Highly reliable 64-channel sequential and parallel tubular reactor system for high-throughput screening of heterogeneous catalysts

Kwang Seok Oh
Department of Chemical & Biomolecular Engineering and Center for Ultramicrochemical Process Systems, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong Yuseong-gu Daejeon, 305-701, Korea

Yong Ki Park
Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, Yuseong. P.O. Box 107, Daejeon, 305-600, Korea

Seong Ihl Woo[a)]
Department of Chemical & Biomolecular Engineering and Center for Ultramicrochemical Process Systems, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong Yuseong-gu Daejeon, 305-701, Korea

Highly reliable 64-channel sequential and parallel tubular reactor for high-throughput screening of heterogeneous catalysts is constructed with stainless steel. In order to have a uniform flow rate at each channel, 64 capillaries are placed between the outlet of multiport valve and the inlet of each reactor. Flow rate can be controlled within ±1.5%. Flow distribution can be easily adjusted for sequential and parallel mode of operation. The reactor diameter is too big to have a uniform temperature distribution. Hence, the reactor body is separated into three radial zones and controlled independently with nine thermocouples. Temperature accuracy is ±0.5 °C at 300 °C and ±1 °C at 500 °C in sequential mode, while it is ±2.5 °C in the range of 250–500 °C in parallel mode. The temperature, flow rate, reaction sequence, and product analysis are controlled by LABVIEW™ software and monitored simultaneously with displaying a live graph. The accuracy in the conversion is ±2% at the level of 73% conversion when all reactors are loaded with same amount of catalyst. A quaternary catalyst library of 56 samples composed of Pt, Cu, Fe, and Co supported on AlSBA-15 (SBA-15 substituted with Al) are evaluated in the selective catalytic reduction of NO at various temperatures with our system. The most active compositions are rapidly screened at various temperatures. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1927076]

I. INTRODUCTION

High-throughput screening (HTS) is drawing more attention in fast lead discovery for novel functional materials than ever. This concept was used initially by Hanak to search for a new semiconductor about 30 years ago.[1] Now, combinatorial methods originally developed to find new drugs are also applied in finding advanced functional materials and catalysts. Schultz and co-workers demonstrated the application of high-throughput experimentation (HTE) in the search of solid material libraries for superconductivity and magnetoresistance.[2,3] Those investigations initiated the application of HTE in material sciences[4] and later also in heterogeneous catalysis.[5]

Reliable multichannel reactors must be used for evaluation of large catalyst libraries in parallel or sequential mode. There are two kinds of HTS: primary and secondary screening. Primary screening system allows the sequential and parallel testing of catalyst libraries of more than 100. The accuracy of this screening can be high enough to have a reasonable relative ranking of the library. On the other hand, secondary screening reactor set up allows the testing of a relatively small library less than 100. The accuracy of secondary screening should be close to that of conventional one-by-one screening. The various types of reactor systems for high-throughput screening of catalyst libraries have been reported by various research groups.[6–12]

Senkan *et al.*[13] reported an 80 array channel microreactor system coupled to mass spectroscopy (MS). Chen[14] has applied modified electrospray ionization tandem mass spectroscopy for the screening of homogeneous catalysts in polymerization reaction. Symyx[15,16] has developed custom-designed MS equipment to monitor product composition by quadrupole mass spectroscopy. Weinberg and co-workers[15,16] constructed a 48-channel gas phase flow reactor for secondary screening of oxidative ethane dehydrogenation catalyst with monitored by gas chromatography (GC).[17] Schüth and co-workers[18] developed a parallel 49-channel reactor system connected with GC for the screening of methane oxidation catalysts.

