A Multiple Microreactor System for Parallel Catalyst Preparation and Testing

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A system containing nine catalytic microreactors for parallel preparation and testing of heterogeneous catalysts is described. The catalyst samples are prepared in the form of thin films coated on thin quartz rods by dip-coating in solutions of different composition. Catalyst-coated rods are placed within thin tubes housed inside a wider tube heated in an electrical furnace. A multiport valve serves to sequentially conduct the reaction products from each microreactor to a mass spectrometer for analysis. The system was tested with the reaction of methane reforming with carbon dioxide over $Pt/Ce_{1-x}Gd_xO_{2-0.5x}$ *and* $Pt/Ce_{1-x}Sm_xO_{2-0.5x}$ *at 650 and 700°C. Individual catalysts were characterized by X-ray analysis, and induction-coupled plasma mass spectrometry for catalyst mass and elemental composition. The measurements showed that* Pt/CeO_2 *had the highest activity among the series of catalysts tested and generally the activity increased with the cerium oxide content. After exposure to the feedstream for 2−3 h at 700°C, most catalysts suffered significant deactivation except the mixed oxides with 25−85% samarium oxide that maintained relatively stable activity.*

Introduction

Parallel processing techniques allow large numbers of materials with systematically varying composition to be prepared and tested simultaneously resulting in vastly higher productivity. Initially developed for biological and medical research, parallel techniques have been recently introduced to the development of heterogeneous catalysts and other solid-state materials. The considerable literature on catalyst development by parallel techniques will not be reviewed here, but reference is made to Senkan's (2001) comprehensive review. Generally speaking, parallel techniques are addressed to two phases of catalyst development: (a) catalyst preparation, including mounting in a reactor and conditioning; and (b) measurement of activity and selectivity in the reaction of interest. Most progress so far has been achieved in phase (a) which is generally the most tedious by conventional techniques. A number of ingenious techniques have also been developed for parallel measurement of activity, but little progress has been possible in parallel measurement of product distribution. In most previous studies, the product distribution was measured sequentially, one catalyst sample at a time. Productivity is still very large when only phase (a) is conducted in parallel. The time taken by a single mass spectrometric measurement, often less than one minute, is much shorter than the hours taken by preparation, mounting in the reactor, calcination, reduction, and other conditioning needed in conventional catalyst testing.

The need for convenient catalyst preparation and mounting in the reactor has been approached by different designs. Systems similar in design to conventional reactors have been used by Hoffmann et al. (1999) and Perez-Ramirez et al. (2000). Senkan et al. (1999) developed an array of reactor channels machined in an alumina block capable of accommodating on the order of 100 catalysts.

Several sophisticated instruments for high throughput catalyst testing are now commercially available. Nevertheless, there also is a need for simple, low-cost, multireactor designs for use in academic and industrial laboratories. There is also significant scope for matching the reactor design with the catalyst preparation protocol. In this article a multireactor design is described that is suitable for testing certain multicomponent oxide catalysts, zeolite catalysts, and supported metal catalysts. The system contains nine microtubular reactors operating in parallel. The catalysts are prepared as thin films coated on quartz or other ceramic rods, although it is also

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possible to use powdered samples. The coated rod geometry facilitates catalyst preparation, loading, and unloading the samples in the reactors.

The multireactor system is tested with the methane-carbon dioxide reaction over platinum supported on rare earth catalysts. This reaction was chosen, motivated by previous reports of methane reforming with carbon dioxide on ceria-supported noble metals (Craciun et al. 1998; Sharma et al. 2000; Wang and Lu 1998; Xu et al. 1999). The addition of another rare earth oxide to cerium oxide was considered as a possible means of increasing oxygen mobility and catalytic activity.

Experimental

Catalyst preparation

Catalyst samples were prepared by dip-coating thin layers of mixed cerium-gadolinium or cerium-samarium oxides on quartz rods (1 mm dia.) and subsequently adding the metal, again by dip-coating. Prior to coating, the quartz rods were roughened with sand paper and cut into pieces 4 cm long, cleaned with water, and subsequently cleaned with acetone in an ultrasonic bath. Mixed rare earth solutions were prepared using the citrate complexation technique (Baythoun and Sale, 1982). Individual solutions of the metal precursors $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa, 99.5%), $Gd(NO_3)_3 \cdot 6H_2O$ (Alfa, 99.9%), or $Sm(NO_3)_3 \cdot 6H_2O$ (Alfa, 99.9%) were prepared by dissolving equal molar amounts of the metal precursor and citric acid in ethanol to a 0.77 M metal concentration. Mixed solutions of cerium with 0, 10, 25, 40, 55, 70, 85 and 100% gadolinium or samarium were prepared by mixing specified amounts of the metal solutions in small vials to a total volume of 3 mL. The mixed solutions were vigorously stirred for 2 h and then 1 mL of 7% (wt./v) ethyl cellulose solution in ethanol was added to the solutions to increase viscosity and binding affinity for coating. The vials were subsequently placed in a multiwell block, while the quartz rods were vertically placed in corresponding positions in another block. The quartz rods were then immersed in the solutions for 30 s after which the vial block was lowered, removing the solutions at a controlled speed of 6.4 cm/min. The coated rods were dried at room temperature for 4 h, further dried at 120°C for 2 h, and calcined at 600°C in air for 4 h resulting in thin films of white oxides. Platinum was added to the coated films by a similar dip-coating procedure using a solution of 0.007 M platinum ($PtCl_4$, Alfa 99.9%) with 3% (wt./v) ethyl cellulose in ethanol and using a pulling speed of 1.2 cm/min. The coated rods were left overnight at room temperature for drying. Each rod had a coated section 2 cm long, and a bare section about 1.5 cm long.

