A Combinatorial Chemistry Method for Fast Screening of Perovskite-Based NO Oxidation Catalyst

Dal Young Yoon,[†] Eunho Lim,[†] Young Jin Kim,[†] Byong K. Cho,[†] In-Sik Nam,*,[†] Jin Woo Choung,[‡] and Seungbeom Yoo[‡]

[†]School of Environmental Science and Engineering/Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San 31 Hyoja-dong, Nam-gu, Pohang 790-784, Republic of Korea

[‡]Exhaust Emission Engineering Team, Research & Development Division, Power Train R&D Center, Hyundai Motor Company, 772-1 Jangduk-dong, Hwaseong 445-706, Republic of Korea

S *Supporting Information*

ABSTRACT: A fast parallel screening method based on combinatorial chemistry (combichem) has been developed and applied in the screening tests of perovskite-based oxide (PBO) catalysts for NO oxidation to hit a promising PBO formulation for the oxidation of NO to NO_2. This new method involves three consecutive steps: oxidation of NO to NO_2 over a PBO catalyst, adsorption of NOx onto the PBO and K_2O/Al_2O_3, and colorimetric assay of the NOx adsorbed thereon. The combichem experimental data have been used for determining the oxidation activity of NO over PBO catalysts as well as three critical parameters, such as the adsorption efficiency of K_2O/Al_2O_3 for NO_2 (α) and NO (β), and the time-average fraction of NO included in the NOx feed stream (ξ). The results demonstrated that the amounts of NO_2 produced over PBO catalysts by the combichem method under transient conditions correlate well with those from a conventional packed-bed reactor under steady-state conditions. Among the PBO formulations examined, $La_{0.5}Ag_{0.5}MnO_3$ has been identified as the best chemical formulation for oxidation of NO to NO_2 by the present combichem method and also confirmed by the conventional packed-bed reactor tests. The superior efficiency of the combichem method for high-throughput catalyst screening test validated in this study is particularly suitable for saving the time and resources required in developing a new formulation of PBO catalyst whose chemical composition may have an enormous number of possible variations.

KEYWORDS: *perovskite-based oxide, NO oxidation, combichem method, colorimetric assay, dual-bed reactor*
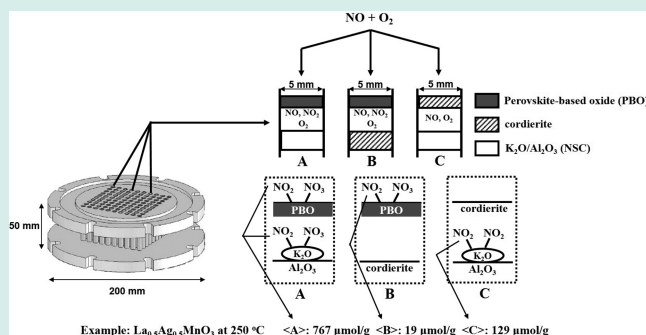
■ INTRODUCTION

The selective catalytic reduction of NOx by urea (urea/SCR) and lean NOx trap (LNT) technologies are regarded as the two most efficient methods for removing NOx from diesel engine exhaust.[1−4] One way to further improve the performance of NOx removal by both technologies, particularly in the temperature range of diesel exhaust (150−250 °C for light duty and 200−350 °C for heavy duty diesel engines), is to preoxidize NO in the upstream exhaust to NO_2, partially or totally depending upon the NOx removal technology to be employed in the downstream.[5−8] Indeed, the low-temperature activity (<250 °C) of a urea/SCR system is significantly improved when NO_2 produced in the diesel oxidation catalyst (DOC) is included in the feed with an equimolar amount of NO, mainly due to the fast-SCR reaction.[5,6] The oxidation of NO to NO_2 is also an essential step for storing NOx on the LNT catalysts under lean conditions, especially for improving its low-temperature activity below 250 °C.[7,8] For oxidizing NO to NO_2 over DOC and LNT catalysts, a noble metal, especially

platinum, is commonly employed due to its superior catalytic oxidation activity.[7−9]

In view of the ever-increasing price of noble metals included in DOC and LNT catalysts and their weak thermal stability by sintering when exposed to the high exhaust gas temperatures, particularly during the regeneration of DPF also installed in the diesel after-treatment system containing DOC and LNT catalysts, perovskite catalysts have recently attracted growing interest as an alternative catalyst for oxidizing NO to NO_2 because of their low cost and high catalytic activity combined with their strong thermal stability.[10,11] The perovskite has a crystal structure in the form of ABO_3, in which a rare-earth or alkaline earth metal such as La, Sr, Ca, etc. occupies the A-site of perovskite and a transition metal such as Mn, Co, Fe, etc. occupies the B-site.[11,12] It may be possible to synthesize several hundred formulations of perovskites by the combination of

those metals in the A- and B-sites of the perovskite. Indeed, an additional huge number of variations of the catalyst formulations may be possible via partial substitutions of both sites. A variety of the perovskite catalysts revealing their own unique oxidation performance have been reported by the alteration of the metals occupying the A- and B-sites as well as the partial substitution of both sites by cations.[13−16]

When Mn or Co was employed as the B-site cation, the propane oxidation performance was higher than that over Cr-, Fe-, or Ni-based perovskite catalysts, regardless of the rare earth metal employed for their A-site.[14] A high performance of the perovskite catalyst for oxidizing NO to NO_2 over $La_{1−x}Ce_xCoO_3$ has been reported by Wen et al.,[15] with $La_{0.8}Ce_{0.2}CoO_3$ exhibiting the highest NO oxidation activity. Kim et al. reported that the platinum-based DOC catalyst can be replaced by a perovskite-type catalyst, such as $La_{0.9}Sr_{0.1}CoO_3$, with outstanding NO oxidation activity.[11] In addition, the catalytic activity of $La_{0.7}Ag_{0.3}MnO_3$ for the simultaneous removal of NOx and diesel soot was higher than that of $LaMnO_3$ below 450 °C.[16]

Developing a new and highly active perovskite-based catalytic system may be very time-consuming and costly because of the enormous number of variations in the chemical formulations arising from the simultaneous alteration or substitution (or both) of both A- and B-sites in the perovskite structure. A variety of high-throughput screening techniques have been proposed as an efficient method for developing a new and active catalytic system, employing various measurement techniques such as optical, mass spectrometric, gas chromatography, and colorimetric assay methods.[17−23] For example, IR thermography was used for the quick screening of catalysts for the oxidation of isooctane and toluene,[17] and the laser-induced fluorescence imaging method (LIFI) was employed for real-time parallel measurements of the oxidation of naphthalene to naphthoquinone on the V_2O_5 surface.[18] On the basis of in situ ionization of reaction products by UV lasers,[19,20] the resonance-enhanced multiphoton ionization (REMPI) method was developed to obtain specific information on gas-phase products.