A reliable multichannel reactor should satisfy three conditions: accurate amount of catalyst loading, narrow temperature distribution, and uniform reactant flow rate at each

[a)]Author to whom correspondence should be addressed; electronic mail: siwoo@kaist.ac.kr
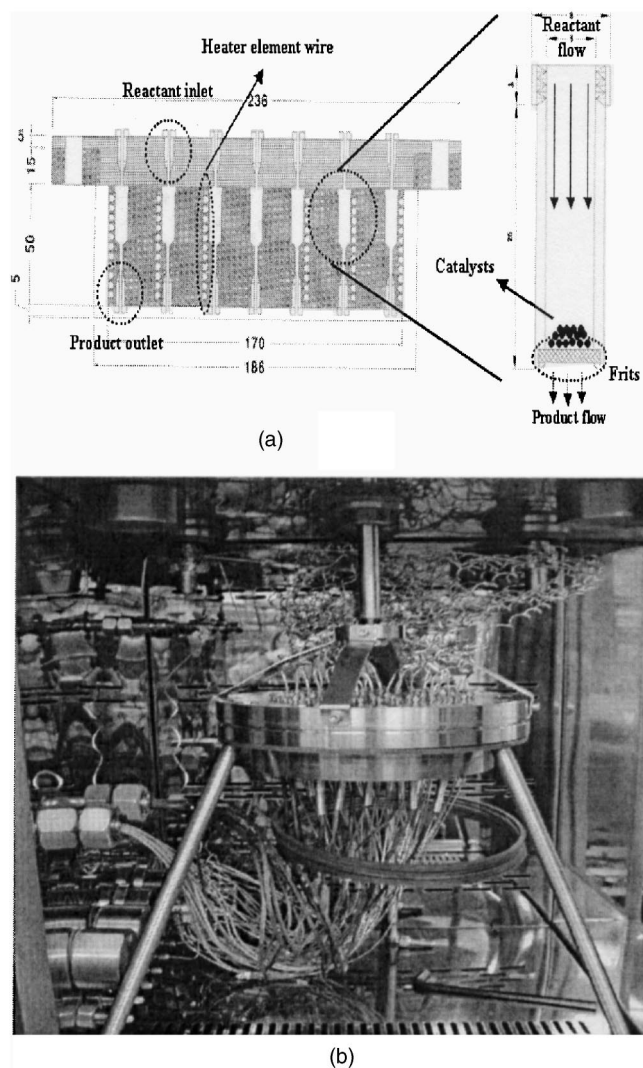
FIG. 1. A schematic drawing of the 64-channel reactor (a) and photograph of reactor.
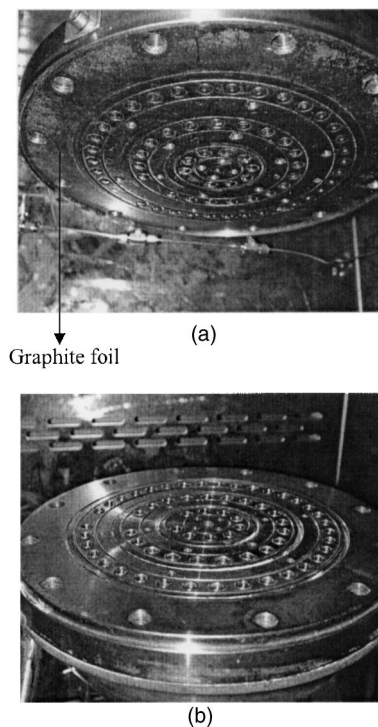

FIG. 2. Removable reactor cover (a) and view of reactor top (b). Graphite foil attached at removable reactor cover is shown in (a) and the edges for complete sealing between graphite foil and removable reactor cover is shown in (b).

channel. Senkan *et al.*[13] prepared a catalyst pellet to control the amount of catalyst loading and for easy mounting. This mounting with a pellet suffers from the channeling of reactant gases, in which a significant amount of reactant gases pass through without contact with the catalyst. This will give a serious error in determining the true catalytic activity. It is highly recommended to use a cartridge for exact weighing of catalyst powder, as reported by Schüth and co-workers.[18] Our design adopted this method. Lauterbach and co-workers[19] controlled the temperature of each channel with high accuracy, but this type of reactor may have a large size in the case of channels more than 50. Our strategy is that the large body of a reactor adopts three-zone heating with the temperature control with the thermocouples nearest to the channel. For the uniform flow rate, each channel was connected to a capillary tube to induce a large pressure drop. In the sequential mode of operation, all the channels except the channel that is used as a reactor were flowed with inert gas not to deactivate the catalyst. The sequential mode of operation can be changed to parallel mode by reversing the initial inlet position of the mixture and inert gas tube that is connected to a multiport valve.

