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Catalysis Today 62 (2000) 281–289

CATALYSIS TODAY

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Application of combinatorial catalysis to the selective reduction of NO by C_3H_6

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Abstract

Selective catalytic reduction of NO by C_3H_6 was investigated using the tools of combinatorial chemistry under both stoichiometric and fuel-lean conditions. Fifty six quaternary Pt–Pd–In–Na combination catalysts were prepared by impregnating γ-Al_2O_3 pellets with precursor solution mixtures prepared automatically using a micro-jet liquid dispensation system. Performances of the catalysts were evaluated in array microreactors using mass spectrometry in the temperature range 200–550°C. A number of multi-metallic combinations showed excellent NO reduction activities under stoichiometric conditions and over a broad temperature range. However, the performance of the entire library under fuel-lean conditions was poor. © 2000 Published by Elsevier Science B.V.

Keywords: Combinatorial heterogeneous catalysis; High-throughput testing; Mass spectrometry; Array microreactors; Autoexhaust emissions control

1. Introduction

The reduction of NO in combustion effluents is one of the most significant challenges in environmental protection. Present day auto exhaust emission control technologies largely depend on the utilization of three-way catalysts (TWC) to simultaneously reduce the emissions of CO, hydrocarbons and NO*x* [1–6]. TWC primarily utilize 0.1–1 wt.% precious metals such as Pt and Rh combinations or Pd deposited on high surface area carrier material primarily composed of γ-Al_2O_3 and CeO_2/ZrO_2 to serve as the oxygen storage component during the fuel-rich transients of the cyclic engine operation. The γ-Al_2O_3 carrier material is also stabilized by the oxides of rare-earth and alkaline-earth metals, such as La and Ba to maintain high surface areas and structural integrity while experiencing high temperatures and water vapor associated with engine exhaust gases [1–6]. The Pt/Rh ratio in current TWC is also typically kept at 5. Since this ratio is significantly lower than the natural abundance ratio of about 17 [2], the development of catalysts with decreased levels of Rh would have considerable economic advantages. Rhodium has been shown to be primarily responsible for NO reduction activity by CO, H_2 and hydrocarbons, while Pt for the oxidation of CO and hydrocarbons. One of the less expensive precious metals explored for TWC is Pd [5,6]. However, Pd is less resistant to deactivation by poisons such as Pb and S [5,6]. This situation has been improved with increased fuel quality, i.e. reduced Pb and S in liquid fuels, as well as with new catalyst formulations some of which involve multi-layer structures [7]. Nevertheless, the progress on the development of new TWC formulations that will reduce the use of high cost precious metals has been slow. This is not surprising since, in the absence of serendipitous

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0920-5861/00/$ – see front matter © 2000 Published by Elsevier Science B.V.
PII: S0920-5861(00)00430-2

discovery, the parameter space that must be considered in search of new catalytic materials is vast.

Combinatorial catalysis, which only recently became practically feasible, as a result of advances made in micro-fabrication, robotics and instrumentation, promises to significantly accelerate the process of discovery and optimization of heterogeneous catalysts by exploring vast parameter spaces quickly. Combinatorial catalysis is a methodology or a set of tools in which large diversities of compositionally and structurally different materials libraries are prepared, processed and tested for desired catalytic activity and selectivity in a high throughput fashion [8–10]. Recently, we developed closely integrated tools for the preparation and parallel testing of large libraries of catalytic materials [11,12]. Specifically a computerized micro-jet liquid dispensation system was developed for the impregnation-based preparation of catalyst libraries. In addition, we developed array microreactors as library structures for the parallel testing of catalysts using either resonance enhanced multiphoton ionization (REMPI) [11], or mass spectrometry [12] as diagnostics.

In this communication, we report on the application of these combinatorial tools for the preparation and testing of a quaternary Pt–Pd–In–Na catalyst library for the reduction of NO by C_3H_6 under both stoichiometric and lean conditions. We chose platinum and palladium because of reasons indicated earlier. Sodium has been shown to be a good promoter under non-oxidizing environments for NO reduction [13–15], and indium has previously been reported to be an active element on a different support material under lean exhaust conditions [16,17]. It should be noted, however, that because combinatorial methodologies allow the rapid creation and screening of catalytic libraries, one can easily choose to evaluate unexplored elements in the periodic table as well.