Catalyst characterization

X-ray powder diffraction analysis of the coated catalysts was carried out using a Scintag Pad V diffractometer with Cu-Kα radiation. Inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer/Sciex Elan 5000A) was used for elemental analysis of individual samples to check the consistency of catalyst loading. Powdered samples prepared by drying the coating solutions and calcining them at 600°C for 4 h were characterized for BET surface area using a Micromeritics ASAP 2000 instrument.

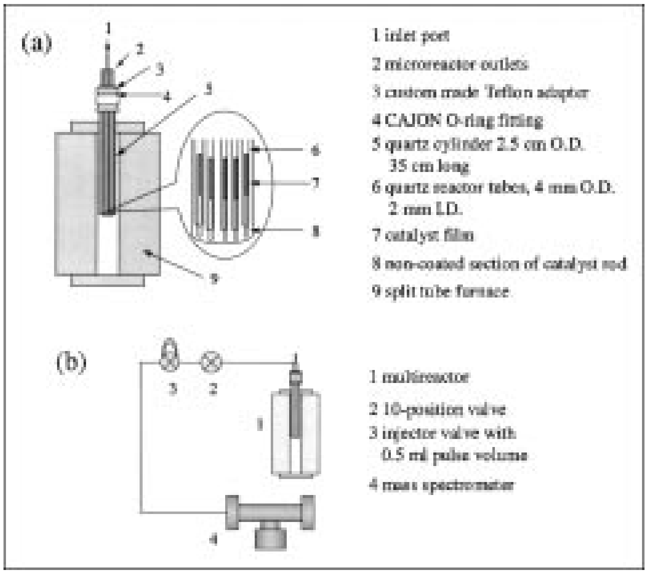

Figure 1. (a) Multireactor system and (b) product line of the multireactor system.

Reactor configuration

The reactor system contained 10 quartz tubes (4 mm OD, 2 mm ID) all surrounded by a 2.5 cm OD quartz cylinder and held in place by a custom made Teflon adapter (Figure 1). One of the tubes was used to house a thermocouple for controlling the temperature of the system, while the other tubes were loaded with the catalyst rods having the noncoated ends resting on the bottom of the reactor system (see Figure 1). The quartz cylinder was placed in a tubular furnace such that the top of the cylinder remained outside of the furnace and was close to ambient temperature. The feed stream was introduced through a common inlet at the top of the quartz cylinder, entered at the bottom, and exited at the top of the individual microreactors. A 10-position valve was used to conduct the product of a particular reactor to a valve used to inject a 0.5 mL pulse of the selected stream to a mass spectrometer (UTI 100C) for analysis. Before testing a new batch of catalysts, the reactor tubes were cleaned with 17% nitric acid in an ultrasonic bath and rinsed with water.

Reaction conditions

The reactor system was heated to 600°C at a heating rate of 10°C/min in an oxygen flow of 50 mL/min and kept at that temperature for 30 min. The temperature was then raised to 650°C at 2.5°C/min, and the system was purged with helium (50 mL/min) for 1 h before switching to a reactant flow of 1:1 CH_4:CO_2 at 30 mL/min. The product composition was monitored for 1 h at 650°C after which the reactor was heated to 700°C at 2.5°C/min and the product composition was measured at that temperature for 3 h. The CO yield was calculated by the expression

$$\text{CO yield}(\%) = 100 \times \frac{[\text{CO}]}{[\text{CH}_4] + [\text{CO}_2] + [\text{CO}]}$$

and used as an indication of catalyst activity, where [CO], $[CH_4]$, and $[CO_2]$ are the gaseous concentrations in the product stream.

Results and Discussion

Catalyst characterization

The catalyst films appeared to be very thin and uniform. X-ray diffraction analysis showed characteristic peaks similar to those of the bulk oxides, although the peaks were very weak due to a very small quantity in each sample. Elemental analysis on replicate samples using ICP-MS revealed that the sample rods contained 64 ± 4 μg of catalyst each, while the platinum content was 0.74 ± 0.04 wt. % of the coating. Due to the very small catalyst loading on each rod, direct measurement of surface area was not possible. Surface areas of catalyst samples were estimated to be less than 10 m^2/g based on values measured for powder samples obtained by drying the coating solutions.