In order to demonstrate the performance of our reactor system, we will present the result of selective catalytic reduction (SCR) of NO with C_3H_6 over quaternary metal catalysts supported on mesoporous AlSBA-15. A detailed procedure for catalyst preparation and operation of our reactor system will be also discussed.

II. OVERALL DESCRIPTION OF 64-CHANNEL REACTOR SYSTEM

A schematic drawing of the reactor and photograph of the reactor system are shown in Figs. 1(a) and 1(b), respectively. This multiple reactor configuration is composed of vertically aligned 64 channels that allow the 64 different gas phase reactions to occur in the sequential or parallel mode. The reactor body with a diameter of 170 mm, and a height of 60 mm is made of stainless steel. For easy mounting and exact weighing of catalyst, catalysts powder is placed in 5 mm inner diameter (i.d.) $\times$ 8 mm outer diameter (o.d.) $\times$ 20 mm long the stainless steel cartridge, which are inserted into the bores and sealed against them with a graphite gasket. A metal frit containing 2-μm pores in the bottom of each cartridges supports the catalyst. The top part of cartridge is machined to have a screw, which will make it easy to take out from each channel. A thermocouple for measuring the reaction temperature is placed at nine positions in whole reactor body. Sealing between the top of the reactor body and the removable reactor cover is secured by using SI-GRAFLEX® graphite foil (SGL technology, thickness of 2 mm), as shown in Fig. 2(a). The top of the reactor was machined so that it has sharp edges to secure the seal between the graphite foil and each reactor channel, as shown in
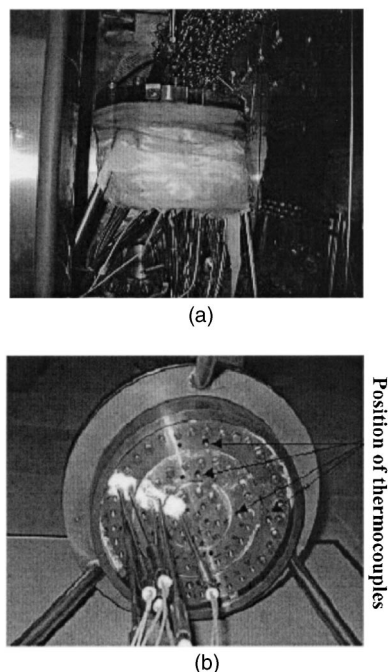
FIG. 3. (a) View of insulated reactor placed in the center of oven and (b) heating element and the position of thermocouples.

Fig. 2(b). As shown in Fig. 3, heating elements are connected to bottom of the reactor body and thermocouples are inserted at thermocouple positions. The heads of thermocouples were screw type, which permitted easy mounting. The assembled reactor body was fixed on the tripod and placed in the center of the oven, which is for additional insulation for the high-temperature reaction. Additionally, we wrapped the outside of the reactor with glass fiber to minimize heat loss.

A. Control of flow rate and operation mode

In order to compare the catalytic activity exactly in each reactor channel, basically the same reaction condition must be maintained until the reaction is finished. The reactant flow rate is one of the most important experimental parameters affecting the conversion. In order to maintain the same flow rate at each reactor channel, a capillary with 1.6 mm o.d., 0.12 mm i.d., and 500 mm long is attached to all the reactor channels via fittings (1/16 in., Valco Instrument Co.) from the removable reactor top to a 16-port two-position valve (SC type, Valco Instrument Co.). In this case, the capillary served two functions. One is that the capillary induced a pressure drop, thus providing an additional flow resistance to have a uniform flow rate at each channel. The other is that they allow the removable reactor top to be moved a long distance from the multiposition valve, which prevents the multiposition valve from being heated over the maximum allowable temperature (200 °C) even though the temperature of the reactor body is above 450 °C. The actual flow rate of each channel controlled at 10 cc min^{-1} of He is shown in Table I. The deviation of the flow rate at each reaction channel is within 0.3 cc min^{-1}. The flow rate varies from 0 to 40 cc min^{-1} within an error of 1.5%.