It has been recognized that the typical combichem system designed to provide a short contact time between the reactant and catalyst under high-throughput experimental conditions may not adequately address the practical issue on the steady-state performance of the catalysts that may be quite different from their transient performance measured by the typical combichem system because of the possible change of reactivity with respect to time on-stream, especially during the initial short period of reaction time.[9,19,21,22] Thus, an attempt to identify a correlation between the catalytic activities obtained from the transient combichem method and those from the conventional fixed-bed reactor system under the steady-state conditions has been rarely made.

One approach to evaluating the effect of time on-stream on the catalyst performance is the use of an array of microreactors with which the time on-stream can be readily varied as desired.[9,22] For example, a 16-channel-multitubular reactor and gas chromatography were used in combination to screen the activity of a catalyst library for *o*-xylene hydrogenation, with the results being displayed as a function of time on-stream.[22] In addition, Park et al. developed a fast parallel screening method along with a colorimetric assay to evaluate the NOx storage capacity of LNT catalysts with respect to reaction time, demonstrating the usefulness of the colorimetric assay method

in detecting NOx quantitatively for a large number of catalysts at the same time in a parallel array microreactor system.[23]

Here, we introduce a transient combichem methodology for developing a new catalyst formulation of the perovskite-based oxide (PBO) catalysts for the oxidation of NO to NO_2 and validate its integrity via a systematic quantitative analysis of the transient combichem data. The proposed system consists of a dual-bed reactor with a PBO catalyst in the front bed and K_2O/Al_2O_3 as a NOx storage component (NSC) in the rear bed. A colorimetric assay is then employed for directly determining the amount of NOx extracted from both PBO catalysts and K_2O/Al_2O_3. Results of the catalyst screening by the combichem method are directly compared with those obtained from the steady-state conventional packed-bed flow reactor, and a certain correlation between these two results is determined to ensure the integrity and practical value of the results from the transient combichem methodology developed. Finally, we identify the most active chemical formulation of the PBO catalysts among all screened.

■ EXPERIMENTAL PROCEDURES

Catalyst Preparation. PBO with the chemical formulation of $A_{1−x}A'_xBO_3$ (A = La, Pr, Y, A′ = Ag, Ba, K, Sr, B = Fe, Mn, Co, x = 0.1−0.5) were prepared by the citric acid method.[11] $La(NO_3)_3·6H_2O$ (Yakuri Pure), $Pr(NO_3)_3·6H_2O$ (Aldrich), $Y(NO_3)_3·5H_2O$ (Aldrich), $Sr(NO_3)_2$ (Aldrich), $AgNO_3$ (Kojima), KNO_3 (Junsei), and $Ba(NO_3)_2$ (Aldrich) were used as the precursors for A-site metals of PBO, and $Mn(NO_3)_2·6H_2O$ (Kanto), $Co(NO_3)_2·6H_2O$ (Aldrich), and $Fe(NO_3)_3·9H_2O$ (Aldrich) were used for B-site metals. Appropriate stoichiometric amounts of the precursors were dissolved in distilled water, and 10 wt % excess of the monohydrate form of citric acid (Kanto) was added to the solution to form a complete complexation of the related metals. The solution was stirred at room temperature for 1 h and then heated to 80 °C with continuous stirring. The temperature of the solution was maintained at 80 °C to evaporate water before the viscous gel was formed. The obtained gel was oven-dried at 110 °C overnight and precombusted in a muffle furnace at 250 °C to prevent the loss of the PBO by the explosive removal of nitrates in the catalyst during the calcination procedure up to 700 °C for 5 h. Note that the catalyst designation "$A_{1−x}A'_xBO_3$" is based on the stoichiometric composition of the PBO (i.e., the molar ratio of A- and B-site metals), not on the structural phase composition of perovskite. In addition, the substituted metals such as K, Sr, Ba, and Ag examined in the present study were incorporated into mainly the A-site of the PBO catalyst because of their large ionic radius (r > 0.090 nm).[12,13]

A K_2O/Al_2O_3 (K = 10 wt %) employed as an NSC was prepared by the incipient wetness method with an aqueous solution of CH_3COOK (Aldrich) for impregnating K onto γ-Al_2O_3 (Puralox SCFa-160, Sasol).[24] The prepared catalyst was then oven-dried at 110 °C overnight, and calcined in air at 500 °C for 5 h.

Catalyst Characterization. X-ray powder diffraction (XRD) patterns of PBO catalysts were obtained by the XPERT PRO MPD X-ray diffractometer (PANalytical) using Cu Kα radiation (wavelength = 1.54056 Å), and the spectra were collected in the region of 2θ = 20−80° at 40 kV and 30 mA of the X-ray gun.

Conventional Catalytic Activity Test for NO Oxidation. For the purpose of benchmarking, the NO oxidation activity of PBO catalysts was measured over a conventional packed-bed

Scheme 1. Schematic Diagram of a Base Activity Set in the 10 × 10 Array of Combichem Microreactors