2. Experimental

2.1. Catalyst preparation

A 56 member quaternary catalyst library composed of Pt, Pd, In, and Na as active components were prepared by impregnating γ-Al_2O_3 pellets with precursor solutions prepared by computer-controlled micro-jet dispensation technique. This was accomplished by dissolving H_2PtCl_6, $PdCl_3$, $InCl_3$ and $NaNO_3$ compounds in deionized water to prepare stock solutions. Relative concentrations of each component in the solution were adjusted so that Pt, Pd, and In loadings (wt.%) in the final catalyst pellets were in the range 0–1% with 0.2% increments, whereas Na loadings were kept in the 0–10% range with 2% increments. After dispensing appropriate amounts of precursor solutions to the solution library well plate, each site was diluted to 50 μl with deionized water, after which 30 mg γ-Al_2O_3 pellets (4 mm diameter by 1 mm high cylinders) were introduced into each well. Impregnation was allowed until all of the solution evaporated at room temperature. A picture of the liquid dispensation and impregnation system is shown in Fig. 1. After impregnation, the entire library was dried for 2 h at 90°C, and for another 2 h at 120°C. The library subsequently was calcined for 4 h at 600°C under an air atmosphere. Pellets were then placed into the array microreactors and reduced under H_2 for 2 h at 350°C at 60,000 GHSV prior to testing.

2.2. Catalyst testing

Details of the catalyst testing system have been described before [12], thus, only a brief description will be provided. Catalyst testing was accomplished using four microreactor arrays that were placed inside a temperature controlled heating block. Each array contains 20 parallel channel microreactors, thus, it was possible to simultaneously test 80 different catalysts. In the present experiments, duplicates of selected combinations of catalysts as well as plain γ-Al_2O_3 pellets were used to fully utilize the availability of 80 test channels. Reactor effluents were analyzed for NO, C_3H_6 and CO_2 by withdrawing small samples from the microreactor exit using a capillary sampling probe followed by gas analysis by on-line mass spectrometry. The reactor block was placed on a computer controlled *x-y-z* movement mechanism, thus it was possible to automatically and sequentially analyze the exhaust streams of each reactor channel. The complete analysis of the entire library took about an hour.

Reactor feed gas compositions were kept at 3500 ppm of NO and 3500 ppm C_3H_6 while the O_2 levels were changed to be at 1.575, 4 and 10% O_2

