

# High-Throughput Parallel Reactor System for Propylene Oxidation Catalyst Investigation

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A high-throughput reactor system was designed for catalyst testing, which includes two important sections: the gas flow splitters and the parallel reactor. Each gas flow splitter could split one gas stream to 64 streams ( $8 \times 8$ ). The current system has two gas splitters that could feed two kinds of gases (from mass flow controllers) to a 64-channel ( $8 \times 8$ ) parallel fixed-bed reactor. The reactor is composed of tube connectors, a reactor tube array, a heating block, a product collector, and a temperature controller. The reactor system could test 64 catalysts simultaneously and give results, which are comparable with a regular single-channel microreactor. For the purpose of verifying the validity of the reactor system, propylene oxidation to prepare acrolein was used as the probing reaction. In order to analyze the reaction products, a high-throughput colorimetric diffusion–reflection imaging method was developed for the analysis of acrolein. By comparing the results from colorimetric diffusion–reflection imaging analysis with that from the traditional gas chromatography spectrometer with thermal conductivity detectors, a colorimetric diffusion–reflection imaging method was confirmed to be reliable and accurate in acrolein analysis.

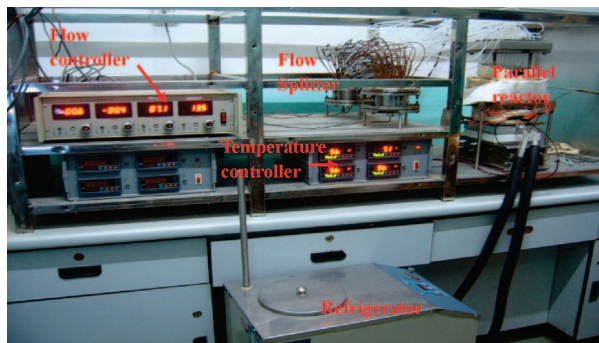
## 1. Introduction

Combinatorial chemistry has been widely applied in catalyst discovery and optimization.<sup>1–4</sup> Hundreds or even thousands of catalysts could be prepared and tested by combinatorial chemistry methodology in a short time, such as the applications of combinatorial chemistry in catalyst screening and optimization for photodegradation reaction,<sup>5,6</sup> aniline synthesis reaction,<sup>7</sup> CO oxidation,<sup>8</sup> and hydrogen oxidation.<sup>9</sup> However, in the investigation of developing combinatorial methodology in catalysis chemistry, there are three problems that need to be resolved: (1) flow or pressure control, (2) catalytic reactor design, and (3) high-throughput product analysis. There have been extensive investigations devoted to this area.<sup>9–12</sup> Sekan<sup>13</sup> had developed a resonance-enhanced multiphoton ionization (REMPI) technique with an microreactor array for catalyst screening in cyclohexane dehydrogenation to prepare benzene. The microreactor array was composed of isolated channels that were micromachined on a substrate. However, the author did not mention the flow management to deliver equal gas flows into reactor channels. Both Urschey<sup>14</sup> and Scheidtmann et al.<sup>15</sup> reported gas-controlling systems to deliver gas streams into reactor channels, in which many mass flow controllers were employed to control the gas flows. Obviously, this kind of system would be very costly and would occupy a lot of space. Claus et al.<sup>16</sup> reported a capillary flow distribution device to split flows for a microreactor array. The capillary channels were carved on a flat substrate, and catalysts were also prepared in those capillary channels. However, due to the heterogeneity and phase segregation of catalyst components,

the resistances among channels could be different. Hence, the flows could vary among channels. Scientists at Symyx<sup>17</sup> had described a reactor system based on a microfabricated glass capillary flow distributor. Relatively better flow management was reached. However, the flows for channels were still not adjustable. There were still about 10% relative error from channel to channel. Wang et al.<sup>18</sup> also reported a flow distribution device, whereas the detail was not mentioned and the errors were not clear yet. In order to obtain results comparable with that obtained from traditional microreactors, an accurate flow management for a microreactor array is the key issue in catalytic reactor design. An ideal flow-controlling device should be flexible in flow adjusting of an individual channel and relatively cheap to fabricate. On the subject of combinatorial fixed-bed catalytic reactor design, there have been many reports.<sup>10,19</sup> The key issues for this part of the investigation are the heating and sealing of the reactor channels. Attempting to connect or disconnect individual reactor channels will be labor intensive and will not be a high-throughput way to work. The ideal way to work in this area is to design a quick parallel connector to simultaneously connect or disconnect all of the reactor channels.

For catalyst discovery and optimization in combinatorial chemistry, product analysis is usually the bottleneck. Developing a high-throughput analysis method is of the same importance as designing a parallel reactor. After reaction, the products must be analyzed to evaluate the efficiency of catalysts. Recently, IR thermography,<sup>9,20,21</sup> photofluorescence imaging,<sup>22</sup> laser-induced resonance-enhanced multiphoton ionization,<sup>13</sup> microprobe sampling mass spectrometry,<sup>23,24</sup> and fluorescence indicators have been developed for high-throughput analysis.<sup>25,26</sup> Most of the analysis technologies

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**Figure 1.** Integrated reactor system, which is composed of mass flow controllers, flow splitters, a parallel reactor, a temperature controller, and a refrigerator.

were developed for the product analysis of specific reactions. Zhou et al. designed a colorimetric diffusion-reflection imaging (CDRI) system for organic or inorganic compound analysis,<sup>27</sup> which could be widely applied in product analysis. In the current work, the CDRI technique was employed to analyze acrolein.