Example: $La_{0.5}Ag_{0.5}MnO_3$ at 250 °C (Table 2)   <A>: 767 μmol/g <B>: 19 μmol/g <C>: 129 μmol/g
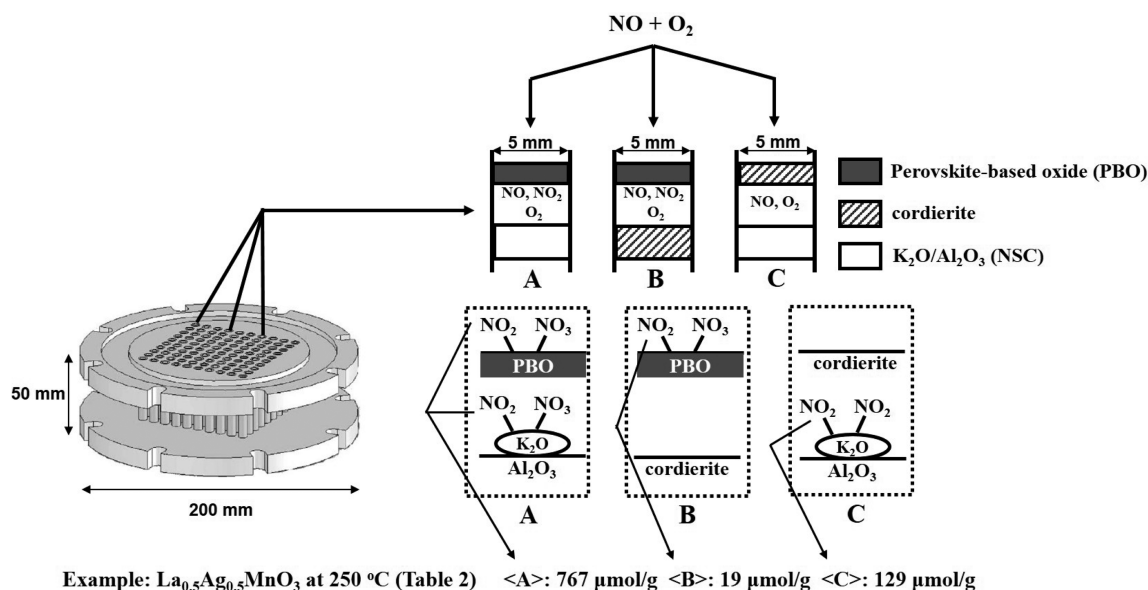
flow reactor under steady-state condition.[25] The feed gas composition was 1000 ppm of NO, 8% O_2, 10% H_2O, and N_2 balance, and the gas-phase concentrations of NO and NO_2 in both the feed and exit streams were measured by an FT-IR equipped with a 2 m gas cell (Nicolet 6700, Thermo Electron Co.) heated to maintain 165 °C. Note that the IR calibration curves for analyzing the concentrations of NO and NO_2 were fit well with linear equations in a high degree of accuracy (Supporting Information (SI) Figure S1). An identical amount (1 mL) of the catalyst pellets in the 0.60−0.84 mm size (i.e., 20/30 mesh size) was charged into a 9.5 mm o.d. quartz tube reactor. Both external and internal mass transfer resistances were negligible under the present experimental conditions as indicated in SI Figures S2a and S2b. The amount of NO_2 produced over the PBO catalyst was recorded in the unit of (μmol of NO_2/cc of bulk catalyst). The reactor space velocity was maintained at 60 000 h^{-1} with a total flow gas rate of 1 L/min through the reactor. All the catalysts were pretreated in 8% O_2 and N_2 balance at 500 °C for 1 h before each activity test.

Catalytic Activity Test by Combichem Method. On the basis of high-throughput combichem, a fast, new screening method has been developed to properly screen the NO oxidation activity of PBO catalysts and identify the one with the highest NO oxidation activity.[23,24] The screening test was conducted over a parallel reactor system with 10 × 10 microreactor arrays,[26] as illustrated in Scheme 1. It also shows the screening procedure for discovering the most active PBO catalyst for NO oxidation. Combichem reactors A, B, and C, as shown in Scheme 1, contain (PBO + K_2O/Al_2O_3), PBO, and K_2O/Al_2O_3, respectively, as active participants in the NO oxidation and NOx adsorption processes. Cordierite was used as an inert material for maintaining identical pressure drops across all three reactors. The back diffusion of NO_2 produced in the combichem reactor may occur through the individual exit channels (20 mm long) after mixing of the individual exit streams with neighboring ones, as can be seen in SI Scheme S1; however, this back-diffusion of NO_2 through the individual exit channel may be assumed negligible according to the axial Peclet number (N_{Pe}) presented in P5 (SI). Indeed, N_{Pe} for the exit channel flow from the bottom end of the combichem reactor to

the end of the individual exit channel (20 mm) is greater than 10 over the entire reaction temperature range covered (SI Table S1), indicating the back-diffusion of NO_2 is negligible because of the faster forward rate of the convective mass transfer.[27]

For convenience, we introduce base and average activity sets in the description of the combichem reactor arrays as follows: A collection of all three reactors, including reactors A, B, and C, forms a base activity set from which the NO oxidation activity of a PBO formulation can be determined. For each PBO formulation, there are three identical base activity sets comprising an average activity set from which a statistical average of the NO oxidation activity can be calculated. Thus, the catalytic performance of a PBO formulation is the average catalytic activity obtained from the average activity set consisting of nine reactors containing three base activity sets (3A + 3B + 3C reactors).

The total volume of reactor B or C was kept identical to that of reactor A by adjusting the volumetric amount of the cordierite powder to maintain an identical pressure drop across all three reactors, thereby removing any effect of the reactor pressure drop on the NO oxidation and NOx adsorption performance of the packed-bed array of the microreactor system. In separate experiments, the adsorption capacity of cordierite for NOx was found to be negligible, confirming that the main role of the cordierite particles in the dual-bed microreactor system is solely in equalizing the pressure drops across the parallel 10 × 10 arrays of the microreactors. In addition, the adsorption capacity of a PBO catalyst ($La_{0.5}Ag_{0.5}MnO_3$) for NO was found to be much smaller than that for NO_2. All catalyst samples charged into the 10 × 10 reactors were tested simultaneously, and unused reactors were packed with the same volume of cordierite powder to maintain the same pressure drop across each microreactor for a uniform flow distribution among them.

The dual-bed reactor A contains PBO catalyst (10 mg) in the front bed and K_2O/Al_2O_3 (30 mg) in the rear bed, as shown in Scheme 1. NO_2 produced over the PBO catalyst in the front bed can be adsorbed onto either the PBO catalyst itself in the front bed or the K_2O/Al_2O_3 in the rear bed. Reactors B and C

containing the PBO catalyst and K_2O/Al_2O_3, respectively, were employed to measure the amount of NOx adsorbed onto the PBO and K_2O/Al_2O_3, respectively. The amount of NO_2^- or NO_3^- stored onto the PBO catalysts or K_2O/Al_2O_3 was readily extracted by water and estimated by a colorimetric assay of the extracts through the Griess diazotization reaction.[28] The color of the solution changed from colorless to deep red by the presence of NO_2^- or NO_3^- in the extracts. The chemistry of the colorization by the Griess reagent has been reported elsewhere.[23]

The catalyst samples [particle size below 0.075 mm (200 mesh)] were charged into each individual microreactor (5 mm i.d.) of the 10 × 10 parallel array reactor system whose overall reactor assembly diameter was 200 mm o.d., as depicted in Scheme 1. The catalysts were placed between glass wool packings in each microreactor. The samples in the micro-reactors were pretreated with 8% O_2 and N_2 balance at 500 °C for 1 h prior to each screening test. The feed gas composition to the parallel reactor system was 1000 ppm of NO, 8% O_2, 10% H_2O, and N_2 balance with a total flow rate of 3 L/min to the reactor assembly and an individual flow rate of ∼30 mL/min to each individual microreactor.

