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Research Note

Colorimetric assay for a fast parallel screening of NO_x storage

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Abstract

A fast parallel method for determining the capacity of an automotive catalyst to trap and especially store NO_x has been established. A three-step approach, including parallel adsorption of NO onto the catalyst samples, water extraction of trapped NO_x in the form of $NO_2{}^-$ and $NO_3{}^-$ in an aqueous solution, and colorimetric assay based on the sensitive and dramatic color change from colorless to deep red of the organic dye through the Griess diazotation reaction has been performed sequentially to give a fast parallel and quantitative evaluation of the amount of NO_x trapped over promising automotive catalysts. The results correlate well with those obtained by means of traditional, time-consuming techniques, such as temperature-programmed desorption.

Keywords: Colorimetric assay; NO_x storage-reduction catalyst; Naked eye sensing; Nitrite sensor

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1. Introduction

The abatement of CO_2, as well as the emission of air pollutants into the atmosphere, is a hot topic of global significance. Although highly energy-efficient automotive engines have been developed, automobiles remain a major source of energy consumption and air pollutants (e.g., NO_x, CO, and hydrocarbon). A recently developed lean-burn engine that operates with a higher air/fuel ratio than conventional gasoline engines is quite promising for reducing fuel consumption and CO_2 emissions. The excess air to the engine serves as an oxidizing agent for the removal of the unburned hydrocarbons and CO over a conventional three-way catalyst, but it hardly reduces NO_x emission from a lean-burn engine [1,2]. One way to solve the problem of the lean-burn engine may be to develop an NO_x storage-reduction catalyst, where under lean conditions, NO_x is trapped on the catalyst surface, and under rich conditions, the stored NO_x is released and reduced to N_2 over a short period.

The NO_x storage capacity for trapping and retrapping NO_x through the oxidation and reduction reactions of NO_x over the catalyst samples is the key parameter in developing an NO_x storage catalyst [3,4]. In the past, the NO_x storage capacity was evaluated and developed using various tedious and time-consuming techniques, including temperature-programmed desorption (TPD), mainly by repeated characterization and measurement of the storage capacity until further improvements are no longer justified. Serial testing of the hundreds or even thousands of candidate catalysts would require an unthinkable amount of time and effort. A fast parallel screening method would be an alternative for discovering and optimizing a new or improved catalyst within a reasonable period [5–10].

Recent fast assay screening of heterogeneous catalysts by means of infrared (IR) imaging has been successfully used to simultaneously analyze NO_x emissions from catalysts [7]. Moates et al. [8] used background-corrected IR thermography to monitor an array of catalyst samples for the exothermic hydrogen/oxygen reaction to examine the catalytic activity. Busch et al. [9] used a dye, 2,2′-azinobis(3-ethylbenzthiazoline-6-

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sulfonic acid) (ABTS), to evaluate the partial quantitative concentration of NO emitted from the array of catalyst samples.

In the present study, a combination of extraction and colorimetric assay was used to develop a novel parallel, quantitative assay for measuring the amount of NO_x trapped on a catalyst sample. Such a method should be easy and economical, and provide a way to examine a large number of catalyst samples at once. The goal of the present study was to establish a fast, parallel, quantitative assay for screening the amount of NO_x adsorbed on the surface of heterogeneous catalysts. It is a reliable test of NO_x storage capacity of catalyst samples prepared by impregnation of mixed metal nitrate solutions. The new method was compared with traditional, time-consuming techniques, such as TPD.

2. Experimental

2.1. Catalyst preparation

NaY (CBV100) and two alumina supports were obtained from Zeolyst and Aldrich, respectively. The alumina supports are referred to as AldI (Al_2O_3; Aldrich catalog No. 26, 774-0), and AldII (Al_2O_3; Aldrich catalog No. 30, 911-7). Catalysts (1 wt% Pt/AldII, 10 wt% Ca/AldII, and 20 wt% Ba/AldII) were prepared by incipient wetness impregnation of the alumina support (AldII) with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ (Aldrich), $Ca(NO_3)_2 \cdot 4H_2O$ (Aldrich), and $Ba(NO_3)_2$ (Aldrich). The 1% Pt/5% Ba/AldII and 1% Pt/20% Ba/AldII samples, comparable to commercial NO_x storage catalysts, were prepared by impregnating the calcined Ba/AldII with a solution of $Pt(NH_3)_4(NO_3)_2$. The samples were then dried overnight in air at 110 °C and finally calcined at 500 °C for 5 h.

