complete ion exchange with little K is not active for the reaction. Unlike Pt-based catalyst, the presence of NO_2 does not inhibit catalytic activity. Co/$K_xTi_2O_5$ was resistant to the presence of SO_2 less than 10 ppm. High-NO oxidation activity and high resistance to SO_2 and NO_2 make Co/$K_xTi_2O_5$ a promising catalyst for NO oxidation.

Keywords: NO oxidation; Co/$K_xTi_2O_5$; Co/TiO_2; SO_2 poisoning

1. Introduction

Lean burn engines, of which diesel engine is a common example, are generally more fuel-efficient than stoichiometric engines, thereby giving a longer traveling distance per unit of fuel and, consequently, reduced CO_2 emission [1]. However, emission standards of diesel engines are becoming more and more severe. In 2005, for example, soot and NO_x productions were limited to 25 mg km^{-1} and 250 mg km^{-1}, respectively, according to Euro IV regulations, twice as low as Euro III standards [2]. In order to meet NO_x emission levels, three approaches can be used: NO_x storage and reduction (NSR), selective catalytic reduction (SCR) and continuously regenerating trap (CRT) [3–8].

For adopting these technologies, it becomes evident now that NO_2 plays a decisive role [9,10]. For the NO_x storage and reduction (NSR), NO is first oxidized to NO_2 on platinum and then stored on BaO as nitrate [11]. For selective catalytic reduction (SCR) technology, it has been proved that SCR reaction rate can be substantially increased, when a fraction of NO in the exhaust is converted to NO_2. This effect is more pronounced at lower temperatures (200–300 °C) when the reaction mixture contains equimolar amounts of NO and NO_2 (fast SCR process) [12–14]. For continuously regenerating trap (CRT), NO_2 is used as a strong oxidizer to oxidize soot collected on a particulate filter at comparably low temperatures. These temperatures are much lower than the ignition temperature of soot in air, which is typically around 550 °C.

However, nitrogen oxides ($NO + NO_2$) produced by combustion engines consist mainly of NO. Thus, the oxidation of NO to NO_2 is an important step for the after treatment reactions. At present, it is mainly achieved by using Pt-based catalyst or plasma. Pt-based catalysts have been comprehensively studied by many authors in the area of oxidation efficiency with NO and O_2; influence of Pt particle size; effects of precursors and support, SO_2, water and CO [14,15,17–23]. Kinetic modeling and simulations have also been carried out. For commercial application of Pt-based catalysts, however, many problems remain to be solved [2,16,24,25]. Pt has shown a decrease of activity when it was exposed to $NO + O_2$ at 250 °C [2,19,26]. This deactivation was attributed, according to

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[*] Corresponding author at: San 31, Hyoja-Dong, Nam-Ku, Pohang 790-784, Republic of Korea. Tel.: +82 54 279 2267; fax: +82 54 279 5528.
E-mail address: jsc@postech.ac.kr (J.S. Chung).

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XPS data, to the oxidation of Pt to PtO or PtO_2, which are less active than reduced platinum. Pt-based catalyst also oxidizes SO_2 to SO_3, which then forms sulfate with support alumina (such as $Al_2(SO_4)_3$), leading to a decrease in the catalytic activity [2,17,21,33]. Mulla et al. [22] have reported that the presence of water vapor in the feed results in an irreversible decrease in the active Pt surface area and a corresponding loss of NO conversion, for both Pt-K/Al_2O_3 and Pt/Al_2O_3 catalysts. The blocking of the Pt sites caused possibly by the migration of impurities from the support is believed to be the reason of the water poisoning. Zhu et al. [27] have also concluded that silica is not a good support when water is present although silica has been found to be better than alumina in the absence of water.

There has been little attempt to search substitute for Pt-based catalyst. Kantcheva et al. [28,29] have reported that Co^{3+} ions are able to oxidize NO to NO^{2-} and NO^{3-} species at room temperature, which could be a promising substitute for Pt-based catalyst. Mulla et al. [22] observed a lower apparent activation energy for Pt/K/Al_2O_3 catalyst (60 kJ mol^{-1}) compared to Pt/Al_2O_3 catalyst (82 kJ mol^{-1}). The turnover rate was also higher on Pt/K/Al_2O_3 catalyst. This promotional effect of K on Pt was by a factor of about 2 at 300 °C. They attributed it to the enhancement of O_2 absorption on Pt/K/Al_2O_3 surface.