The high-throughput screening tests were conducted from 200 to 350 °C for 20 min. After each screening test, all catalyst samples were purged with N_2 to remove the physisorbed NO remaining on the surface of PBO and K_2O/Al_2O_3 as well as NOx in the gas phase. For the fast transfer of the catalyst samples from the combichem reactor assembly to the 10 × 10 microtubes (each volume: 1.1 mL, plasticware-type strip tube, Simport), the sample ejector was placed right on the top of the 10 × 10 microreactor assembly, and all three devices were correctly aligned in the top-to-bottom order of ejector–microreactors–microtubes, as shown in SI Scheme S2b. Then all catalyst samples were simultaneously transferred from the combichem microreactors to the microtubes by pushing down the plunger cap of the ejector, as illustrated in SI Scheme S2b. Distilled water (0.7 ml) was then added to each of the collected samples in microtubes under vigorous mixing for 20 min by a shaker (Lab Companion SI-300 Benchtop Shaker, GMI) to extract the NO_2^- and NO_3^- stored on the samples. The samples were then centrifuged at 13 000 rpm to obtain clear extracted solutions. The obtained solutions were diluted with distilled water at a mixing ratio of 1:20 for chemical analysis, and the amounts of NOx in the extracts were determined by a wet chemical analyzer (Auto Analyzer 3, Bran+Luebbe).

To examine the effect of the NO and NO_2 feed concentrations on the amount of NOx adsorbed on K_2O/Al_2O_3, a parallel adsorption test was conducted by using an identical amount of K_2O/Al_2O_3 packed into each of the 10 × 10 microreactors (100 reactors in total) with a feed gas stream containing 1000 ppm of NOx (NO + NO_2), 8% O_2, 10% H_2O, and N_2 balance at 250 °C for 20 min. The amount of NOx adsorbed onto K_2O/Al_2O_3 was determined by colorimetric assay. To investigate the effect of the reaction temperature on the adsorption efficiency of NO_2 onto NSC, we conducted a set of separate adsorption experiments with 300 mg of NSC in a flow type transient packed-bed adsorption system at 200, 250, 300, and 350 °C for 20 min of the on-stream time at each temperature with a flow rate of 300 mL/min so that the reactor residence time was kept identical to that of the combichem reactor (30 mg of NSC in a flow of 30 cc/min). The feed gas composition was 1000 ppm of NO_2, 8% O_2, 10% H_2O, and N_2

balance, and the NO_2 concentrations at the inlet and outlet of the adsorption system were measured by an online FT-IR.

■ RESULTS AND DISCUSSION

XRD Patterns of the Perovskite-Based Oxide Catalysts Prepared. The catalysts prepared in the present study are in the structural form of PBO, as shown in Figure 1. As mentioned
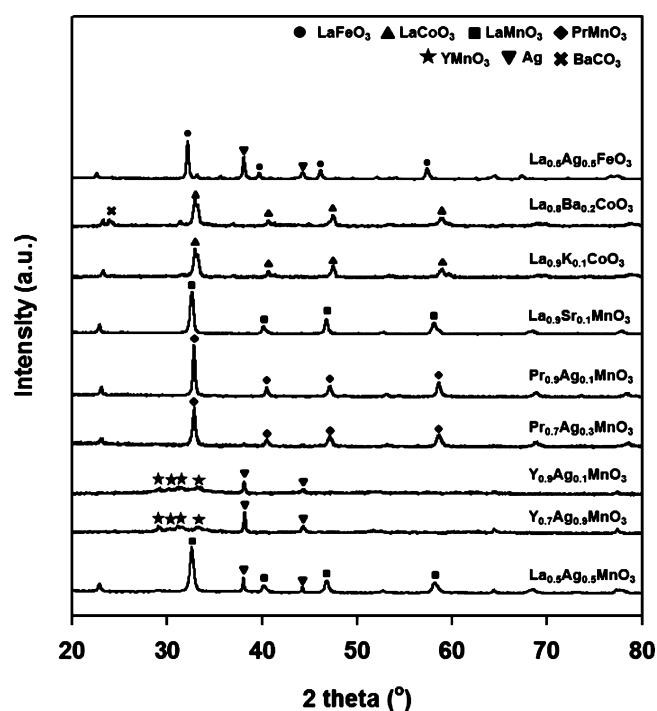

Figure 1. XRD patterns of the perovskite-based oxide catalysts prepared.

earlier, the designation of a PBO catalyst (e.g., $A_{1-x}A'_xBO_3$) is based on the stoichiometric composition of the PBO (i.e., the molar ratio of A- and B-site metals), not on the structural phase composition of perovskite. The XRD pattern of $La_{0.5}Ag_{0.5}FeO_3$ reveals the typical perovskite-type structure of $LaFeO_3$ (JCPDS 74-2203) with the metallic Ag phase (JCPDS 4-783). Indeed, the secondary phases may be commonly formed on the perovskite during preparation due to the excess substitution of A- or B-sites in the ABO_3 structure.[15,16,29] Although the 0.1 mol of K is partially substituted into the A-site of the $LaCoO_3$ perovskite, the XRD diffraction peak of $LaCoO_3$ (JCPDS 25-1060) is still clearly observed in $La_{0.9}K_{0.1}CoO_3$ without any segregated phase, such as KOH and K_2CO_3, suggesting that K might be fully incorporated into the perovskite structure of $LaCoO_3$ or that the secondary phase formed may be amorphous or too small to be detected by XRD, whereas a new diffraction peak assigned to $BaCO_3$ (JCPDS 45-1471) appears in the XRD pattern of $La_{0.8}Ba_{0.2}CoO_3$ catalyst. Similarly, $La_{0.9}Sr_{0.1}MnO_3$ and $Pr_{1-x}Ag_xMnO_3$ (x = 0.1, 0.3) reveal the diffraction pattern of $LaMnO_3$ (JCPDS 75-0440) and $PrMnO_3$,[30] respectively, regardless of the partial substitution of A-site by Sr and Ag. In addition, $Y_{1-x}Ag_xMnO_3$ (x = 0.1, 0.3) and $La_{0.5}Ag_{0.5}MnO_3$ are in the perovskite structure of $YMnO_3$ (JCPDS 25-1079) and $LaMnO_3$ (JCPDS 75-0440), respectively, with an additional phase of metallic Ag (JCPDS 4-783).