The operation of the multichannel reactor can be easily adjusted to sequential mode or parallel mode by selecting three-way valves. The parallel mode allows permanent on-stream of reactant gases to all the channels; in this way time-on-stream activity measurement can be performed. On the other hand, only one channel is flowed with reactant and the others are flowed with inert gas at the operation of the sequential mode. An initial deactivation rate measurement can be performed in this mode. Compared with our multiple reactor, the inlet system of multiple reactor reported by Baerns and co-workers[10] and Schüth and co-workers[18] was designed to distribute the flow rate through one common inlet. This inlet system guarantees the homogeneous flow rate of each reactor channel with the capillary behind the reactor, but cannot allow to flow inert gas to the inactive reactor channel. The selection of sequential and parallel mode depends on the type of analytical instrument. Since we focused on exact evaluation of product gas from DeNO$_x$ reaction as a case study, we have chosen to employ GC and mass spectroscopy.

TABLE I. Flow rate distribution of each reaction channel (flow rate: He 10 cc min^{-1} at each reaction channel).

| Channel number	Flow rate (cc/min)	Channel number	Flow rate (cc/min)	Channel number	Flow rate (cc/min)	Channel number	Flow rate (cc/min)
1	9.9	17	9.7	33	9.7	49	9.8
2	9.9	18	9.8	34	9.8	50	9.9
3	9.8	19	9.9	35	9.9	51	9.9
4	9.7	20	9.8	36	9.8	52	9.7
5	9.9	21	9.8	37	9.8	53	9.7
6	9.7	22	9.9	38	9.9	54	9.9
7	9.8	23	9.7	39	9.7	55	9.8
8	9.8	24	9.8	40	9.8	56	9.8
9	9.8	25	9.8	41	9.7	57	9.8
10	9.7	26	9.9	42	9.8	58	9.9
11	9.7	27	9.9	43	9.9	59	9.9
12	9.9	28	9.7	44	9.8	60	9.7
13	9.9	29	9.7	45	9.8	61	9.7
14	9.8	30	9.9	46	9.9	62	9.9
15	9.7	31	9.8	47	9.7	63	9.8
16	9.7	32	9.8	48	9.8	64	9.8
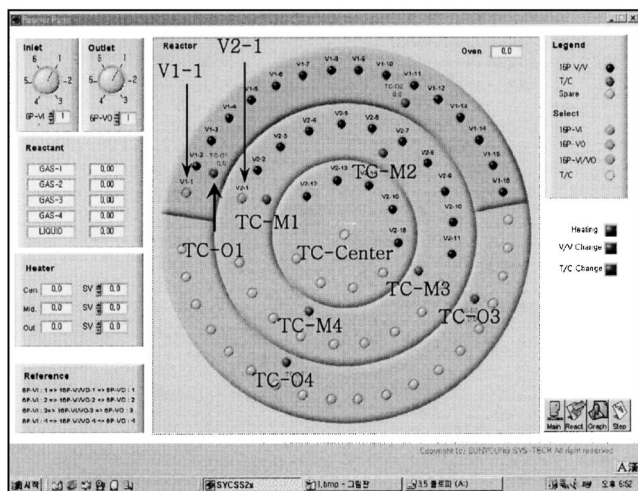
FIG. 4. Main screen of our HTS system in LABVIEW software. [V1-1 to V1-16 correspond to channels 1–16 and V2-1–V2-16 correspond to channel 17–32, thermocouple (TC) is assigned to TC-O1, O2, O3, and O4 placed in the most outer part of reactor, TC-M1, M2, M3, and M4 placed in the middle of reactor, and TC-center in the center of reactor.]

These instruments can be operated with only the sequential mode. Therefore, the catalytic properties of each channel reactor are sequentially evaluated.

B. Temperature control

The large size of the reactor makes it hard to maintain a homogeneous temperature profile over the whole range of the reactor. We divided the reactor into three heating zones inserted with highly heat conductive materials to avoid inhomogeneity of the temperature profile. Temperature is measured via nine thermocouples placed on reactor body, which gave a feedback to the power supply to control the temperature with nine independent proportional, integral, and derivative controllers. These nine thermocouples allowed more accurate temperature control in parallel and sequential modes than other similar types of multichannel reactors,[10,18] because the reaction temperature of the reported reactor is controlled individually by only 3–4 thermocouples placed in each concentric ring of the reactor channel. As shown in Fig.