In the current investigation, we are not trying to design a catalytic reactor system to run large catalyst libraries (such as more than 100 catalysts in a library). We think that testing 50–100 catalysts in each library is reasonable. Hence, the high throughput in situ synthesis of catalysts was not explored in this work. In most cases, the stabilization of catalysts in online reaction takes several hours or even several days. The catalyst loading does not require too much time. Hence, in each run, testing 50–100 catalysts is reasonable. The goal of the current work is to introduce a high-throughput catalytic reaction system design with a CDRI high-throughput method for acrolein analysis. The catalytic oxidation of propylene to prepare acrolein is chosen as the testing reaction in the evaluation of the reaction system.

## 2. Experimental

**2.1. Reaction System.** The current reaction system was built for the selective oxidation of hydrocarbons. The whole reaction system includes two sections: the gas flow splitters and the parallel fixed-bed reactor. There are two mass flow controllers to control the flows of oxygen (or air) and hydrocarbon gas, such as propylene or propane. The two gas streams are fed into two flow splitters, respectively. In the flow splitter, each stream of reactant gases is split to 64 equal streams, and then, each stream of hydrocarbon gas combines with one stream of oxygen (or air) to mix the two reactant gases and is fed into one of the reactor tubes in the parallel reactor. The parallel reactor has 64 reactor tubes (each reactor tube contains one catalyst and accepts one stream of gas mixture), which could run 64 catalysts simultaneously. The catalyst beds were heated by cartridge heaters in an aluminum block. The reactor system is shown in Figure 1. The products from the parallel reactor are analyzed by specific methods depending on the properties of the compounds. In the current investigation, propylene oxidation was used as a testing reaction to verify the reaction system. In the reaction, acrolein is the desired product. Hence, we can analyze acrolein by the CDRI method described before by Zhou et al.<sup>27</sup>

**2.2. Configuration of the Splitter.** Figure 2 shows the detail of the splitter design. The splitter is composed of three major pieces: the top plate, the compartment, and the bottom plate. All of the three parts are made from stainless steel. On the top piece, there is a gas inlet. The top piece is tightened together with the compartment piece by nuts and sealed by silicon rubber O-rings. In the compartment piece, an  $8 \times 8$  channel array is machined. For detail, see the right diagram of Figure 2. At the bottom of each channel, a porous stainless steel disc (pore size  $40 \mu\text{m}$ , diameter  $1/8$  in.) was placed. Above the porous stainless steel disc, poly tetrafluoroethylene (Teflon) beads ( $100 \mu\text{m}$ ) were filled and then another piece of porous stainless steel disc was placed above the Teflon beads. Above the porous stainless steel disc, a stainless steel pushing tube (diameter  $1/8$  in., 15.0 mm in length) was placed, and above the pushing tube, there was an adjustable screw thread (6.0 mm in diameter and 12.0 mm in length). The gas flow in an individual channel is adjusted by turning the top screw thread. The screw thread pushes the pushing tube to drive the top piece porous stainless steel disc downwards to compress the Teflon beads to adjust the flow. Before installing the flow splitter, the flow of each channel was adjusted to the same value at a constant pressure.

**2.3. Parallel Reactor.** The parallel reactor includes three parts as shown in Figure 3. The top piece is a parallel connector, which is used to connect the reactor tubes with the tubes from the gas splitters. Silicon O-rings are used to make a seal between the tubes and parallel connector. The current parallel reactor has 64 channels ( $8 \times 8$ ). The reactor tubes could be stainless steel or glass tubes, which are organized into an  $8 \times 8$  array. The reactor tube array is heated up by an aluminum block (an  $8 \times 8$  hole array is drilled in it) with cartridge heaters. The aluminum heating block is packed in glass wire insulator. A digital temperature controller is used to control the temperature of the aluminum heating block. The catalyst beds are located in the hot zone. After going through the hot zone of the aluminum heating block, the reactor tubes lead to a cooling plate (also made from aluminum block) that is cooled by a refrigerator to condense the products (as shown in Figure 1). Below the cooling plate, there is an acceptor plate (Teflon) drilled with an  $8 \times 8$  well array to accept samples. The detail of the parallel reactor is shown in Figure 3.

**2.4. Sample Collection.** Acrolein samples from individual reactor tubes were collected in an  $8 \times 8$  well-array acceptor plate. Each well has a volume of 2.0 mL. In each well, 1000  $\mu\text{L}$  of deionized water was added. Gas mixtures from the reactor array were bubbled through the water in the wells of the acceptor plate to absorb acrolein. The sample collection could take any desired period of time. In the current case, we usually take 30 min to collect samples, but sometimes, when too much acrolein was formed over catalysts, shorter collecting times were used, such as that in the collection of samples in catalyst library 2; here, the samples were collected within 15 min. After the absorption, 500  $\mu\text{L}$  of solution from the wells of the acceptor was transferred to the corresponding wells on the analysis well-array plate ( $14 \times 14$  wells, well volume 4.0 mL, each well contains 2.0 mL of fuchsin sulfate

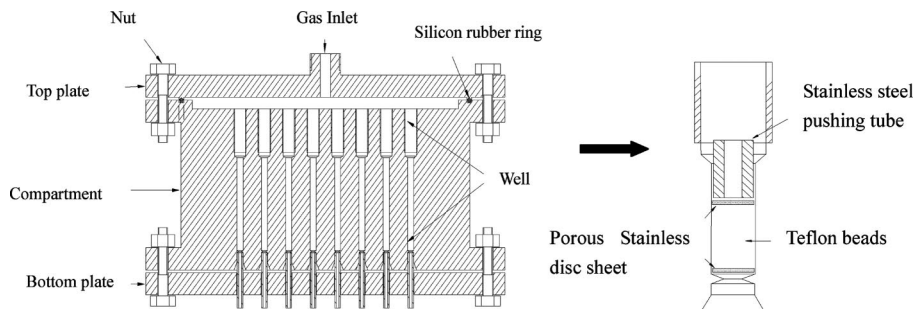


Figure 2. Assembly Drawing of the Splitter and Detail of One Splitter Channel.