NO Oxidation Performances over the Perovskite-Based Oxide Catalysts in Conventional Packed-Bed

Reactor. Figure 2 shows the NO oxidation performance of the PBO catalysts determined in a conventional packed-bed reactor
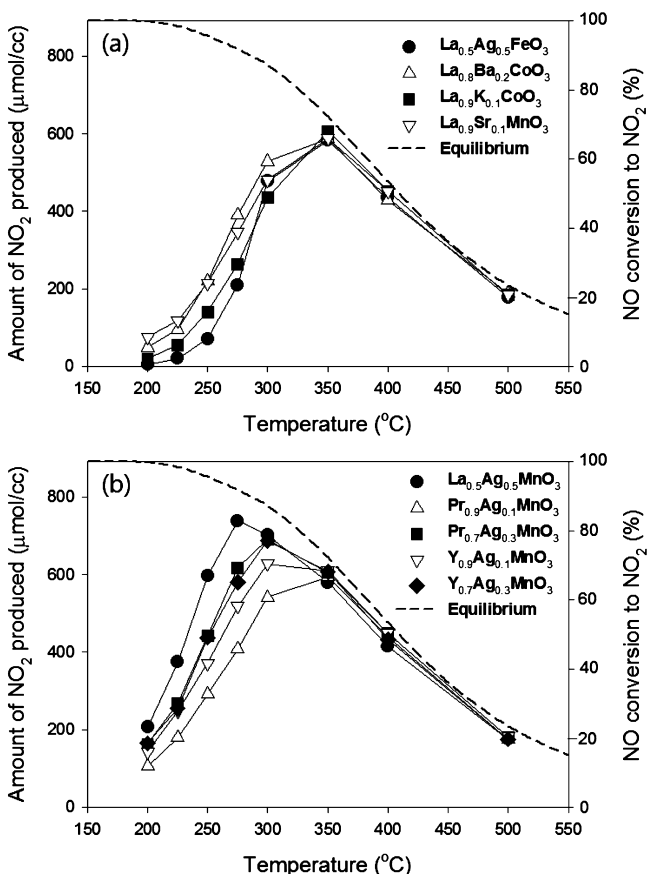

Figure 2. NO oxidation performance over the perovskite-based oxide catalysts. Feed gas composition: 1000 ppm of NO, 8% O_2, 10% H_2O, and N_2 balance; SV = 60 000 h^{-1}.

under steady-state conditions, and their averages and standard deviations are listed in SI Table S2. Note that the largest standard deviation is 5.2% over the entire reaction temperature range covered. NO oxidation activity of $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.8}Ba_{0.2}CoO_3$ was higher than that of $La_{0.5}Ag_{0.5}FeO_3$ and $La_{0.9}K_{0.1}CoO_3$, particularly in the low temperature range from 200 to 325 °C, as shown in Figure 2a. However, their high temperature activity above 350 °C was quite similar, regardless of the catalyst formulation, because of the limitation of thermodynamic equilibrium of the oxidation reaction of NO to NO_2.[11,15]

In Figure 2b, the NO oxidation activity over $A_{1-x}Ag_xMnO_3$ (A = La, Pr, Y) is higher than that over $La_{1-x}A'_xBO_3$ (A′ = Ba, K, Sr; B = Mn, Co) without Ag in Figure 2a, regardless of the substitution ratio (x) of the A-site with A′ cations in the latter. When x increases from 0.1 to 0.3, the amount of NO_2 produced over $Y_{1-x}Ag_xMnO_3$ and $Pr_{1-x}Ag_xMnO_3$ increases in the low temperature range below 300 °C, with the increase being particularly significant over $Pr_{1-x}Ag_xMnO_3$, yielding an increase by as much as 50% at 275 °C. This indicates that the NO oxidation activity of the Ag-based PBO varies with the amount of Ag substituted into the A-site of PBO as well as with the host metal in the A-site.

Indeed, the catalytic oxidation activity of the perovskite is strongly influenced by the partial substitution of the A-site by a cation with an oxidation state distinct from that of the host

metal in the A-site.[31,32] It may be due to the variation of the chemical valence in the perovskite structure, which may lead to an enhanced redox property of the perovskite by an increase in the amount of the surface oxygen adsorbed thereon.[31,33,34] Because a variety of metals may form A- and B-sites of perovskite and those sites can be partially substituted by a variety of cations, an enormous number of perovskite compounds may be formulated, prepared, and examined to develop a highly active PBO catalyst for NO oxidation, particularly in the low temperature region below 250 °C.

Preparatory Procedure for Combichem System before Catalyst Screening. As a preparatory step for developing a combichem system in the present study, we examined both the uniform flow distribution among the microreactors and the effect of NOx feed composition on the NOx adsorption efficiency onto K_2O/Al_2O_3, as described in Catalytic Activity Test by Combichem Method. First, the uniformity of flow distribution to each microreactor in the 10 × 10 array was indirectly determined by an adsorption test conducted at 250 °C over the reactor assembly with each microreactor containing 30 mg of K_2O/Al_2O_3, under a feed gas condition containing 1000 ppm of NO_2, 8% O_2, 10% H_2O, and N_2 balance. Results in Figure 3a indicate a fairly uniform amount of NOx was adsorbed onto the NSC in each 100 combichem microreactor. The average amount of NOx
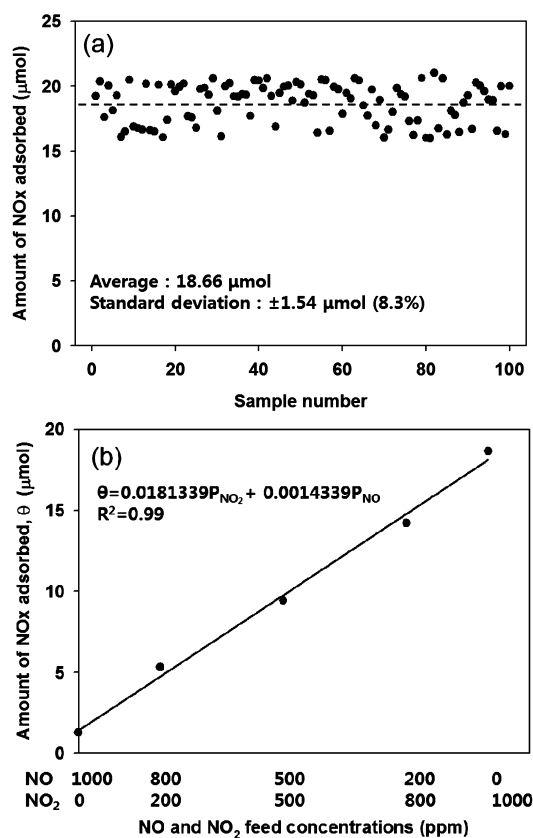

Figure 3. Uniformity of flow distribution over the 10 × 10 array of microreactors (a), and the effect of NOx feed concentration on NOx adsorption efficiency onto NSC (b). Feed gas composition: 1000 to 0 ppm of NO, 0 to 1000 ppm of NO_2, 8% O_2, 10% H_2O and N_2 balance. Temperature, 250 °C; amount of NSC, 30 mg; θ, amount of NOx adsorbed on NSC (μmol); P_{NO}, feed concentration of NO; P_{NO_2}: feed concentration of NO_2.

adsorbed onto the NSC is 18.66 μmol with a standard deviation of 1.54 μmol (8.3%), indicating that the flow distribution over the 10 × 10 array of the microreactors is sufficiently uniform for proper screening of PBO catalysts for NO oxidation, and the catalyst bed packing is reasonably uniform across all the microreactors.