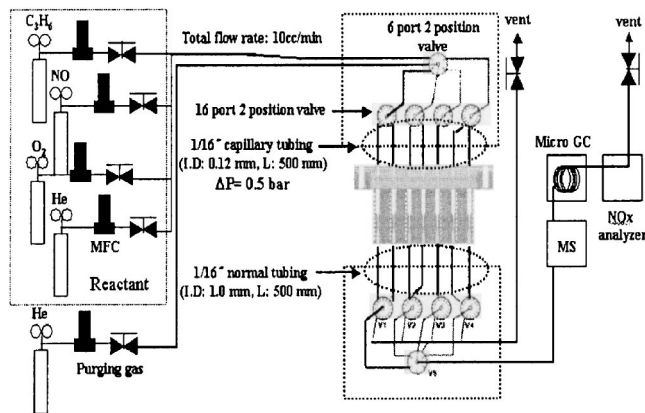FIG. 5. Time schedule control panel for high-throughput screening.

FIG. 6. Schematic diagram of an experimental apparatus for measuring an activity of catalyst library.

4, the thermocouples are placed in the middle circle (TC-M#, # is indicating the number), outer (TC-O#) circle of reactor, and center circle of reactor (TC-center). A circle of V1-1 indicates the starting reaction channel, where reaction and analysis are first in the sequential mode operation. V1-1 to V1-16 correspond to channels 1–16 and V2-1–V2-16 correspond to channels 17–32. In order to control the temperature more accurately, temperature control is achieved by TC-O1 when the reaction progresses from channel 1 to channel 6. From channels 7 to 16, temperature control is achieved by TC-O2, TC-M1 is responsible for controlling the temperature of channels 17–19, TC-M2 is for channels 20–25, TC-M3 is for 26–27, and TC-center is for 28–32. As a result, the temperature deviation at 250–500 °C is observed within ±1 °C, across the entire reactor channel. Temperature control at parallel mode was easily performed by selection of the temperature control mode in operation software. The raw temperature data of nine thermocouples were first compared, and the software then selected a thermocouple shown to have the highest temperature deviation. Hereafter, the thermocouple of interest was adjusted to the desired temperature. In this way, the temperature deviation was ±2.5 °C at 250–500 °C at parallel mode. The temperature of all the thermocouples was recorded and several temperature data points per second were monitored for all nine thermocouple simultaneously while displaying a live graph.

C. Operation of the reactor system by LABVIEW™ software

Our reactor system runs automatically by commercial LABVIEW software. Current temperature and flow rate can be monitored, controlled, and stored. All information about catalyst testing is saved to a MS-EXCEL™ file until the reaction is finished. The time schedule option is adopted to operate the reactor efficiently. The time schedule option controls the sequence of the experiment and sends a signal to micro-GC for starting the analysis, as shown in Fig. 5. This time schedule requires information on reaction temperature, valve change interval, and GC analysis interval. The operation procedure of typical HTS experiment is done as follows. Channel 1 is a default channel when the software is opened. Reactant gas flows in channel 1 and inert gas flows in the
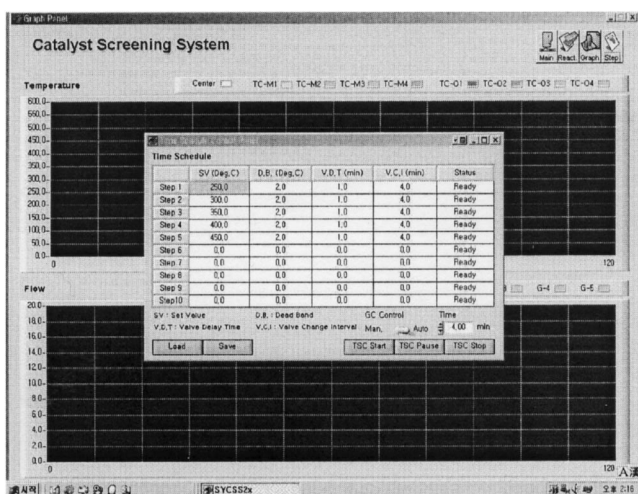
TABLE II. Composition of 56-member library.