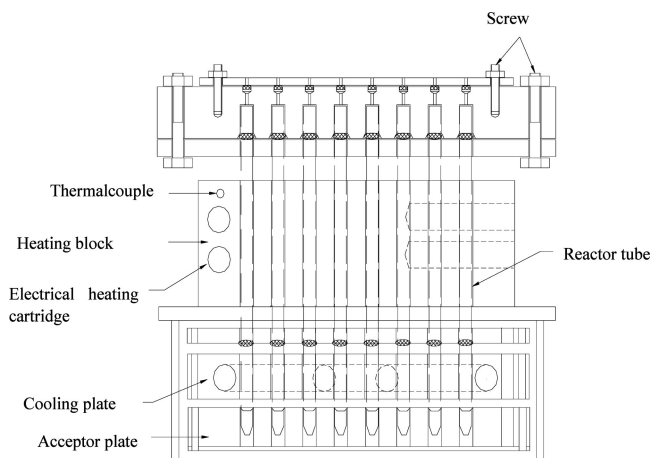


Figure 3. Schematic Drawing of the Parallel Reactor.

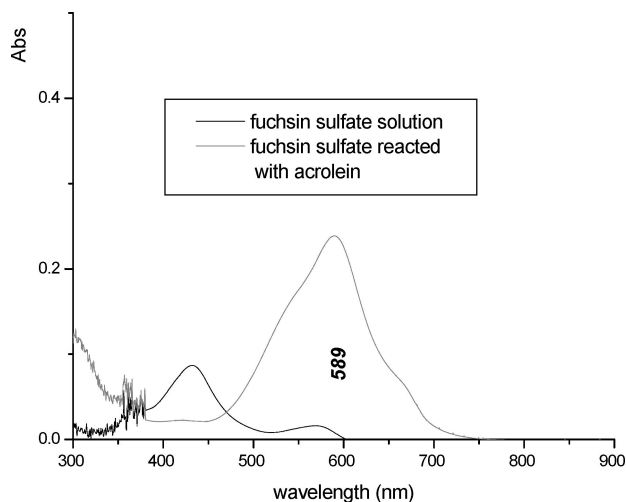


Figure 4. UV spectra of fuchsin sulfate and product of reaction between acrolein and fuchsin sulfate.

solution (0.000 20 M)). The standard acrolein solutions were also transferred into the analysis well-array plate for calibration in the analysis. The concentrations of the acrolein standard solutions were 0.50, 0.40, 0.30, 0.20, 0.10, 0.050, and 0.010 M. After acrolein solutions were mixed with the fuchsin sulfate solutions in the wells of the analysis well-array plate, the samples were analyzed according to the following method.

**2.5. Analysis of Acrolein.** In propylene selective oxidation, acrolein is our desired product. Fuchsin sulfate was used as indicating reagent to quantify acrolein. As shown in Figure 4, fuchsin sulfate solution did not show absorption above 600 nm, but after reacting with acrolein, a strong absorption peak appeared in the UV spectra. From the spectrum

information of the fuchsin sulfate solution and the product(s) of fuchsin sulfate reacting with acrolein, we can use the CDRI method to analyze acrolein, which we described elsewhere.<sup>27</sup>

**2.6. Preparation of Catalysts. 2.6.1. Synthesis of 4.0 wt % NiO/Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> Catalyst.** In the synthesis of 4.0 wt % NiO/Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> catalyst, 29.046 g of NH<sub>4</sub>VO<sub>3</sub> was dissolved in 750.0 mL of water at 80 °C to obtain a solution, and then, 175.348 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O was added to the NH<sub>4</sub>VO<sub>3</sub> solution at 80 °C; this was stirred for 10 min to obtain a V-Mo solution. Then, 25.084 g of H<sub>2</sub>TeO<sub>4</sub>·2H<sub>2</sub>O was mixed with the V-Mo solution, and this was stirred for 15 min to form a yellow V-Mo-Te solution. Next, 15.95 g of Nb<sub>2</sub>O<sub>5</sub> powder was added to the V-Mo-Te solution to obtain a slurry, which was stirred for 30 min to obtain the Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> precursor. The molar ratio of the Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> precursor was Mo:V:Te:Nb = 1.0:0.25:0.11:0.12. The Ni precursor solution was prepared by directly dissolving 45.675 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 250.0 mL deionized water. The concentration of Ni was 1.0 M (based on the metal atoms). Then, 77.1 mL of Ni(NO<sub>3</sub>)<sub>2</sub> solution (1.0 M) was added to the above Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> precursor to obtain a mixture. The mixture was dried for 15 h at 120 °C and calcined at 500 °C for 2 h to give the catalyst, which has a formula of 4.0 wt % NiO/Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub>. The catalyst was used for reactor system testing. In each channel of the reactor, 1.00 g of catalyst (80~100 mesh) was loaded.