The effect of NOx feed composition on the NOx adsorption efficiency onto NSC was investigated in a series of NOx adsorption experiments conducted over a parallel adsorption system consisting of 10 × 10 microreactor arrays with the feed gas containing 0−1000 ppm of NOx (i.e., NO + NO_2), 8% O_2, 10% H_2O, and N_2 balance. The average amount of NOx adsorbed onto NSC charged into each of 100 microreactors was measured with respect to the NOx feed composition by the colorimetric assay method. The amount of NOx adsorbed onto the NSC depends strongly on the feed concentration of NO_2, but weakly on that of NO as shown in Figure 3b.[35,36] The amount of NOx adsorption (θ) increased from 1.29 to 18.66 μmol as the feed concentration of NO_2 increased from 0 to 1000 ppm (and that of NO decreased simultaneously from 1000 to 0 ppm) in 1000 ppm of NOx, resulting in a linear correlation in terms of both NO (P_{NO}) and NO_2 concentrations (P_{NO_2}) with a relative correlation factor >99%, when both NO and NO_2 were present in the feed gas stream. This excellent linear correlation indicates, in particular, that the NO_2 produced over the PBO catalyst in the front bed of the dual-bed reactor A is adsorbed on NSC in the rear bed in proportion to its gas-phase concentration. It indicated that the adsorption efficiency of NO_2 is essentially independent of both NO_2 and NO concentrations and further suggests that the effect of any interaction between NO and NO_2 on their adsorption on K_2O/Al_2O_3 is insignificant.

NO Oxidation Activity of the Perovskite-Based Oxide Catalysts Determined by Combichem Method. The oxidation activity of the PBO catalysts can be determined by measuring the amount of NO_2 formed over the PBO by the combichem method developed in the present study. In measuring the amount of NO_2 formed, it is important to note that there are three different pathways for the formed NO_2 to go through: It may adsorb on the PBO catalyst surface [NO_2 (P)], or it may move along with the exit gas stream from the PBO bed to the rear bed containing NSC (i.e., K_2O/Al_2O_3), where it may either adsorb onto K_2O/Al_2O_3 [NO_2 (K)] or move out of the K_2O/Al_2O_3 bed along with the exit gas stream from the rear bed [NO_2 (g)]. In view of these three pathways available for NO_2 molecules produced, the total amount of all three NO_2 species (NO_2 produced = [NO_2 (P) + NO_2 (K) + NO_2 (g)]) can be obtained from the combichem experimental data according to eq 1, which is basically a mass balance equation for NO_2 over reactor A:

$$NO_2 \text{ produced} = \langle B \rangle + [\langle A \rangle - \langle B \rangle - \xi \langle C \rangle]/\alpha \tag{1}$$

where $\langle A \rangle$ and $\langle B \rangle$ are the amount of NOx adsorbed onto the catalysts in reactors A and B, respectively, and $\langle C \rangle$ is the amount of NO adsorbed onto the NSC for the reference feed concentration of NO to reactor C (i.e., 1000 ppm), measured by the colorimetric assay (μmol/g). α is the adsorption efficiency of NSC for NO_2 defined by

$$\alpha = \frac{\text{amount of } NO_2 \text{ adsorbed on NSC}}{\text{amount of } NO_2 \text{ in feed gas to NSC}} \tag{2}$$

and ξ is the time-average fraction of NO included in the NOx stream emitted from the front bed containing the PBO catalyst in reactor A during the on-stream time of 20 min employed in the present study.

The first term on the right-hand side of eq 1, $\langle B \rangle$, is essentially the same as the amount of NO_2 adsorbed on the PBO [NO_2 (P)] in reactor B during the oxidation of NO to NO_2 because the adsorption of NO onto the PBO is negligibly small compared with that of NO_2, as already mentioned earlier. $\langle A \rangle - \langle B \rangle$ is the amount of NOx adsorbed onto K_2O/Al_2O_3 in the rear bed of reactor A, whereas $\xi \langle C \rangle$ is the amount of NO adsorbed onto K_2O/Al_2O_3 after NO oxidation reaction over the PBO catalyst in the front bed of reactor A. Thus, the numerator in the second term on the right-hand side of eq 1, [$\langle A \rangle - \langle B \rangle - \xi \langle C \rangle$], represents the amount of NO_2 adsorbed onto K_2O/Al_2O_3 [NO_2 (K)] after the oxidation of NO to NO_2 over the PBO catalyst in the front bed of reactor A, and the denominator, α, is the adsorption efficiency of NSC for NO_2. By the definition of α in eq 2, the second term on the right-hand side of eq 1 thus corresponds to the total amount of NO_2 in the feed gas stream to the NSC bed before splitting into the two different pathways of [NO_2 (K)] and [NO_2 (g)] in the NSC bed. As a result, the right-hand side of eq 1, $\langle B \rangle + [\langle A \rangle - \langle B \rangle - \xi \langle C \rangle]/\alpha$, is equal to [$NO_2$ (P) + NO_2 (K) + NO_2 (g)].

Figure 4 shows the transient response of NO_2 concentration in the exit stream from the NSC bed as a function of the time-
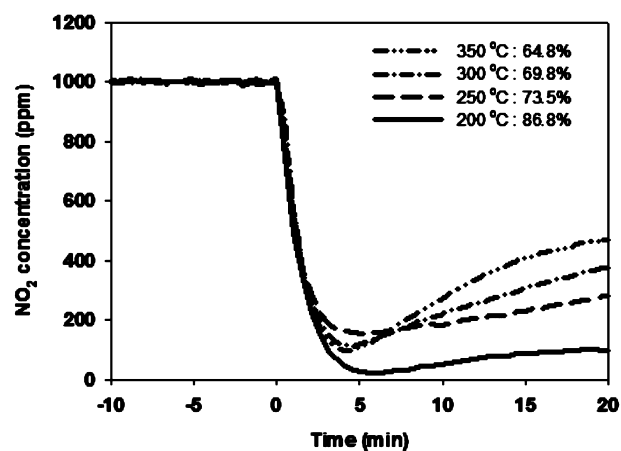

Figure 4. Transient NO_2 concentration profile as a function of time on-stream in a packed-bed adsorption system at adsorption temperatures from 200 to 350 °C. Feed gas composition: 1000 ppm of NO_2, 8% O_2, 10% H_2O, and N_2 balance. Feed gas flow rate, 300 cc/min; amount of NSC, 300 mg.

on-stream, which can be used to determine the adsorption efficiency of NSC for NO_2. The experiment was conducted in a packed-bed adsorption system using a feed gas containing 1000 ppm NO_2, 8% O_2, 10% H_2O, and N_2 balance (300 mL/min). The NO_2 concentration profiles from the adsorption system were measured by an online FT-IR. When the NSC temperature increased from 200 to 350 °C, the adsorption efficiency of K_2O/Al_2O_3 for NO_2 decreased from 86.8% to 64.8% as determined by the integration of the NO_2 concentration profiles during the on-stream time of 20 min, revealing that the adsorption efficiency of the NSC for NO_2 depends on the temperature of the NSC. The values of α obtained from Figure 4 are listed in Table 1 as a function of NSC temperature.