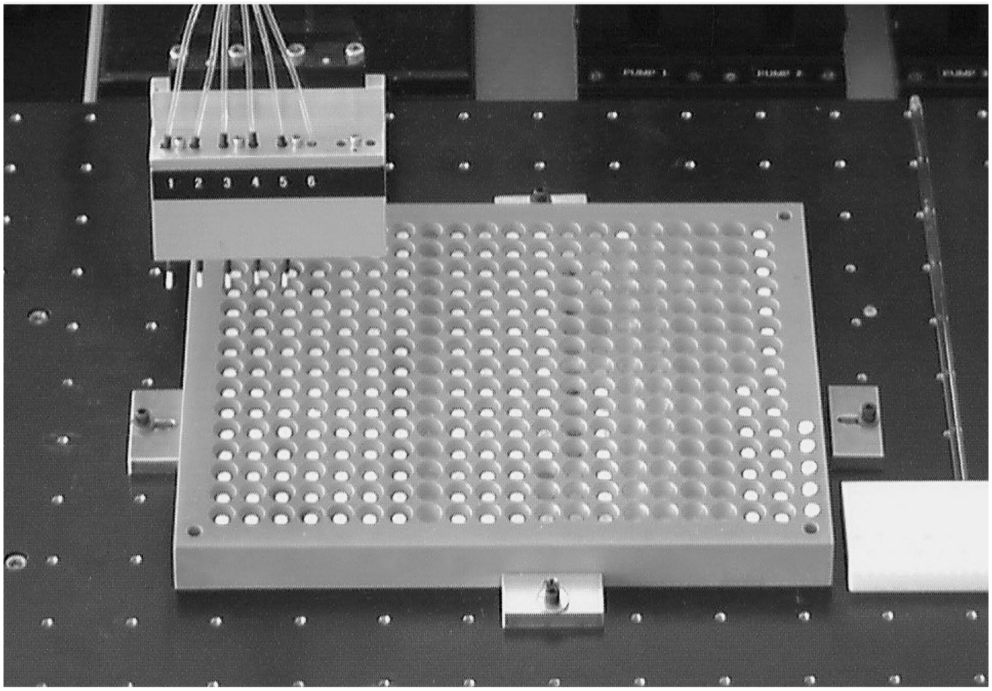

Fig. 1. Catalyst library preparation using micro-jet solution dispensation and impregnation.

in helium. These oxygen concentrations correspond to stoichiometric and different extents of fuel-lean conditions, respectively. Premixed gases of NO and C_3H_6 in helium were acquired from standard sources (Matheson, Cucamonga, CA). Gas flow rates were regulated by digital mass flow controllers (MKS, Andover, MA). In all of the experiments reported here only dry feed was used. We recognize that significant amounts of water vapor exist in engine exhaust streams and that this has a major impact on the activities, selectivities and operational lifetimes of catalysts [5,6]. However, since the primary purpose of the present investigation was to demonstrate the viability of combinatorial approach for the discovery and optimization of selective NO reduction catalysts, our efforts were directed towards this direction. The experimental facilities are currently being modified to accommodate water vapor, and future studies will allow the incorporation of this important component in the combustion products.

Total GHSV through each microreactor was kept at about 60,000 h^{-1}, very close to the values used in practical exhaust emission control catalysts. It is particularly interesting to note that in our current array microreactor design gases flow over one of the flat sides of the catalytic pellet [5,6], which is similar to the flow patterns encountered in commercial monolithic TWC. This is in contrast to flow through powder bed designs traditionally used by many investigators.

3. Results and discussion

The selective reduction of NO by C_3H_6 using the quaternary Pt–Pd–In–Na catalyst system was explored by monotonically increasing the temperature in range of 200–550°C in 50°C intervals. The 56 catalyst library, together with duplicates and blank pellets were reduced first under pure H_2 atmosphere at 350°C for 2 h before the experiments were started. Catalyst screening was accomplished by monitoring the NO (mass 30) signal at the reactor exit together with that for C_3H_6 (mass 41). Mass 41 was selected to monitor C_3H_6, as opposed to mass 42, because it provided a better signal quality. The possibility of other species contributing to these mass signals were also considered, but determined to be insignificant under the stoichiometric conditions investigated. Under fuel-lean conditions, the possible formation of NO_2 as a product may also contribute to NO signals at mass 30, caused by the electron impact fragmentation of NO_2. However, since both NO and NO_2 are pollutants, monitoring mass 30 still represents a good primary screening diagnostic signal for NO*x* emissions.

It may be possible to form ammonia in the reduction of NO with olefins [18]. Unfortunately, the NH_3 signal (mass 17) would be masked by a strong signal from the OH fragment (mass 17) from water (mass 18) which is also produced during the reaction. However, the 17/18 mass ion ratios were noted to correspond to that for water, suggesting insignificant ammonia production in our experiments. Clearly, once promising catalysts are identified using this quick screening methodology, further tests would be needed to ascertain the formation of byproducts.

In Fig. 2 the actual results of one screening test are presented at a temperature of 350°C. In this figure, the mass abundances are presented in terms of arbitrary units as a function of microreactor channel number or time. Signal peaks correspond to levels present in the reactor effluent and sharp increases and/or decreases represent signals acquired during the transit of the capillary probe from one channel to another. As evident from Fig. 2, decreases in NO signals are always associated with decreases in the C_3H_6 signal, clearly suggesting the close coupling of these species in the NO reduction process. On the other hand, for some catalysts while the C_3H_6 signals were significantly decreased, no reduction in the NO signals was observed. An example of this behavior can be seen in channel 19. Evidently, some catalysts were very efficient towards oxidizing C_3H_6, thereby depriving the NO reduction reaction for the necessary hydrocarbon species. The CO_2 mass signals (mass 44), that are also presented in Fig. 2 clearly support this picture. In the present experimental protocol, the microreactors at the ends of the arrays were always left blank, i.e. channels 1, 20, 21, 40, 41, 60, 61 and 80. This led to no conversion of NO and C_3H_6, and no CO_2 formation at these channels, as can be seen in Fig. 2.