Catalyst number	Loading (atomic fraction)				Catalyst number	Loading (atomic fraction)			
	Pt	Cu	Fe	Co		Pt	Cu	Fe	Co
1	0.0	0.0	1.0	0.0	31	0.0	0.6	0.2	0.2
2	0.2	0.0	0.8	0.0	32	0.8	0.0	0.0	0.2
3	0.0	0.2	0.8	0.0	33	0.6	0.2	0.0	0.2
4	0.4	0.0	0.6	0.0	34	0.4	0.4	0.0	0.2
5	0.2	0.2	0.6	0.0	35	0.2	0.6	0.0	0.2
6	0.0	0.4	0.6	0.0	36	0.0	0.8	0.0	0.2
7	0.6	0.0	0.4	0.0	37	0.0	0.0	0.6	0.4
8	0.4	0.2	0.4	0.0	38	0.2	0.0	0.4	0.4
9	0.2	0.4	0.4	0.0	39	0.0	0.2	0.4	0.4
10	0.0	0.6	0.4	0.0	40	0.4	0.0	0.2	0.4
11	0.8	0.0	0.2	0.0	41	0.2	0.2	0.2	0.4
12	0.6	0.2	0.2	0.0	42	0.0	0.4	0.2	0.4
13	0.4	0.4	0.2	0.0	43	0.6	0.0	0.0	0.4
14	0.2	0.6	0.2	0.0	44	0.4	0.2	0.0	0.4
15	0.0	0.8	0.2	0.0	45	0.2	0.4	0.0	0.4
16	1.0	0.0	0.0	0.0	46	0.0	0.6	0.0	0.4
17	0.8	0.2	0.0	0.0	47	0.0	0.0	0.4	0.6
18	0.6	0.4	0.0	0.0	48	0.2	0.0	0.2	0.6
19	0.4	0.6	0.0	0.0	49	0.0	0.2	0.2	0.6
20	0.2	0.8	0.0	0.0	50	0.4	0.0	0.0	0.6
21	0.0	1.0	0.0	0.0	51	0.2	0.2	0.0	0.6
22	0.0	0.0	0.8	0.2	52	0.0	0.4	0.0	0.6
23	0.2	0.0	0.6	0.2	53	0.0	0.0	0.2	0.8
24	0.0	0.2	0.6	0.2	54	0.2	0.0	0.0	0.8
25	0.4	0.0	0.4	0.2	55	0.0	0.2	0.0	0.8
26	0.2	0.2	0.4	0.2	56	0.0	0.0	0.0	1.0
27	0.0	0.4	0.4	0.2					
28	0.6	0.0	0.2	0.2					
29	0.4	0.2	0.2	0.2					
30	0.2	0.4	0.2	0.2					

other channels until reaction temperature is reached to the desired reaction temperature. After the temperature of channel is maintained within ±2 °C from the reaction temperature for 1 min, GC starts to analyze the reaction product from channel 1. This sequence is repeated for all the channel reactors. After the catalysts are tested at the desired temperature, the other reaction temperature is chosen and the whole procedure is repeated as mentioned above. Our software is interfaced with the GC data system by remote control cable; thus, it is possible to trigger the beginning of the GC analysis. The software of the GC data system makes a new file after analysis. Consequently, each run number can be assigned to the position of the channel tested. The GC raw data are saved to an ASCII file containing the peak areas of all the products from two different columns. A schematic diagram of the entire reaction system can be seen in Fig. 6.

III. CASE STUDY OF DeNO$_x$ REACTION

A. Preparation of catalysts

The performance of our reactor systems was verified in the selective catalytic reduction of NO with C_3H_6 over a 56-member of catalyst library. A quaternary catalyst library containing Pt, Cu, Co, and Fe supported on mesoporous AlSBA-15 was prepared as follows.

The synthesis of SBA-15 was carried out in the same manner as reported in literature.[20] 10.0 g of Pluronic P123 was dissolved in 1.6 M HCl solution, heated at 35 °C during stirring, and then 22.0 g of tetraethyl orthosilicate was added in mixture. This mixture was kept at 35 °C for 24 h and
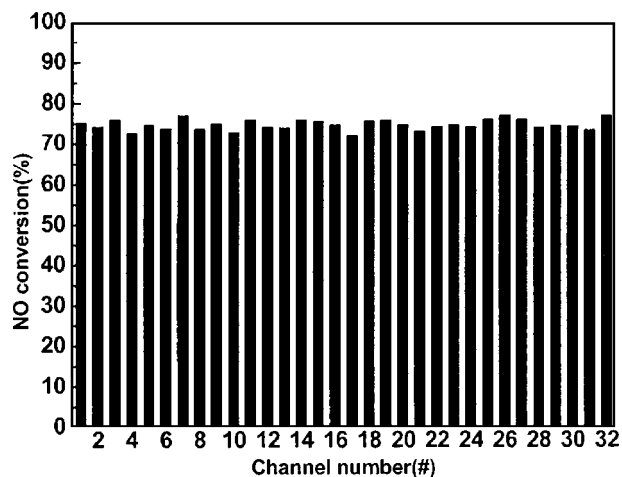