Table 1. Adsorption Efficiency of K_2O/Al_2O_3 for NO_2 (α) and NO (β) As a Function of NSC Temperature

	temp, °C			
value	200	250	300	350
α^a	0.868	0.735	0.698	0.648
β^b	0.054	0.048	0.043	0.038

^{a}Obtained from the data in Figure 4. ^{b}Obtained from the combichem data of F and $\langle C \rangle$.

Note that the exit stream from the PBO catalyst bed, which is the feed stream to the NSC bed, contains <1000 ppm of NO during the combichem screening tests as a result of the NO oxidation activity of the PBO catalysts charged into the front bed, although 1000 ppm of NO is always present in the feed gas stream to the NSC bed in reactor C. To compensate for this difference in the NO feed concentrations, the time-average fraction of NO (ξ) included in the NOx stream was introduced in eq 1.

Now ξ can be obtained from the combichem experimental data obtained from reactors A, B, and C according to eq 3, which is a mass balance equation for NOx over K_2O/Al_2O_3 in reactor A:

$$\frac{\langle A \rangle - \langle B \rangle}{F - \langle B \rangle} = \alpha(1 - \xi) + \beta\xi \qquad (3)$$

, where F is the total amount of NO fed to the PBO catalyst in the front bed of reactor A during the combichem experiment through the feed gas stream (μmol/g), and β is the adsorption efficiency of NSC for NO defined by

$$\beta = \frac{\text{amount of NO adsorbed on NSC}}{\text{amount of NO in feed gas to NSC}} \qquad (4)$$

Listed in Table 1 are the values of β obtained from the amount of NO in the feed gas steam (F) and that adsorbed onto NSC in reactor C, $\langle C \rangle$, as a function of the NSC temperature.

The numerator on the left-hand side of eq 3, $\langle A \rangle - \langle B \rangle$ is the amount of NOx adsorbed onto NSC in the rear bed of reactor A, as mentioned earlier, and the denominator, $F - \langle B \rangle$ is the amount of NOx in the feed gas to the NSC bed resulting from the NO oxidation over the PBO catalyst in the front bed of reactor A. Physically, the left-hand side of eq 3 represents the adsorption efficiency of NSC for NOx produced by the oxidation of NO to NO_2 over the PBO catalyst in the front bed of reactor A, and the right-hand side of eq 3 describes the adsorption efficiency of NSC for both NO and NO_2 in terms of ξ so that ξ can be calculated therefrom.

Table 2 illustrates the amount of NO_2 produced over the $La_{0.5}Ag_{0.5}MnO_3$ catalyst by the combichem method as an example. Listed in column 1 is the amount of NO in the feed gas stream, and columns 2, 3, and 4 present the amounts of NOx (columns 2 and 3) and NO (column 4) adsorbed in reactors A, B, and C, respectively. (The amount of NOx adsorbed in reactor B is essentially the same as that of NO_2 because NO adsorption is negligible on PBO, as mentioned earlier.) Columns 5 and 6 determine the amount of NOx adsorbed onto the NSC in the rear bed of reactor A and that fed to the NSC in the rear bed of reactor A, respectively, which are used to calculate ξ in column 7 according to eq 3. Finally, the total amount of NO_2 produced over the PBO is obtained by eq 1 as listed in column 8.

Figure 5 shows the amount of NO_2 produced over various PBO catalysts over the reaction temperature from 200 to 350
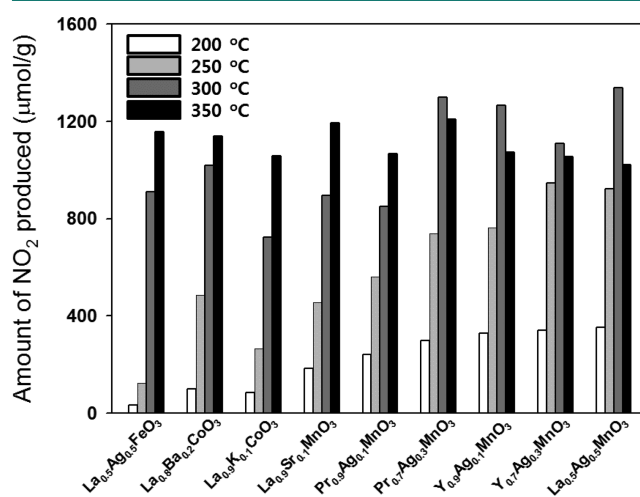

Figure 5. Amount of NO_2 produced by the oxidation of NO over the perovskite-based oxide catalysts in the reaction temperature from 200 to 350 °C. Feed gas composition: 1000 ppm of NO, 8% O_2, 10% H_2O, and N_2 balance.

°C, obtained from the experimental data by the combichem method as described in eqs 1 and 3. The averages and standard deviations of all data are listed in SI Table S3. The NO oxidation activity of the $La_{0.5}Ag_{0.5}FeO_3$ catalyst at 200 and 250 °C is lower than that of the Mn- and Co-based catalysts, regardless of the cation partially substituted in the A-site as also determined by the oxidation results from the conventional packed-bed flow reactor. Similarly, the amounts of NO_2 produced over the partially substituted Ag-based catalysts are

Table 2. Amount of NO_2 Produced over $La_{0.5}Ag_{0.5}MnO_3$ Catalyst by the Combichem Method^a

	column							
	1	2	3	4	5	6	7	8
T (°C)	F^b (μmol/g)	$\langle A \rangle^c$ (μmol/g)	$\langle B \rangle^d$ (μmol/g)	$\langle C \rangle^e$ (μmol/g)	$\langle A \rangle - \langle B \rangle$ (μmol/g)	$F - \langle B \rangle$ (μmol/g)	ξ^f	NO_2 produced (μmol/g)
200	2679	438	21	146	417	2658	0.874	354
250	2679	767	19	129	748	2660	0.661	921
300	2679	993	5	115	988	2674	0.502	1338
350	2679	725	4	101	721	2675	0.620	1020

^{a}Amounts (μmol/g) in columns 1−4 were normalized with respect to the amount of perovskite catalyst (g) in reactor A. ^{b}Amount of NO fed to each of microreactors through the feed gas stream. ^{c}Amount of NOx adsorbed in reactor A containing PBO and NSC. ^{d}Amount of NO_2 adsorbed in reactor B containing PBO. ^{e}Amount of NO adsorbed in reactor C containing NSC. ^{f}The time-average fraction of NO included in the NOx stream emitted from the PBO bed in reactor A.

greater than those over the partially substituted Ba-, K-, or Sr-based catalysts at temperatures below 250 °C for the PBO catalysts, including Mn or Co in the B-site.