2.2. Parallel adsorption, extraction, and colorimetric assay

Three steps (parallel adsorption, extraction, and colorimetric assay) were performed sequentially to develop a method for the fast parallel screening of candidate NO_x storage-reduction catalysts [11]. Parallel adsorption involves the uptake of NO by the catalyst samples (AldI, AldII, NaY, 20% Ba/AldII, 1% Pt/AldII, 1% Pt/5% Ba/AldII, 10% Ca/AldII, and 1% Pt/20% Ba/AldII). Eight quartz tubes containing about 20 mg of each catalyst were placed in a fixed-bed reactor adsorption system designed and fabricated for the present study. The samples were activated in situ by simultaneously heating to 500 °C at a ramp rate of 10 °C/min, kept for 2 h in a total flow of 500 cc/min containing 79% He and 21% O_2, and then cooled to 200 °C. Then NO was adsorbed for 1 h at 200 °C in a total flow of 500 cc/min of 3000 ppm NO and 8% O_2 in He. The adsorption system had been purged by He at 200 °C for 1 h to remove free and physisorbed NO species, similar to a conventional TPD procedure.

Water seems to be the most reliable solvent for completely dissolving and recovering the NO_x adsorbed on the catalyst surface. The extracted solution was simultaneously centrifuged or filtered using a multichannel pipette for fast colorimetric assay. NO_x adsorbed onto the eight catalyst samples was extracted in 1.5 cc of H_2O for 10 min, and the samples were centrifuged or filtered to obtain a clear extract.

The NO_x extracted from the catalyst samples was mainly in the anionic form of NO_2^- and/or NO_3^- in the extract, as confirmed by liquid chromatography (LC). The amount of NO_2^- and/or NO_3^- was estimated by the fast combination method, through the Griess diazotation reaction [12,13]. The parallel assay is based on the sensitive and dramatic color change of the organic dye from colorless to deep red due to the presence of NO_2^- in the extract. NO_3^- in the solution was successfully reduced to NO_2^- by adding hydrazine sulfate to the extract for the measurement of the catalyst's NO_x storage capacity. The chemical sensor was the Griess reagent, containing N-1-naphthylethylenediamine dihydrochloride (NED) and sulfanilic acid. The color change was visible to the naked eye. The chemistry of the colorization by the Griess reagent is given in Fig. 1.

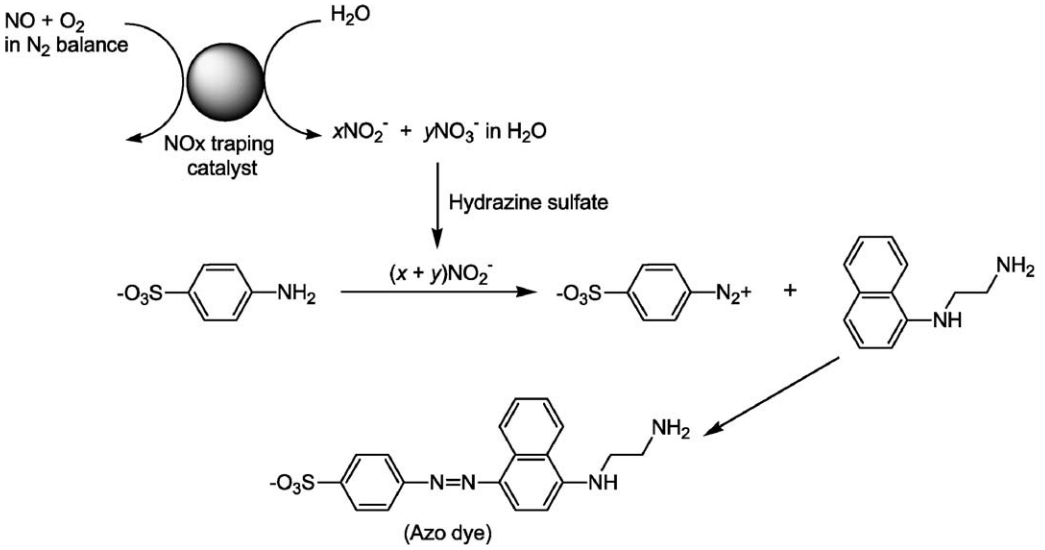

Fig. 1. Diagram of the fast colorimetric screening of NO_x trapped over automotive catalysts.