In Fig. 3, the microreactor exit concentrations of NO are presented for the quaternary Pt–Pd–In–Na catalyst library at different reaction temperatures for the stoichiometric conditions (i.e. 1.575% O_2 in the

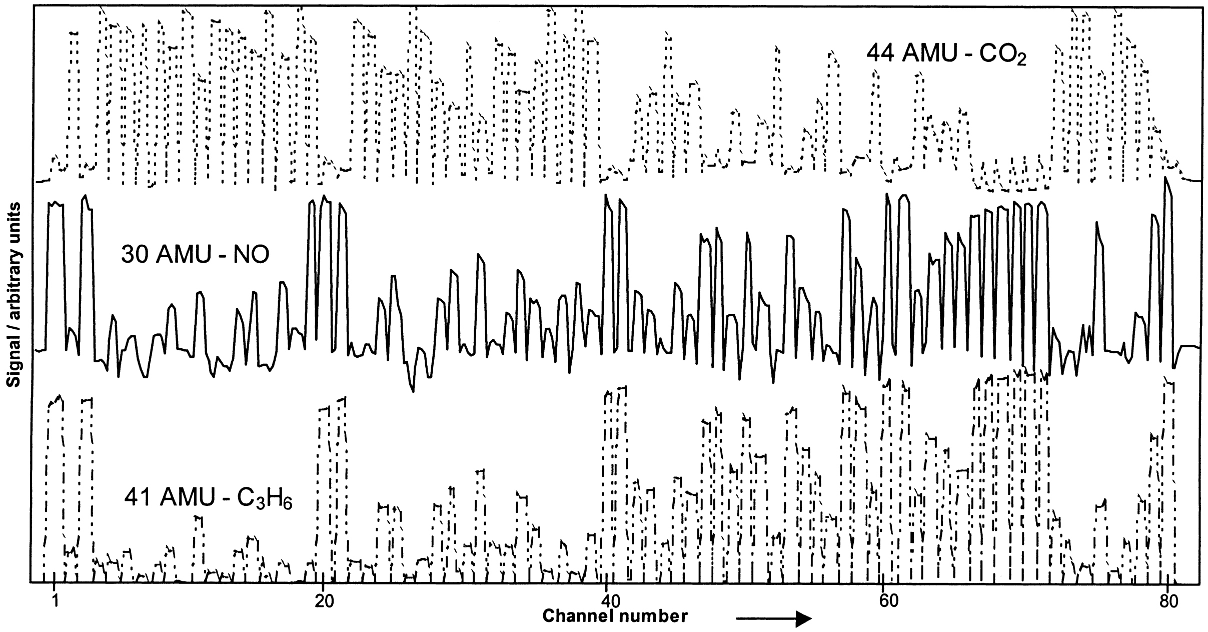

Fig. 2. Signal intensities for NO, C_3H_6 and CO_2 at the microreactor exit as a function of channel number.