Among the catalysts examined, the $La_{0.5}Ag_{0.5}MnO_3$ catalyst produces the largest amount of NO_2, consistent with its superior NO oxidation performance discussed in Figure 2b. It is worth noting that an increasing amount of NO was oxidized over all PBO catalysts with the increasing reaction temperature from 200 to 300 °C, and the identical trend was also observed in their NO oxidation activity over a conventional packed-bed flow reactor (Figure 2). Again, similar amounts of NO_2 were produced at 350 °C, regardless of the PBO formulation, primarily attributable to the limitation of thermodynamic equilibrium of the oxidation reaction of NO to NO_2 at high temperatures above 350 °C.[11,15] Note that the largest standard deviation for producing NO_2 in the combichem reactor was 10.7% over the entire reaction temperature range covered (SI Table S3).

Correlation of the NO Oxidation Activity of the Perovskite-Based Oxide Catalysts Determined by Conventional Steady-State Packed-Bed and Transient Combichem Reactors. Among other correlations observed (SI Figure S3), Figure 6 (i.e., SI Figure S3a) shows the best
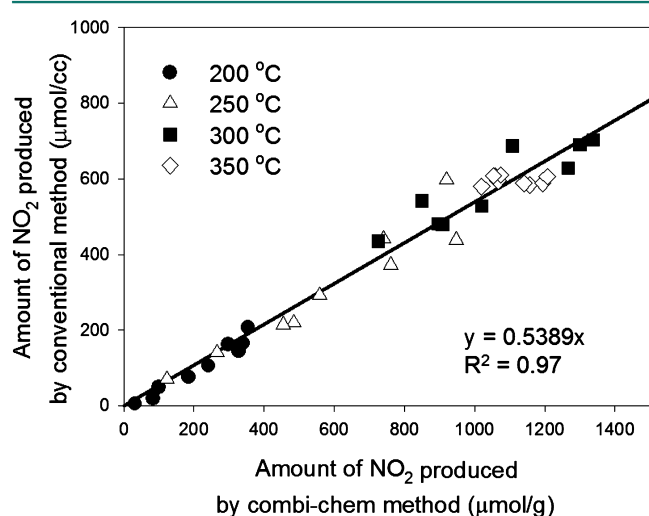

Figure 6. Correlation of the NO oxidation activity of perovskite-based oxide catalysts: the combichem reactor vs the conventional steady-state packed-bed reactor.

linear correlation between the NO oxidation activity of the PBO catalysts obtained by the transient combichem method developed in the present study and that by the conventional fixed-bed reactor under steady-state conditions. Interestingly, however, the amounts of NO_2 produced by the combichem reactor were about twice as large as those by the conventional fixed-bed reactor. This difference in the NO_2 yield may be attributed mainly to the different reaction conditions because the NO_2 production in the combichem experiment was measured during the first 20 min of time on-stream under the transient condition at the reactor space velocity of 260 000 h^{-1}, whereas the conventional fixed-bed reactor experiment was carried out under the steady-state condition at 60 000 h^{-1}.

From these observations, it can be concluded that the combichem method developed in the present study in combination with the colorimetric assay method is a highly effective tool for comparative kinetic studies in search of a new

catalyst formulation. The method is particularly suitable for high-throughput screening of the NO oxidation activity of the PBO catalysts, which have an enormous number of possible variations in their chemical formulation. Furthermore, it can also be used to predict the NO oxidation activity of a conventional fixed-bed reactor containing the same PBO catalyst under steady-state conditions.

Indeed, the conventional NO oxidation experiment for each catalyst sample requires at least 10 h, including 2 h for the catalyst pretreatment and 8 h for the NO oxidation activity test. It requires 90 h for measuring the NO oxidation activity of nine PBO samples. However, the new screening test developed in the present study can be completed within 4 h, including the pretreatment and activity test of nine samples at once, as shown in Table 3. Because only 10 mg of PBO is required for the

Table 3. Comparison of the Required Catalyst Screening Time for Oxidation of NO to NO_2 over the Perovskite-Based Oxide Catalysts by Conventional and Combichem Methods

Conventional Packed-Bed Method		
experiment	pretreatment	2 h
	reaction	8 h
total (1 EA)		10 h
total (9 EA)		90 h
Combichem Method		
experiment	pretreatment/reaction	3 h
	extraction/analysis	1 h
total (9 EA)		4 h

catalyst activity test by the combichem method, the catalyst preparation time can be reduced further. Clearly, the new combichem method developed in this study is highly effective for simultaneously evaluating a large number of catalyst formulations for a promising new NO oxidation catalyst.

■ CONCLUSIONS

A new combichem method, based on transient catalytic reaction and adsorption measurements using parallel arrays of microreactors, has been developed for the efficient and cost-effective screening of various PBO catalyst compositions to identify the best chemical formulation of the catalyst for oxidation of NO to NO_2. The consecutive steps of the oxidation of NO to NO_2 over the PBO catalyst and the subsequent adsorption of NOx onto the PBO and K_2O/Al_2O_3 were quantitatively analyzed by the use of a colorimetric assay method developed previously, whose results were successfully incorporated into the data analysis of the combichem screening system along with three critical parameters: the adsorption efficiency of NSC for NO_2 (α) and NO (β) and the time-average fraction of NO included in the NOx stream (ξ).

The results yielded an excellent linear correlation between the amount of NO_2 produced over the PBO catalysts in the combichem microreactors and the oxidation activity of NO to NO_2 over the identical PBO catalysts obtained from conventional packed-bed reactors, demonstrating the practical usefulness of the combichem method proposed. Among the PBO catalyst formulations tested for the oxidation of NO, $La_{0.5}Ag_{0.5}MnO_3$ was identified as the best chemical formulation of the PBO catalyst. This finding was confirmed in conventional fixed-bed activity tests, and it validates the excellent capability of the combichem method developed in the present study in providing a high-throughput experimental tool for

finding a commercially promising PBO catalyst for NO oxidation and possibly for other applications as well.

ASSOCIATED CONTENT

$\circledS$ Supporting Information

Calibration of FTIR for analyzing NO and NO_2 concentrations; effect of internal and external mass transfer resistances; effect of back-diffusion of produced NO_2 after mixing with neighbor exit streams; schematic diagram of the lab-prepared ejector; accuracy of NO oxidation activity measured over perovskite-based oxide catalysts; and comparison of NO_2 production performance: combichem reactor vs conventional fixed-bed reactor. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: +82-54-279-2264. Fax: +82-54-279-8299. E-mail: isnam@postech.ac.kr.

Notes

The authors declare no competing financial interest.

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