2.3. TPD

TPD was performed in a quartz tubular fixed-bed microreactor. The catalyst samples were activated in situ by heating to 500 °C at a rate of 10 °C/min, kept for 2 h in a total flow of 100 cc/min containing 79% He and 21% O_2, cooled to 200 °C, and adsorbed for 1 h at 200 °C in a total flow of 100 cc/min containing 3000 ppm NO and 8% O_2 in He. After flushing with He at 200 °C for 1 h to remove physisorbed species, the catalyst was heated to 800 °C at 10 °C/min under flowing He (100 cc/min STP), while continuously monitoring the reaction products by on-line mass spectrometry (Pfeiffer/Balzers Quadstar QMI422 and QME125). Note that NO is a main product during TPD and that negligible amounts of N_2, NO_2, and N_2O are found [14].

3. Results and discussion

The parallel colorimetric assays of NO_2^- and $NO_2^- + NO_3^-$ (reduced to NO_2^- by hydrazine) for the eight catalyst samples (Figs. 2A and 2B) reveal many of degrees of red, which may be directly related to the NO_x concentration in the extract solution. To confirm the results of the parallel colorimetric assay, LC with an IC-Pak Anion HR column and a UV detector was used to analyze NO_2^- and NO_3^- in the extract. The LC peaks for NO_2^- and NO_3^- were nicely separated within 6 min of operating time, and the peak areas and the calibration curves for standard NO_2^- and NO_3^- solutions were used to quantify the NO_2^- and NO_3^- concentrations in the solution.

To compare and confirm the capacity of the eight catalyst samples to trap NO_x and to use them as probe catalysts for the method developed in the present study, TPD experiments were performed in a quartz tubular fixed-bed microreactor. Ba- or Ca-containing catalysts exhibited unique desorption features with respect to the alumina support (Fig. 3). The amount of NO_x trapped and the adsorption strength (up to 650 °C) increased after alkaline earth metal was added to the catalyst. However, the NO desorption peak of the Pt-containing Ba/AldII catalyst shifted to lower temperatures compared with the catalyst without the noble metal [14]. The amount of NO desorbed from the eight samples was evaluated from the TPD peak area and a standard calibration curve for NO.

Fig. 4 reveals that the NO_x storage capacity, evaluated by the present parallel colorimetric assay, is linear with the time-consuming traditional analysis (i.e., LC and TPD). Furthermore, the nitrogen content of the eight catalysts was quantified by a Vario EL CHN elemental analyzer equipped with an autosampler. Samples of ca. 20 mg rather than the usual 2 mg were used to improve precision. As shown in Fig. 4, the elemental analysis of nitrogen confirmed the validity of the parallel method developed in the present study. It also reflects that the amount of NO_x trapped on the catalyst samples can be completely recovered, including the extraction of NO_x from the samples by water.

Fig. 5 gives the reaction scheme of the parallel assay. Gaseous NO_x is a complex mixture of nitrogen species including NO, NO_2, N_2O_4, and N_2O_3 [15]. These compounds interact with the surface of the catalysts and are chemically adsorbed on its surface. The chemisorbed NO_x species exist in chelating, bridging, linear, bidentate, and monodentate forms [16]. In the TPD study, the NO_x species adsorbed on the catalyst surface are released and decomposed thermally, and the resulting gaseous nitrogen compounds (NO, NO_2, N_2O, and N_2) are identified by on-line mass spectroscopy or gas chromatography.

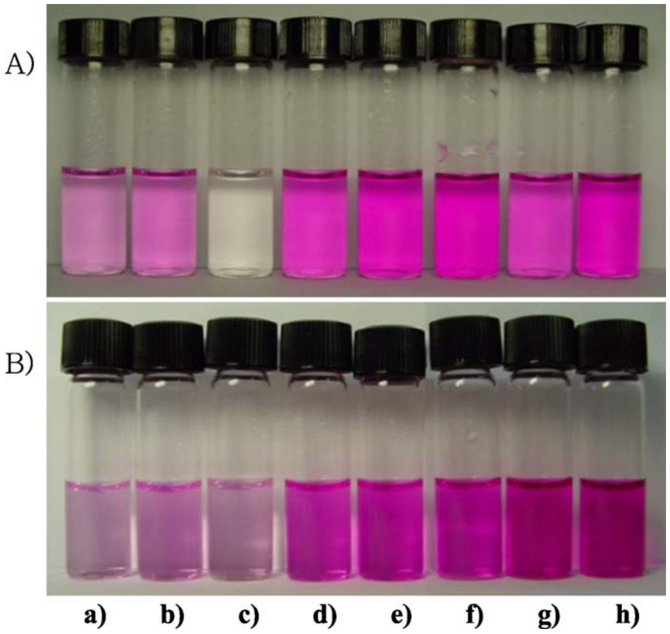

Fig. 2. Colorimetric assay of (A) NO_2^- and (B) $NO_2^- + NO_3^-$ reduced by hydrazine sulfate for (a) AldI, (b) AldII, (c) NaY, (d) 20% Ba/AldII, (e) 1% Pt/AldII, (f) 1% Pt/5% Ba/AldII, (g) 10% Ca/AldII, and (h) 1% Pt/20% Ba/AldII, respectively, through Griess diazotation reaction.