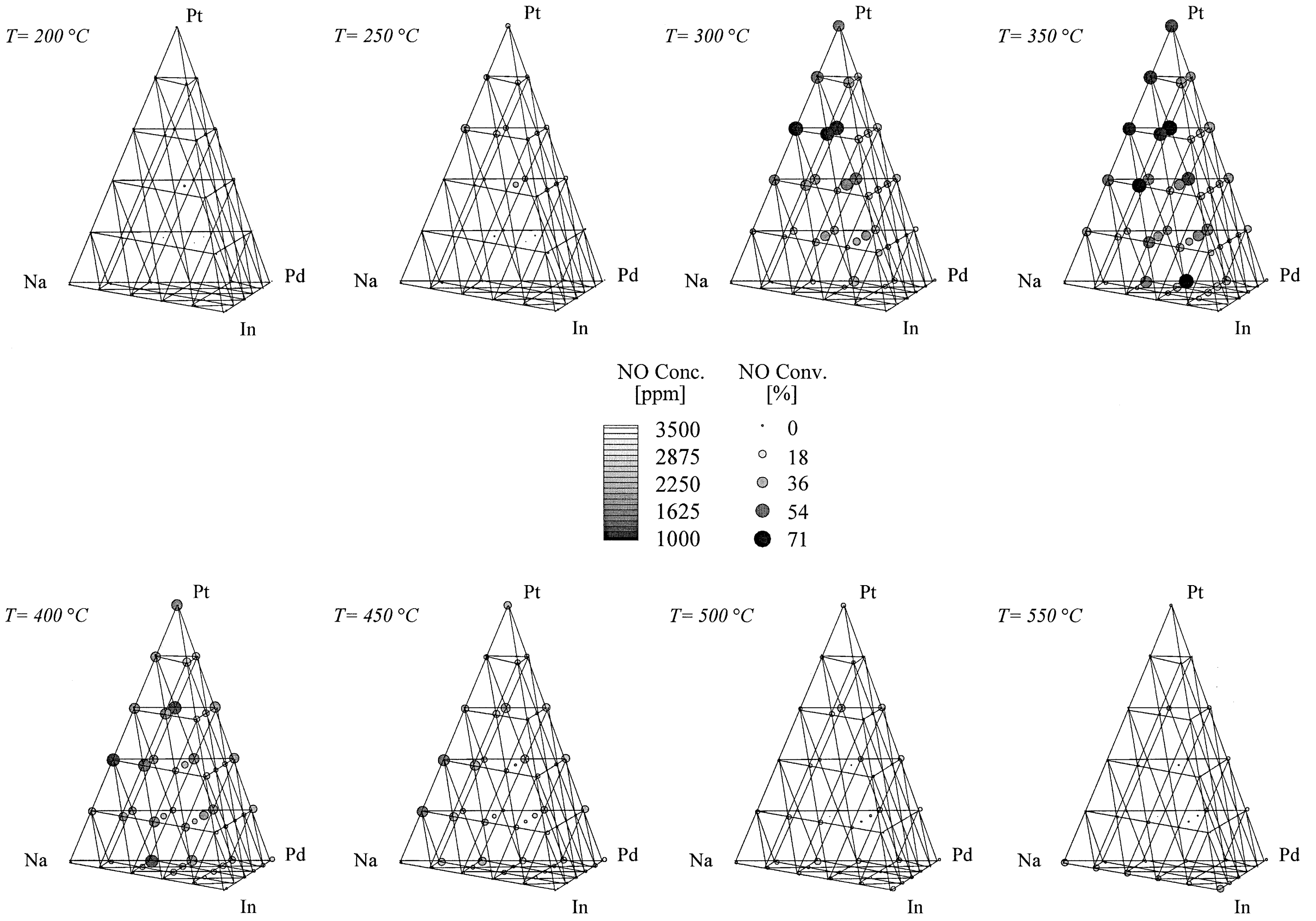

Fig. 3. NO concentration and conversion (gray scale and spot size) at the exit of the array microreactors as a function of catalyst formulation and reaction temperature under fuel-rich conditions.

feed). In this figure, different library compositions are represented as discrete coordinates on the equilateral tetrahedron, in accordance with the preparation method described earlier. Each corner of the tetrahedron corresponds to pure elements as indicated. Exit NO concentrations are represented as variations in gray scale and size from small white circles (3500 ppm, no conversion) to large black circles (1000 ppm, corresponding to about 75% conversion) in accordance with the legend also shown in Fig. 3. Consequently, catalysts that exhibit increasingly darker and larger circles are better performers as far as NO reduction process is concerned.

An examination of Fig. 3 indicates several significant features. First, the NO reduction activities of the catalyst formulations, when present, increased first and then decreased with increase in temperature. This feature can easily be seen in Fig. 3 by the appearance and then disappearance of black circles upon increase in temperature. This trend is in complete agreement with the literature and our current understanding of the interplay that exists between the reactions with NO and combustion of hydrocarbons [19]. The examination of the reactor exit levels of C_3H_6 and CO_2, presented in Figs. 4 and 5, respectively, suggest that C_3H_6 combustion to CO_2 is largely responsible for the observed decrease in NO reduction activity at high temperatures. As noted earlier, the oxidation of hydrocarbons ultimately starves the NO reduction process of the much-needed hydrocarbon, thereby decreasing the NO conversion at higher temperatures.