It is widely accepted that TiO_2 is more resistant to SO_x. Therefore, a catalyst composing of Co, K and TiO_2 might have a potential for NO oxidation to NO_2 and low SO_x poisoning. Recently it has been found that $K_2Ti_2O_5$ exhibits the highest catalytic activity and photoluminescence compared with other layered titanates [30]. The present study reports a new catalyst of Co/$K_xTi_2O_5$ as alternative of Pt-based catalysts. Study includes preparation and characterization of the catalysts and activity comparison with Pt-based catalysts for the NO oxidation. The reaction was investigated by varying concentration of oxygen, nitrogen oxide and GHSV. The active species and the promotion effect of support for NO oxidation were also studied. Deactivation of the catalysts in the presence SO_2 and NO_2 was also evaluated.

2. Experimental

2.1. Catalyst synthesis

The flow chart of the synthesis of Co/$K_xTi_2O_5$ catalysts is outlined in Fig. 1. $K_2Ti_2O_5$ was first prepared by solid-state reaction. Potassium carbonate (Yakuri Pure Chemical Co., Ltd.) and titanium dioxide (Hombikat UV 100) were mixed together with a proper amount of water (molar ratio of K_2CO_3:TiO_2:H_2O = 1:2:15), and subjected to ball milling for 24 h. After being dried and crushed to fine powder, it was calcined at 850 °C for 10 h in air to obtain $K_2Ti_2O_5$. Co/$K_xTi_2O_5$ was prepared by introducing 2 g $K_2Ti_2O_5$ powder into 200 ml aqueous solution of $Co(NO_3)_2$ (Junsei Chemical Co., Ltd.). After the solution was kept stirring for a certain time, it was filtered and dried and this was followed by calcination at 500 °C for 5 h in air. By controlling the exchange time and the concentration of the Co precursor solution, we could get catalysts having different amount of K and Co loading.

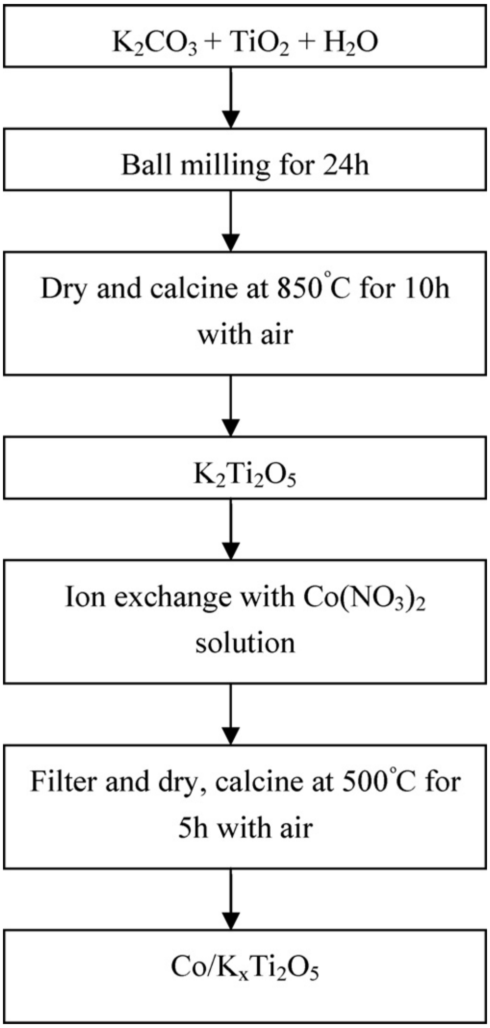

Fig. 1. Procedure of preparing Co/$K_xTi_2O_5$.

For comparison purpose, 20 wt.%Co/TiO_2 and 5 wt.%Co/TiO_2 catalysts were prepared by impregnation method. $Co(NO_3)_2$ (Junsei Chemical Co., Ltd.) solution was added to TiO_2 powder (Hombikat UV 100) drop by drop to the incipient wetness. 5 wt.%Co-1 wt.%K/TiO_2 catalysts were also synthesized with different kinds of K precursors, including potassium carbonate (Yakuri Pure Chemical Co., Ltd.), potassium nitrate (Shinyo pure chemicals CO., Ltd.) and potassium acetate (Sigma–Aldrich, 99 + % A.C.S reagents) by the same impregnation method. They were then dried at 105 °C over night and calcined at 500 °C for 5 h in air. All catalysts in present work were calcined using a box furnace in a static air environment.

2.2. Catalyst characterization

The compositions of the Co/$K_xTi_2O_5$ catalysts were examined by atomic absorption analysis (Model Spectra AA 800). BET surface area were obtained by measuring the amount of adsorbed N_2 at liquid N_2 temperature by means of Micromeritics ASAP 2010 sorption analyzer. The samples