**2.6.2. Synthesis of Catalyst Libraries 1 and 2.** The Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub> precursor (denoted as M<sub>1</sub>) was prepared by the same method as that described in section 2.6.1. The M<sub>1</sub> precursor was transferred to the glass bottles (in each bottle, 11.71 mL of the precursor mixture was transferred) in an array of 8 × 8 under stirring. The Cu, Ni, Cd, Co, Ce, Ag, and Fe precursor solutions (1.0 M) were prepared by dissolving 8.55 g of CuCl<sub>2</sub>·2H<sub>2</sub>O, 14.55 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 9.15 g of CdCl<sub>2</sub>, 6.50 g of CoCl<sub>2</sub>, 21.70 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 8.50 g of AgNO<sub>3</sub>, and 20.20 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in deionized water, respectively. The solutions of CuCl<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, CdCl<sub>2</sub>, CoCl<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, AgNO<sub>3</sub>, and Fe(NO<sub>3</sub>)<sub>3</sub> were added into the glass bottles containing M<sub>1</sub> precursor to prepare catalyst library 1 according to the compositions listed in Table 1. The percentages in Table 1 are calculated according to the weight percentages of CuO, NiO, CdO, Ce<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Ag. The library was dried at 120 °C for 15 h and, then, calcined at 500 °C for 2 h in air to obtain catalyst library 1.

**Table 1.** Compositions of Catalysts in Library 1<sup>a</sup>

2.0%Cu/M <sub>1</sub>	2.0%Ni/M <sub>1</sub>	2.0%Cd/M <sub>1</sub>	2.0%Ce/M <sub>1</sub>	2.0%Co/M <sub>1</sub>	M <sub>1</sub>	2.0%Fe/M <sub>1</sub>	
4.0%Cu/M <sub>1</sub>	4.0%Ni/M <sub>1</sub>	4.0%Cd/M <sub>1</sub>	4.0%Ce/M <sub>1</sub>	4.0%Co/M <sub>1</sub>	M <sub>1</sub>	4.0%Fe/M <sub>1</sub>	
6.0%Cu/M <sub>1</sub>	6.0%Ni/M <sub>1</sub>		6.0%Ce/M <sub>1</sub>	6.0%Co/M <sub>1</sub>	M <sub>1</sub>	6.0%Fe/M <sub>1</sub>	2.0%Ag/M <sub>1</sub>
8.0%Cu/M <sub>1</sub>	8.0%Ni/M <sub>1</sub>	8.0%Cd/M <sub>1</sub>	8.0%Ce/M <sub>1</sub>	8.0%Co/M <sub>1</sub>	M <sub>1</sub>	8.0%Fe/M <sub>1</sub>	
	10%Ni/M <sub>1</sub>	10%Cd/M <sub>1</sub>	10%Ce/M <sub>1</sub>	10%Co/M <sub>1</sub>		10%Fe/M <sub>1</sub>	4.0%Ag/M <sub>1</sub>
14%Cu/M <sub>1</sub>	14%Ni/M <sub>1</sub>	14%Cd/M <sub>1</sub>	14%Ce/M <sub>1</sub>	14%Co/M <sub>1</sub>		14%Fe/M <sub>1</sub>	8.0%Ag/M <sub>1</sub>
18%Cu/M <sub>1</sub>	18%Ni/M <sub>1</sub>	18%Cd/M <sub>1</sub>	18%Ce/M <sub>1</sub>	18%Co/M <sub>1</sub>			10%Ag/M <sub>1</sub>
22%Cu/M <sub>1</sub>	22%Ni/M <sub>1</sub>	22%Cd/M <sub>1</sub>	22%Ce/M <sub>1</sub>	22%Co/M <sub>1</sub>		22%Fe/M <sub>1</sub>	

<sup>a</sup> Note: M<sub>1</sub> stands for Mo<sub>1.0</sub>-V<sub>0.25</sub>-Te<sub>0.11</sub>-Nb<sub>0.12</sub>-O<sub>n</sub>. The numbers in the table are weight percentages of CuO, NiO, CdO, Ce<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Ag.

**Table 2.** Compositions of Catalysts in Library 2<sup>a</sup>

10%Na/M <sub>2</sub>	10%Ca/M <sub>2</sub>	10%Fe/M <sub>2</sub>	10%W/M <sub>2</sub>	10%Cd/M <sub>2</sub>	10%Cu/M <sub>2</sub>	10%Sn/M <sub>2</sub>	10%Sb/M <sub>2</sub>
1.0%Na/M <sub>2</sub>	1.0%Ca/M <sub>2</sub>	1.0%Fe/M <sub>2</sub>	1.0%W/M <sub>2</sub>	1.0%Cd/M <sub>2</sub>	<b>1.0% Cu/M<sub>2</sub></b>	1.0%Sn/M <sub>2</sub>	1.0%Sb/M <sub>2</sub>
0.10%Na/M <sub>2</sub>	0.10%Ca/M <sub>2</sub>	0.10%Fe/M <sub>2</sub>	0.10%W/M <sub>2</sub>	0.10%Cd/M <sub>2</sub>	0.10%Cu/M <sub>2</sub>	0.10%Sn/M <sub>2</sub>	0.10%Sb/M <sub>2</sub>
10%K/M <sub>2</sub>	10%Ag/M <sub>2</sub>	10%La/M <sub>2</sub>	10%Ba/M <sub>2</sub>	10%Pb/M <sub>2</sub>	10%Co/M <sub>2</sub>	10%Mg/M <sub>2</sub>	10%Bi/M <sub>2</sub>
1.0%K/M <sub>2</sub>	1.0%Ag/M <sub>2</sub>	1.0%La/M <sub>2</sub>	1.0%Ba/M <sub>2</sub>	1.0%Pb/M <sub>2</sub>	1.0%Co/M <sub>2</sub>	1.0%Mg/M <sub>2</sub>	1.0%Bi/M <sub>2</sub>
0.10%K/M <sub>2</sub>	0.10%Ag/M <sub>2</sub>	0.10%La/M <sub>2</sub>	0.10%Ba/M <sub>2</sub>	0.10%Pb/M <sub>2</sub>	0.10%Co/M <sub>2</sub>	0.10%Mg/M <sub>2</sub>	0.10%Bi/M <sub>2</sub>
M <sub>2</sub>	M <sub>2</sub>	M <sub>2</sub>	M <sub>2</sub>				