Second, multi-component formulations, in general, provided superior NO reduction performances compared to single component Pt and Pd catalysts under stoichiometric conditions. As evident from the results presented in Fig. 3, 1% Pt alone exhibited peak activity of about 60% in the 300–400°C range, while Pd itself showed almost no NO reduction activity over the entire temperature range studied. Single component In and Na catalysts showed very little activity and only at temperatures 500–550°C, and this activity may even be associated with the activity of the support material. However, Na exhibited a significant promotional effect around 2–4% loading in a number of multi-component catalyst formulations in the temperature range of 300–450°C. The promotional effect of Na has been attributed to the increased strength of the Pt–NO chemisorption, concomitant with the weakening of the N–O bond [13–15]. Consequently, the dissociative chemisorption of NO proceeds easily on Na promoted surfaces. Clearly, such a mechanism would be valid when NO and C_3H_6 compete for the surface sites, as would be the case in stoichiometric systems.

A closer examination of Fig. 3 also reveals that the catalyst formulation of 0.6% Pt, 0.2% Pd and 2% Na had the best NO conversion performance under the stoichiometric conditions investigated, resulting in nearly 75% reduction at 350°C. This is a result which is considerably better than the 60% conversion observed with the 1% Pt catalyst. The fact that improved NO reduction can be achieved with a catalyst having a lower loading of Pt is significant towards reaching the goal of reducing the cost of TWC for commercial applications. It is also important to note that under the conditions considered, the multi-component catalyst formulations had superior performance compared to the 1% Pt catalyst over a broader temperature range.

In Figs. 4 and 5, the exit concentrations of C_3H_6 and CO_2 are presented. The comparison of these figures with Fig. 3 also reveal insights regarding the role C_3H_6 plays in the selective catalytic reduction of NO. Most importantly, catalysts that were good hydrocarbon oxidation catalysts were poor NO reduction catalysts, a result that is in complete harmony with existing literature [19]. Since most metallic catalysts become increasingly more effective towards combustion at high temperatures, their effectiveness toward NO reduction decreases with increasing temperature. It is important to note that N_2O may also form and therefore can contribute to mass 44 in the present experiments. In fact, the lack of perfect correlation between C_3H_6 disappearance (Fig. 4) and CO_2 appearance (Fig. 5) may be attributed to this event. It should be noted that, some CO can also form under the conditions investigated; this can also adversely affect the correlation between C_3H_6 and CO_2 signals.

A close inspection of the results presented in Figs. 3–5 reveal that pellets containing binary combinations of Na and In were poor catalysts both for NO reduction and C_3H_6 conversion. Yet both Na and In were useful promoters in Pt and Pd formulations. It was particularly interesting to note the behavior of the 0.2% Pt and 8% Na catalyst for C_3H_6 combustion. At lower temperatures, this catalyst exhibited increasing combustion activity with increasing temperature. However, after 500°C, its conversion activity