FIG. 7. NO conversion over 1 wt. % Pt/AlSBA-15 at each reaction channel (reaction condition; 2000 ppm of NO, 2700 ppm of C_3H_6, 3.2% of O_2 and He balance, total flow rate 10 cc min^{-1}, weight of catalyst 10 mg, reaction temperature 300 °C).
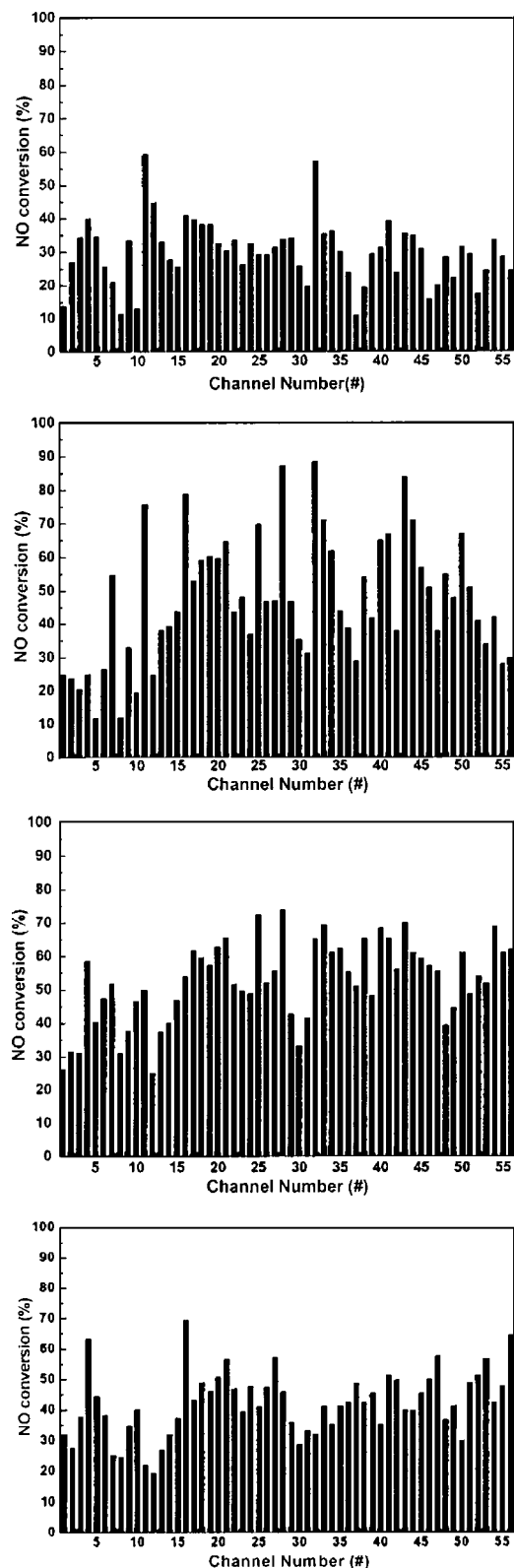
FIG. 8. NO conversion of catalyst sample library between the sample numbers 1 and 56 at various temperatures: (a) 250 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C.

heated to 100 °C for 12 h. After reaction, the resulting gel was dried at 110 °C and added the EtOH+HCl solution (EtOH:HCl=600 ml:2 g) for removing the surfactant with vigorous stirring. Then, synthesized SBA-15 was separated by filtration, followed by repeated washing with EtOH and

subsequent dryness at room temperature in a vacuum oven. After drying, the sample powder was calcined at 500 °C for 3 h under a ramping speed of 1 °C min⁻¹. For calcination temperature was maintained at 400 °C for 3 h to prevent the hexagonal structure from destruction in the process of calcination. The addition of aluminum ions to SBA-15 was carried out by postsynthesis modification method.[21] $Al(NO_3)_3 \cdot 9H_2O$ was used as the precursors of aluminum. This metal precursor was dissolved into distilled water and a predetermined amount of SBA-15 was added to the resulting solution. This slurry was heated at 60 °C under stirring for removal of the water. After removing, the sample powder was dried at 110 °C and calcined in air at 500 °C for 3 h, resulting in AlSBA-15.