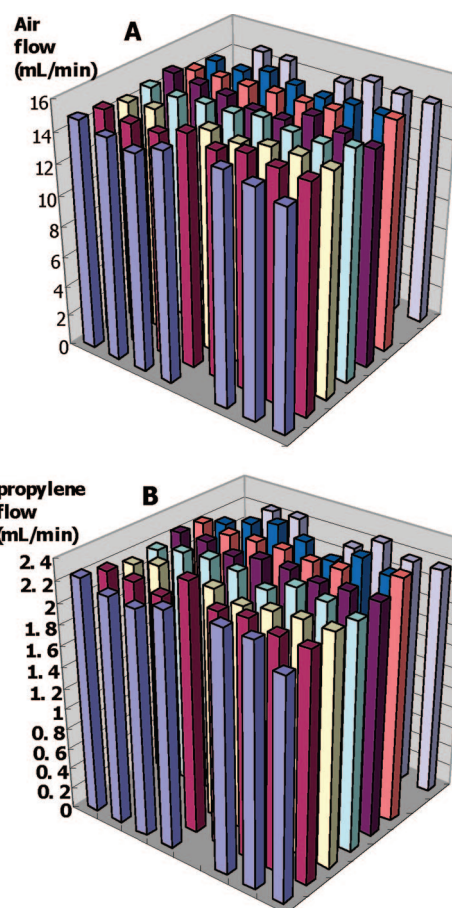
<sup>a</sup> Note: In Table 2, M<sub>2</sub> denotes **4.0 wt % NiO/M<sub>1</sub>**. The numbers in table are weight percentages of CuO, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, MgO, NaOH, KOH, ZnO, SnO<sub>2</sub>, PbO<sub>2</sub>, CaO, La<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, BaO, and Bi<sub>2</sub>O<sub>3</sub>.

After testing of library 1, catalyst **4.0 wt % NiO/M<sub>1</sub>** was found to be the best (in the following description, **4.0 wt % NiO/M<sub>1</sub>** was denoted as M<sub>2</sub>). Hence, it was selected as the “leader” for the preparation of the next generation catalysts (library 2). The preparation of M<sub>2</sub> precursor mixture (before drying) was described in the previous section. According to the above method, 8.50 g of AgNO<sub>3</sub>, 8.55 g of CuCl<sub>2</sub>·2H<sub>2</sub>O, 20.20 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 6.50 g of CoCl<sub>2</sub>, 7.40 g of Mg(NO<sub>3</sub>)<sub>2</sub>, 2.00 g of NaOH, 2.80 g of KOH, 9.15 g of Zn(AC)<sub>2</sub>, 13.05 g of SnCl<sub>4</sub>, 11.50 g of Pb(NO<sub>3</sub>)<sub>2</sub>, and 8.20 g of Ca(NO<sub>3</sub>)<sub>2</sub> were added into deionized water (to make up a total volume of 50.0 mL) to prepare the corresponding solutions (1.0 M), respectively. The solutions of La, W, and Ba with concentrations of 0.10 M were prepared by dissolving 1.625 g of La(NO<sub>3</sub>)<sub>3</sub>, 8.45 g of (NH<sub>4</sub>)<sub>5</sub>H<sub>6</sub>[H<sub>2</sub>(WO<sub>4</sub>)<sub>6</sub>]·H<sub>2</sub>O, and 0.855 g of Ba(OH)<sub>2</sub> in deionized water (to make up a total volume of 50.0 mL), respectively. The Bi precursor solution with a Bi concentration of 0.10 M was prepared by dissolving 1.98 g of Bi(NO<sub>3</sub>)<sub>3</sub> in 1.0 M nitric acid solution (to make up a total volume of 50.0 mL).

In an 8 × 8 glass bottle array, M<sub>2</sub> precursor mixture (under stirring) was added to the corresponding bottles with the same volume of 11.71 mL. Aqueous solutions of Cu, Fe, Co, Mg, Na, K, Zn, Sn, Pb, Ca, La, W, Ba, and Bi salts were added into the individual bottles containing M<sub>2</sub> precursor to prepare a precursor library of library 2 according to the compositions listed in Table 2. The numbers listed in Table 2 were calculated according to the weight percentages of CuO, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, MgO, NaOH, KOH, ZnO, SnO<sub>2</sub>, PbO<sub>2</sub>, CaO, La<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, BaO, and Bi<sub>2</sub>O<sub>3</sub>. The precursor library was dried at 120 °C for 15 h, and then calcined at 500 °C for 2 h to obtain catalyst library 2.