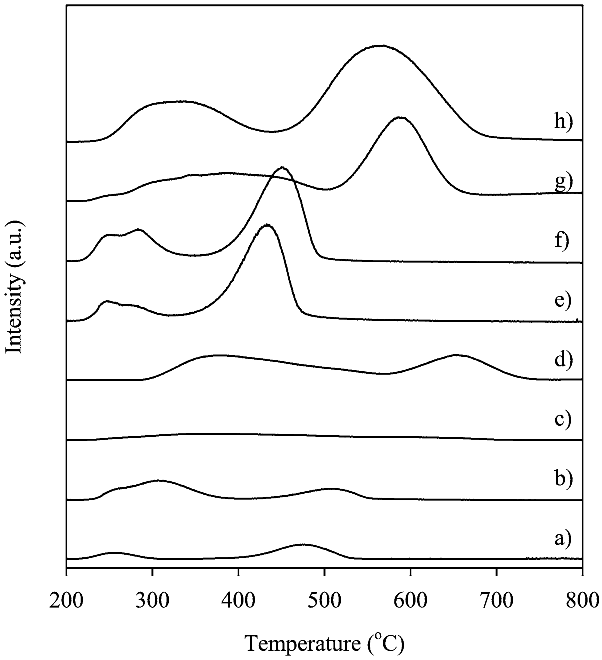

Fig. 3. NO TPD for (a) AldI, (b) AldII, (c) NaY, (d) 20% Ba/AldII, (e) 1% Pt/AldII, (f) 1% Pt/5% Ba/AldII, (g) 10% Ca/AldII, and (h) 1% Pt/20% Ba/AldII.

In the present parallel assay, adsorbed species are dissolved in water and completely converted to NO_2^- and/or NO_3^- anions, depending on the chemical composition of the catalyst. Then they are quickly, inexpensively, and simultaneously measured by a combination of modified hydrazine reduction and colorimetric assay with a Griess reagent. A further test is still underway for a variety of catalysts, including zeolite-type catalysts, to ensure that the method is not specific for the catalyst samples examined here.

The amount of NO_x retrapped by the catalyst sample can be routinely determined by the method developed in the present study after repeating the adsorption and reduction procedure of NO_x, even in a realistic emission gas containing H_2O, CO_2, and SO_2 from the automotive engine. The screening of new NO_x storage catalysts, which are not easily deactivated by SO_2 present in automobile exhaust streams along with NO_x, is ongoing and is relying on the present parallel assay methodology.

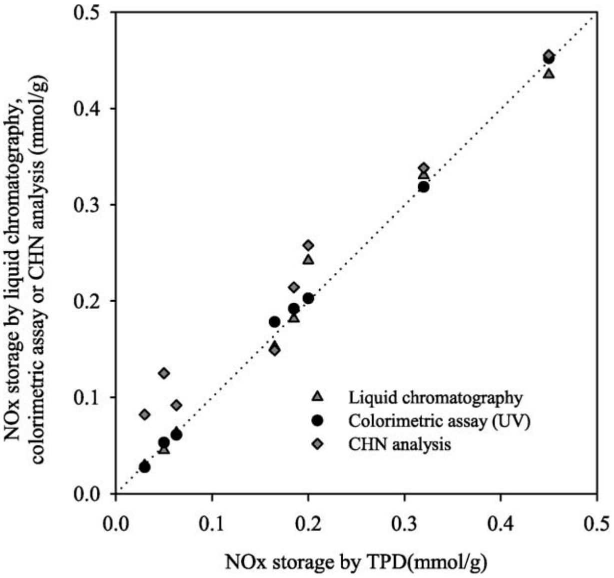

Fig. 4. Correlation of NO_x storage examined by TPD, colorimetric assay (●), liquid chromatography (▲), and CHN analysis (◆).

The conventional TPD experiment for measuring the amount of NO_x adsorbed on a catalyst sample requires at least 6 h, including about 3 h for sample pretreatment, 1 h for adsorption of NO, 1 h for purging the remaining unadsorbed and physisorbed NO, and 1 h for desorption of NO_x. Eight catalyst samples would require at least ca. 48 h, whereas the colorimetric test can be done in ca. 6 h by parallel adsorption, extraction, and colorization. The present method would be most efficient for measuring hundreds of samples.