Four standard stock solutions of 0.05 M chloroplatinic acid, 0.2 M copper nitrate, 0.2 M iron nitrate, and 0.2 M cobalt nitrate were prepared by dissolving in distilled water. Each stock solution was dispensed into 64 wells containing 10 mg of AlSBA-15 powder using a computer-controlled dispensing system (MicroSys™ SQ, Cartesian).[22,23] Relative concentrations of each component in the solution were adjusted so that the target metal loadings in the final catalyst powders were in the range 0–3 wt. % for all metals. After dispensing, the prepared catalyst library was dried at 110 °C for 12 h and calcined at 550 °C for 4 h under air condition. The composition of the 56-member catalyst library containing different metal loadings is shown in Table II.

B. Optimized quaternary composition of catalysts at various temperatures

The total gas flow rate was 10 cc min⁻¹ and 10 mg of catalyst was placed in the reactor. The composition of the reactant gas mixture consisted of 2000 ppm of NO, 2700 ppm of C_3H_6, 3.2 vol. % of O_2 and He balance, and their DeNO$_x$ activity was measured in the temperature range of 250–400 °C using a micro-GC. Prior to screening of catalyst library, C_3H_6-SCR using the same catalyst of 1 wt. % Pt/AlSBA-15 was tested for validation from channel 1 to 32. As shown in Fig. 7, NO conversion of each reaction channel is similar under the same reaction condition and deviation of NO conversion at 300 °C is ±2%.

Among the various catalysts (#1–56) explored in various temperatures, Pt-containing catalysts showed relatively high activity compared to the other catalysts (Fig. 8). However, the optimum catalytic composition was changed significantly depending on the reaction temperature; $Pt_{0.8}Fe_{0.2}$ (#11) and $Pt_{0.8}Co_{0.2}$ (#32) at 250 °C, $Pt_{0.6}Fe_{0.2}Co_{0.2}$ (#28), $Pt_{0.8}Co_{0.2}$ (#32), and $Pt_{0.6}Co_{0.4}$ (#43) at 300 °C, $Pt_{0.4}Fe_{0.4}Co_{0.2}$ (#25), $Pt_{0.6}Fe_{0.2}Co_{0.2}$ (#28), and $Pt_{0.6}Co_{0.4}$ (#43) at 350 °C, and $Pt_{0.4}Fe_{0.6}$ (#4), $Pt_{1.0}$ (#16), and $Co_{1.0}$ (#56) at 400 °C showed the highest activity. It is quite interesting to observe that $Pt_{0.8}Co_{0.2}$ (#32) and $Pt_{0.6}Co_{0.4}$ (#43) showed a higher NO conversion than pure Pt catalyst (#16) at 300 °C. This result indicates that the composite catalysts of $Pt_{0.6-0.8}-Co_{0.2-0.4}$ can be a potential candidate for SCR of NO at 300 °C, likewise $Pt_{0.4-0.6}Fe_{0-0.4}Co_{0.2-0.4}$ at 350 °C. When the reaction temperature was raised to 400 °C, the catalytic activity of the Pt-containing catalysts decreased rapidly compared to 300 °C. In contrast, the activity of pure Pt catalyst (#16) and

pure Co catalyst (#56) increased with increase in reaction temperature. NO conversions of the composite catalysts not containing Pt were higher at 400 °C than at 300 °C.

We have developed a highly reliable 64-channel sequential and parallel tubular reactor system that allows for the quantitative analysis of heterogeneous catalyst library in a high throughput manner under realistic condition. A quaternary catalyst library of 56 samples composed of Pt, Cu, Fe, and Co supported on AlSBA-15 is optimized in the SCR of NO at various temperatures with our system.

ACKNOWLEDGMENTS

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