### 3. Results and Discussion

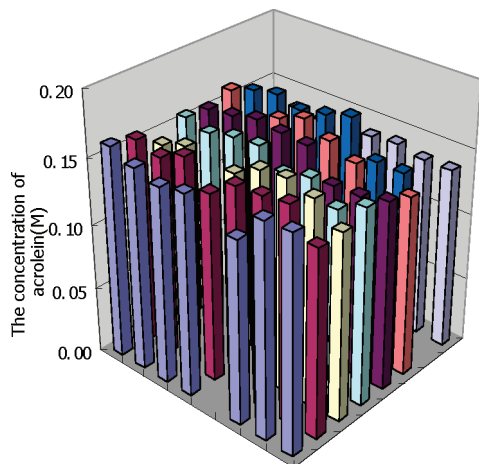
**3.1. Evaluation of Flow Splitter.** In order to demonstrate the usefulness of the flow distribution technology of the reactor system, the flows from channels of the flow splitter were measured. The air and propylene were directly introduced into the primary massflow controllers to deliver constant flows of air and propylene into the flow splitters,



**Figure 5.** (A) Flows of air from the corresponding channels of the flow splitter, when 928.0 mL/min of air was fed into the flow splitter. (B) Flows of propylene from the corresponding channels of flow splitter, when 141.0 mL/min of propylene was fed into the flow splitter.

respectively. Figure 5 shows the flows of air and propylene from channels of the flow splitters (see the Supporting Information for the numbers).

When 928.0 mL/min of air was passed through the flow splitter, an air flow of  $14.5 \pm 0.6$  mL/min was obtained in each channel (Figure 5A). When 141.0 mL/min of propylene was passed through the splitter, a propylene flow of  $2.2 \pm$

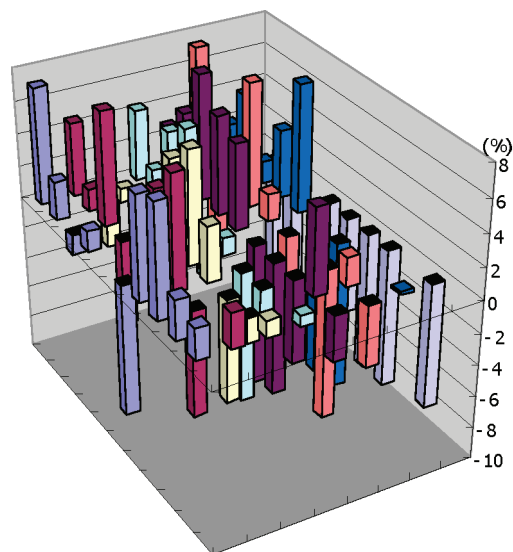


**Figure 6.** Acrolein concentrations of samples from different channels of the parallel reactor loaded with the same amount of catalyst **4.0 wt % NiO/M<sub>1</sub>** (each channel loaded with 1.00 g catalyst). The reactions were carried out at 420 °C. Samples were collected after 4 h of online reaction. The sample collection time was 30 min.

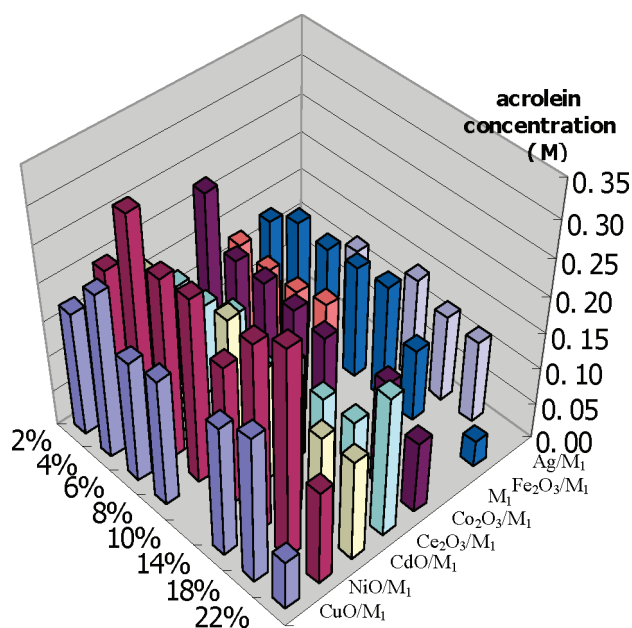
0.15 mL/min was obtained in each channel (Figure 5B). The measurements show that the relative errors for air and propylene are  $\pm 4\%$  and  $\pm 7\%$ , respectively. The relatively large errors for propylene gas might be because the flow in each channel was too small. The measurement itself could generate relatively large errors. We are confident that if the flows of the flow splitters were more carefully fine tuned, more uniform flows could be obtained.

**3.2. Thermal Response of the Reactor.** In the heating section of the parallel reactor, we use aluminum block as the heating media. In order to measure the temperature distribution across the whole aluminum block, the aluminum block was heated to 370 °C by cartridges heaters and controlled by a temperature controller. Temperatures in the center and four corners of the aluminum block (drilled holes for thermal couplers) were measured. Our results show that the temperature differences among the 5 points in the aluminum block are within 2 °C. Generally, 2 °C of temperature difference does not have an apparent impact on chemical reaction. Hence, the aluminum heating block meets the requirement of temperature uniformity in our reaction system.