The time dependence of the amount of NO_x trapped by the catalyst is such that storage of NO_x on the catalysts is nearly complete within 20 min and is strongly promoted by the addition of Pt to the catalyst, particularly the alumina-based catalyst (Fig. 6). Barium and calcium also improve the total NO_x storage capacity of the catalyst. This may be simply due to the enhanced oxidation of NO to NO_2 on platinum, as well as the storage capacity of NO_x on alkaline or alkaline earth metals. This also justifies the adsorption time of NO_x (1 h), as used in the present parallel method.

4. Conclusion

A fast parallel method has been developed for evaluating the NO_x storage capacity of automotive catalysts. Most NO_x species adsorbed on the catalyst surface are readily desorbed in water as NO_2^- and/or NO_3^- anions. The parallel fast screening method developed in the present study may result in new guidelines for the design of a “better” NO_x storage catalyst for application in next-generation vehicles equipped with advanced lean-burn engines.

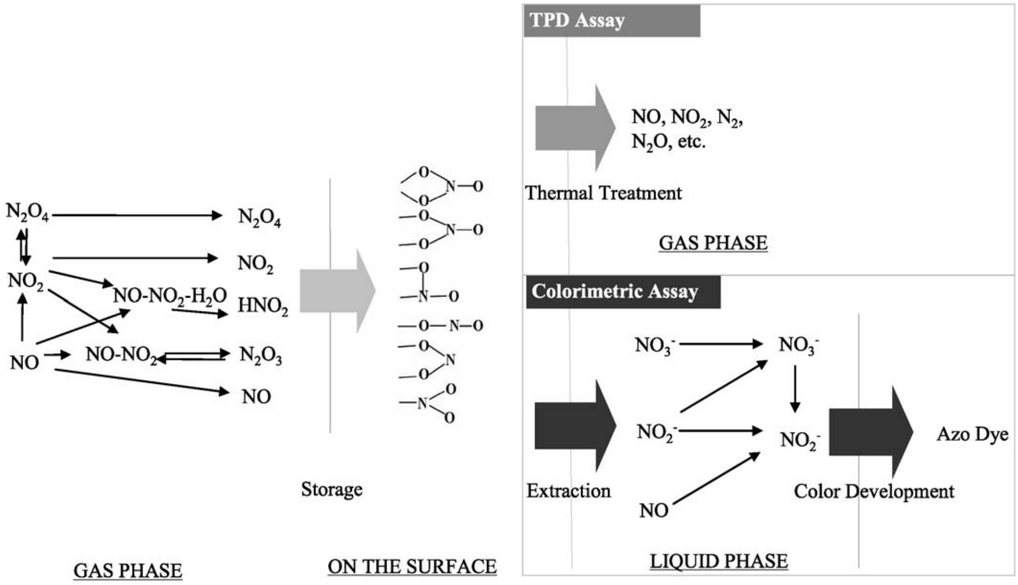

Fig. 5. Diagrams of adsorption and detection of NO_x.

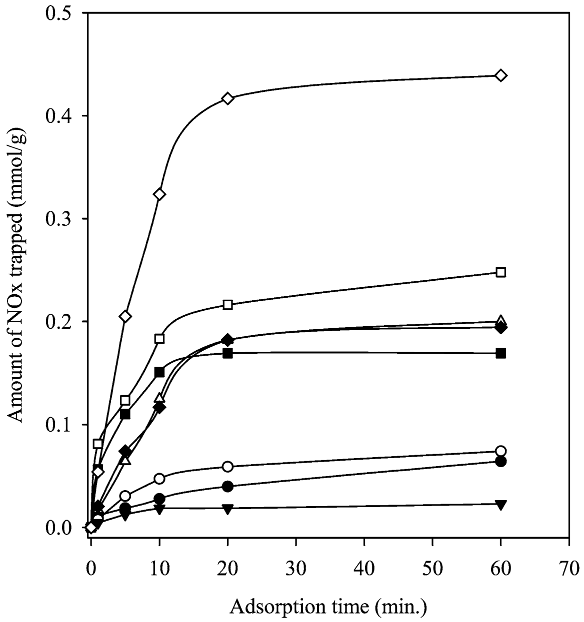

Fig. 6. Amount of trapped NO_x evaluated by the fast colorimetric assay as a function of adsorption time for AldI (●), AldII (○), NaY (▼), 20% Ba/AldII (△), 1% Pt/AldII (■), 1% Pt/5% Ba/AldII (□), 10% Ca/AldII (◆), and 1% Pt/20% Ba/AldII (◇).

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