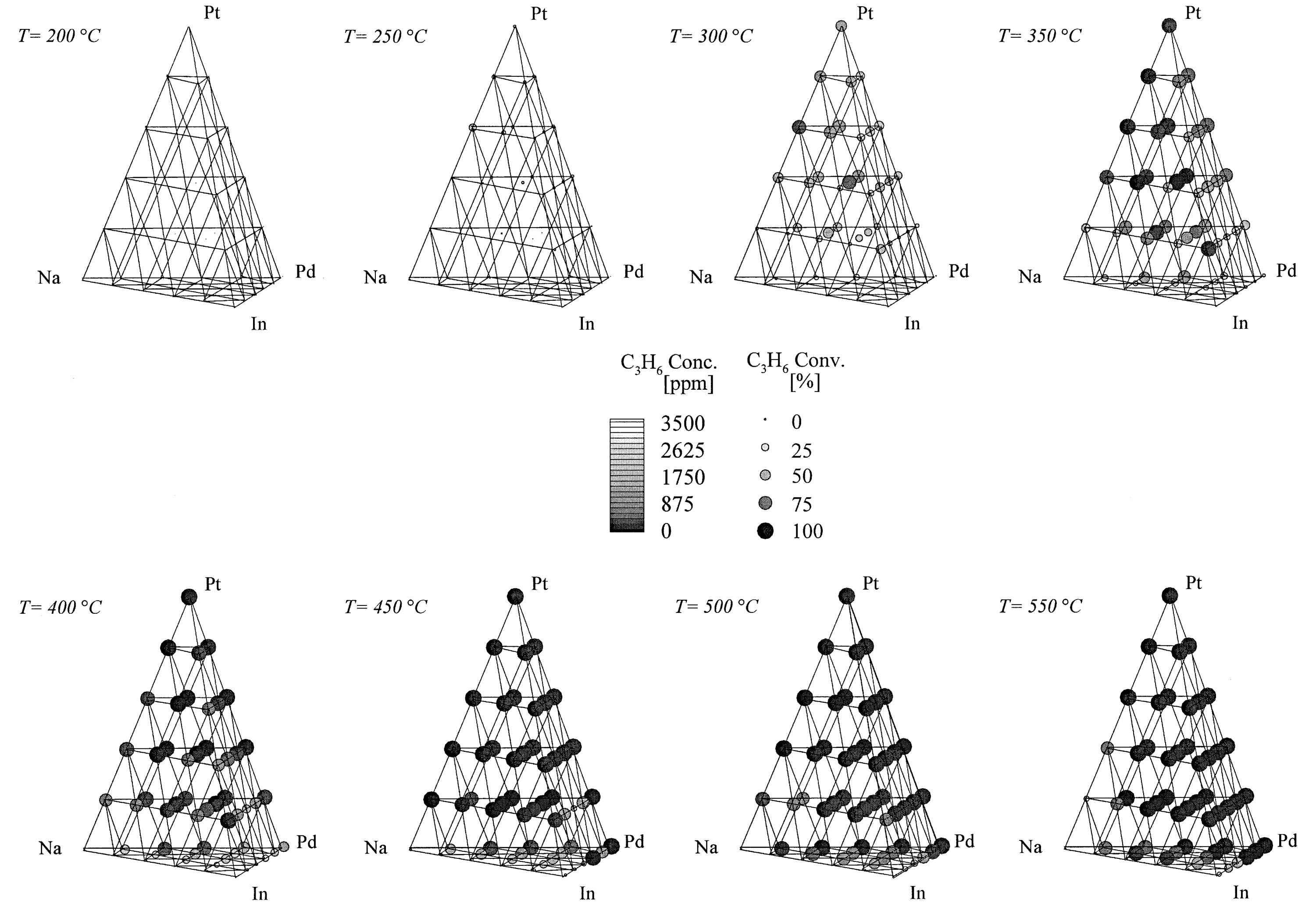

Fig. 4. C_3H_6 concentration and conversion (gray scale and spot size) at the exit of the array microreactors as a function of catalyst formulation and reaction temperature under fuel-rich conditions.