**3.3. Reaction and Product Analysis.** In order to testing the parallel reactor and the CDRI analysis method, 1.00 g of **4.0 wt % NiO/M<sub>1</sub>** catalyst was loaded into each channel of the reactor and the reactions were carried out at 420 °C. The flows of air and propylene were 15.0 and 1.0 mL/min, respectively. The reactions were carried out at atmospheric pressure. After 4 h of online reaction, the acrolein samples were collected and analyzed by the CDRI method described elsewhere.<sup>27</sup> After collection for 30 min, the samples were analyzed by the CDRI method. The concentrations of acrolein from each channel are shown in Figure 6 and the corresponding errors are shown in Figure 7 (some of the channels were not loaded with catalysts, which act as references). The concentration of acrolein in solution from different channels was  $0.15 \pm 0.013$  M. The relative errors are between  $-9$  and  $8\%$ . In our CDRI analysis, the relative errors are also in this region,<sup>27</sup> As a primary evaluation of



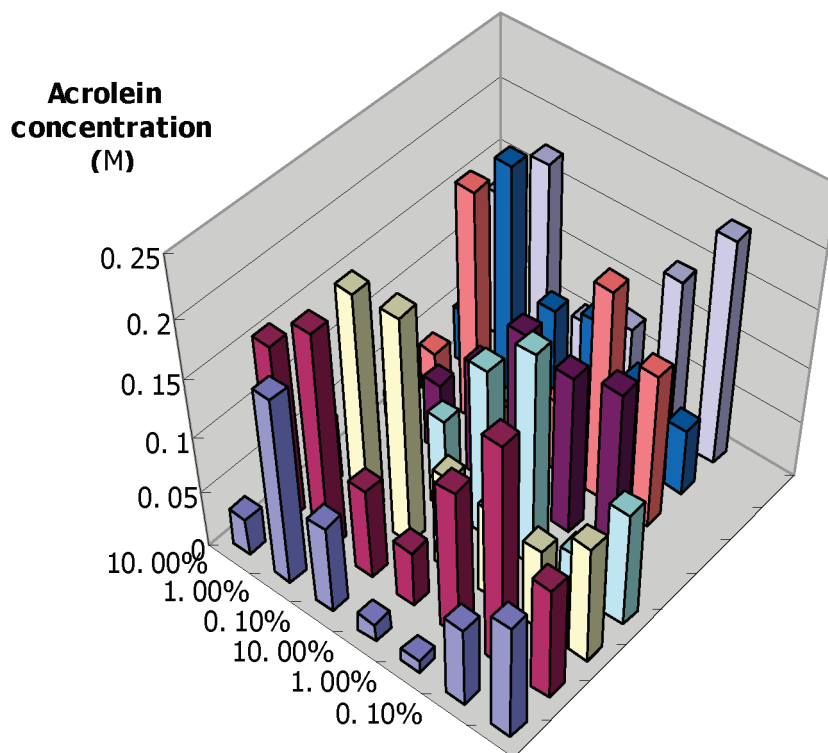
**Figure 7.** Relative errors of the acrolein concentrations shown in Figure 6.



**Figure 8.** Acrolein concentrations of samples from M<sub>1</sub> and other metal ion doped M<sub>1</sub> catalysts (catalyst library 1). The reactions were carried out at 420 °C. The samples were collected for 30 min.

the catalysts, such relative errors are durable. The results show that the parallel reactor system gives reasonable results. It could be used in catalytic reaction.

In catalyst library 1, four of the fundamental catalysts (M<sub>1</sub>) were also tested in the parallel reactor to monitor the reliability of the reactor. The four M<sub>1</sub> catalysts gave almost the same acrolein yields (Figure 8, and also, see the Supporting Information for the numbers). The acrolein concentrations of the four solutions collected from the four M<sub>1</sub> catalysts are 0.128, 0.121, 0.121, and 0.133 M, respectively. The relative average error is from  $-3.7$ – $5.7\%$ . The results over the four M<sub>1</sub> catalysts further confirmed that the parallel reactor and the CDRI analysis worked correctly. The addition of the metal ions and metals Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ce<sup>3+</sup>/Ce<sup>4+</sup>, Co<sup>3+</sup>/Co<sup>4+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup>, and metal Ag to the fundamental catalyst M<sub>1</sub> can generally improve the catalytic activity. Over catalysts doped by these metal and metal



10%Na/M <sub>2</sub>	10%Ca/M <sub>2</sub>	10%Fe/M <sub>2</sub>	10%W/M <sub>2</sub>	10%Cd/M <sub>2</sub>	10%Cu/M <sub>2</sub>	10%Sn/M <sub>2</sub>	10%Sb/M <sub>2</sub>
1.0%Na/M <sub>2</sub>	1.0%Ca/M <sub>2</sub>	1.0%Fe/M <sub>2</sub>	1.0%W/M <sub>2</sub>	1.0%Cd/M <sub>2</sub>	1.0%Cu/M <sub>2</sub>	1.0%Sn/M <sub>2</sub>	1.0%Sb/M <sub>2</sub>
0.10%Na/M <sub>2</sub>	0.10%Ca/M <sub>2</sub>	0.10%Fe/M <sub>2</sub>	0.10%W/M <sub>2</sub>	0.10%Cd/M <sub>2</sub>	0.10%Cu/M <sub>2</sub>	0.10%Sn/M <sub>2</sub>	0.10%Sb/M <sub>2</sub>
10%K/M <sub>2</sub>	10%Ag/M <sub>2</sub>	10%La/M <sub>2</sub>	10%Ba/M <sub>2</sub>	10%Pb/M <sub>2</sub>	10%Co/M <sub>2</sub>	10%Mg/M <sub>2</sub>	10%Bi/M <sub>2</sub>
1.0%K/M <sub>2</sub>	1.0%Ag/M <sub>2</sub>	1.0%La/M <sub>2</sub>	1.0%Ba/M <sub>2</sub>	1.0%Pb/M <sub>2</sub>	1.0%Co/M <sub>2</sub>	1.0%Mg/M <sub>2</sub>	1.0%Bi/M <sub>2</sub>
0.10%K/M <sub>2</sub>	0.10%Ag/M <sub>2</sub>	0.10%La/M <sub>2</sub>	0.10%Ba/M <sub>2</sub>	0.10%Pb/M <sub>2</sub>	0.10%Co/M <sub>2</sub>	0.10%Mg/M <sub>2</sub>	0.10%Bi/M <sub>2</sub>
M <sub>2</sub>	M <sub>2</sub>	M <sub>2</sub>	M <sub>2</sub>				

Note: M<sub>2</sub> stands for 4.0wt%NiO/M<sub>1</sub>.

**Figure 9.** Acrolein concentrations of samples collected from catalysts in library 2. The reactions were carried out at 420 °C. The samples were collected for 15 min.

compounds, the performances of these catalysts at 420 °C show that doping M<sub>1</sub> with 2.00–18.00% of Fe<sub>2</sub>O<sub>3</sub>, 2.00–22.00% of NiO, 2.00–22.00% of CdO, 2.00–10.00% of Co<sub>2</sub>O<sub>3</sub>, or 2.00–10.00% of Fe<sub>2</sub>O<sub>3</sub> improved the efficiency of M<sub>1</sub>. The Ce<sub>2</sub>O<sub>3</sub> and Ag doping did not show apparent improvement on the catalytic activity of M<sub>1</sub>. The best catalysts were found in the NiO doped ones. When 4.00–6.00% of NiO was doped into the fundamental catalyst M<sub>1</sub>, the highest acrolein concentration was obtained. Since the catalyst doped with 4.00% of NiO is better than other catalyst, this catalyst was selected as the “leader” for the optimization of the next generation of catalysts.

The results in library 1 show that NiO has a positive effect on the catalytic activity of Mo<sub>0.10</sub>–V<sub>0.25</sub>–Te<sub>0.11</sub>–Nb<sub>0.12</sub>–O<sub>n</sub> in propylene oxidation to prepare acrolein. Hence, based on the results, we selected 4.0 wt % NiO/M<sub>1</sub> as the fundamental catalyst (denoted as M<sub>2</sub>) and doped it with different metal compounds to prepare catalyst library 2. In the analysis of products from library 2, the samples were collected from the effluents of the parallel reactor for 15 min. The results are shown in Figure 9 (see the Supporting Information for the numbers).

The acrolein concentrations of four samples from the four M<sub>2</sub> catalysts show a run and analysis errors of –1.0–1.9%. Such a small relative error should not provide us from selecting the leader catalyst. The results in Figure 9 indicate that the catalysts in library 2 prepared by doping M<sub>2</sub> with 1.0% CaO, 0.10% Ag, 0.10–1.0% Fe<sub>2</sub>O<sub>3</sub>, 1.0% Ba(OH)<sub>2</sub>, 1.0% CuO, 1.0% SnO<sub>2</sub>, and 0.10% Bi<sub>2</sub>O<sub>3</sub> have higher activities than M<sub>2</sub>. The acrolein yields over these catalysts were much higher than that over M<sub>2</sub>.

**3.3.1. Confirmation of CDRI Analysis.** In the above investigations, the analysis of acrolein samples was conducted by the CDRI method. In order to evaluate the reliability of the analysis method, samples collected from catalysts M<sub>1</sub> and 1.0 wt % CuO/M<sub>2</sub> were analyzed by both GC (6890N) and CDRI. The results are listed in Table 3. The results show that both the GC and CDRI methods gave the same analysis results within an error region of 8%.

## Conclusion

In the current investigation, parallel flow splitters and a parallel reactor were designed and tested in catalyst screening

**Table 3.** Acrolein Concentrations of Samples Collected from Catalysts M<sub>1</sub> and 1.0 wt % CuO/M<sub>2</sub> and Analyzed by CDRI and GC

catalyst	M <sub>1</sub>	1.0 wt % CuO/M <sub>2</sub>
CDRI	0.061 (mol/L)	0.20 (mol/L)
GC	0.066 (mol/L)	0.21 (mol/L)
error	-7.60%	-5.00%

for propylene selective oxidation to prepare acrolein. The flow splitter could split one gas stream to 64 streams with relative errors from  $\pm 4$  to  $\pm 7\%$ , and the parallel reactor could run 64 reactions with relative errors from  $-9$  to  $8\%$ . For primary catalyst screening, such errors are durable. The CDRI high-throughput analysis method was proved to be valid for acrolein analysis. The reactor system and the analysis instrument were designed based on universal application purposes in catalyst investigation. Except the current propylene selective oxidation, these techniques could also be applied in other catalytic reactions.

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**Supporting Information Available.** Tables showing the flows of air and propylene, the relative errors, and the acrolein concentrations over catalysts. This material is available for free of charge via the internet at <http://pubs.acs.org>.

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