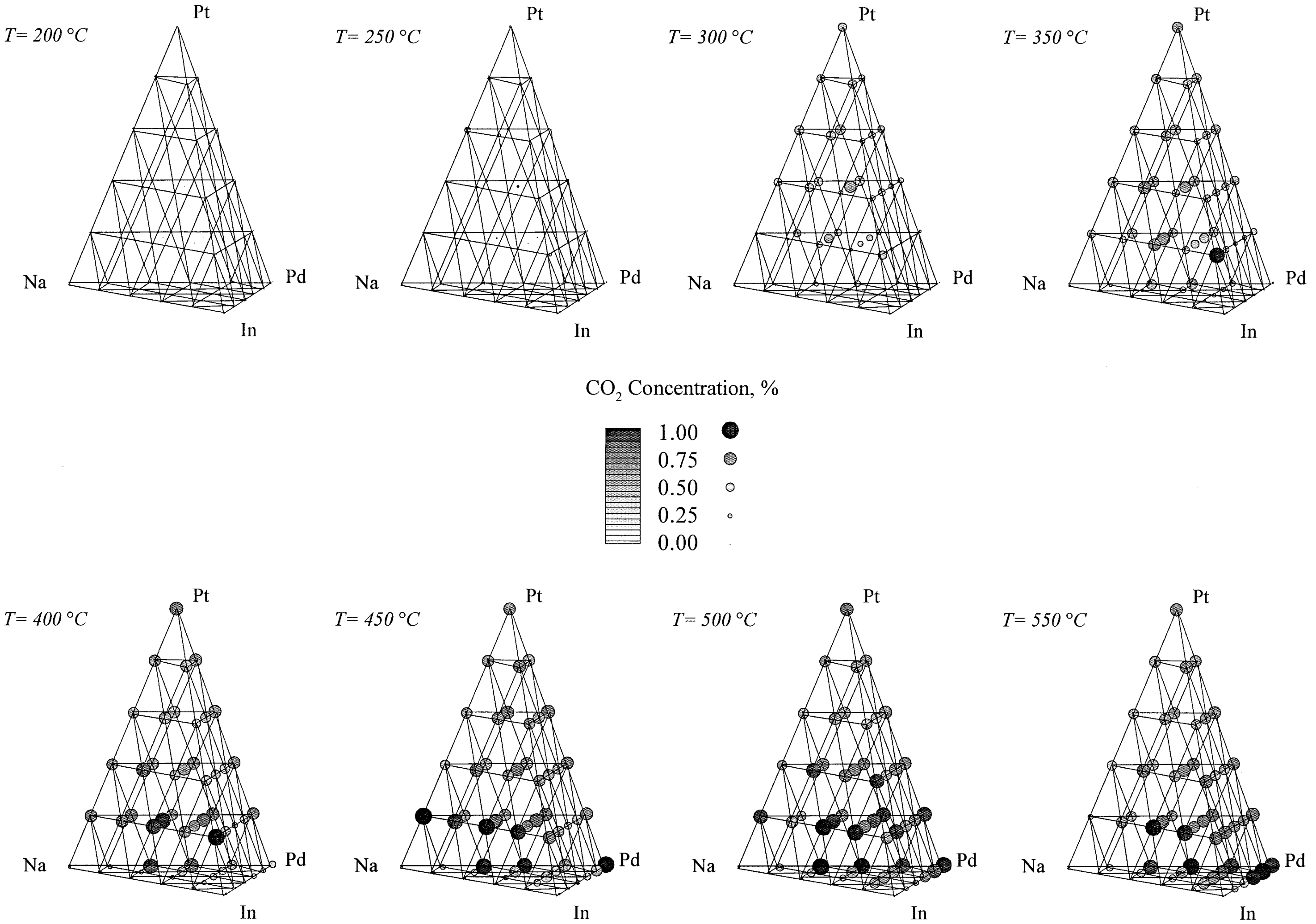

Fig. 5. CO$_2$ concentration (gray scale and spot size) at the exit of the array microreactors as a function of catalyst formulation and reaction temperature under fuel-rich conditions.

diminished. This is an intriguing result that calls for further investigation. The observed deactivation can be due to a number of reasons, including coke formation, sintering, and changes in catalyst morphology and crystal structure, and a variety of surface science techniques can be used to establish the underlying reasons for this.

Similar experiments were also undertaken in the presence of 4 and 10% O_2 in the feed representing different extents of fuel-lean combustion. In both cases, the presence of excess oxygen in the feed had an adverse effect on NO reduction. None of the catalysts exhibited NO reduction activity that was better than 30%, suggesting the absence of Na promotion under fuel-lean conditions. Under fuel-lean conditions, the presence of excess oxygen would be expected to effectively compete and occupy the catalytic sites, thereby inhibit NO chemisorption and thus, result in decreased NO reduction. It should be noted, however, that the Pt–Pd–In–Na library prepared can be a useful starting point to further develop improved lean-burn NO reduction catalysts using a variety of optimization techniques, such as genetic algorithms [20].

Acknowledgements

This research was supported, in part, by the National Science Foundation.

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