Reactor characterization

Measurement of temperature in different microreactor tubes showed uniformity within 5°C. Measurements of the flow rate through seven of the tubes gave equal values within 5%, but the flow rates in the other three tubes were 20–30% higher or lower. The unequal flow in these three tubes was likely due to differences in the constrictions inside the 10-position valve. Therefore, only seven reactor tubes, those with uniform flow rates, were used for catalyst testing in this particular system. Of the three tubes with different flow rates, one was used for blank run, and one was used for inserting the thermocouple for furnace temperature control. The last tube was not used because measurements of catalytic activity for this tube would give considerably higher conversion due to a lower flow rate.

Catalyst testing

Preliminary experiments using identical Pt/CeO_2 catalysts in each reactor gave conversions varying less than ±20%. Runs using rods coated with cerium oxide without platinum and with unsupported platinum gave very low conversions. The very low catalyst activity in the first case could be explained by the absence of the component responsible for methane activation, and in the second case by the very low dispersion of the unsupported metal. Bitter et al. (1997) reported that unsupported platinum black and platinum supported on silica had very low activity, whereas platinum supported on alumina and zirconia had very high activity.

Activities of $Pt/Ce_{1-x}Gd_xO_{2-0.5x}$ catalysts for methane reforming with carbon dioxide were tested at 650 and 700°C, and the CO yields obtained are plotted against the gadolinium content in Figure 2. In all cases, selectivity to hydrogen was low, consistent with the low selectivity to hydrogen at low CH_4 conversion reported by Bradford and Vannice (1998). Because of the difficulty of accurately measuring the low levels of hydrogen, catalyst activity was characterized by the yield of CO that was higher and easier to measure. At 650°C, all catalysts showed induction periods of approximately 1 h during which conversion increased and reached a maximum followed by a slow decline to a steady level. Generally, the activity decreased with increasing gadolinium content and was highest for the Pt/CeO_2 catalyst. After the reaction temperature was raised to 700°C, the catalysts with either high cerium or high gadolinium content reached their maximum conversion level within 10 min, but the catalysts with intermediate composition of the mixed oxides took 40–50 min to reach the maximum. A trend of decreasing activity with increasing gadolinium content was also observed at 700°C. At this temperature, all catalysts underwent gradual deactivation after 1-2 h, reaching significantly lower, but steady, activities.

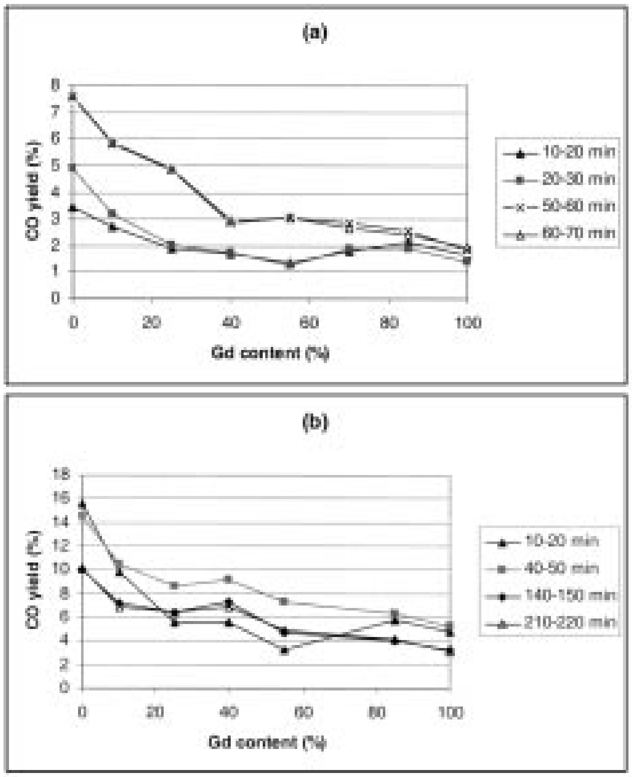

Figure 2. CO yield from CH_4 reforming with CO_2 on $Pt/Ce_{1-x}Gd_xO_{2-0.5x}$ at (a) 650°C and (b) 700°C at different times onstream.

The CO yields from reaction over $Pt/Ce_{1-x}Sm_xO_{2-0.5x}$ at 650 and 700°C are presented in Figure 3. At 650°C the Pt/CeO_2 catalyst had significantly higher activity than the samarium oxide containing catalysts. Catalysts with 40–70% samarium content gave very low CO yields and possibly were not fully activated at 650°C within the 1 h of reaction. After 1 h of exposure to the reactant stream at 700°C, the 40–70% samarium catalysts became activated giving yields of CO only slightly lower than that obtained with Pt/CeO_2. Interestingly, catalysts with at least 25% samarium oxide maintained relatively constant activity for 2–3 h at 700°C, while Pt/CeO_2 underwent significant deactivation within the same period. The standard error in Figures 2 and 3 is about 20%.

The induction time is correlated with the reducibility of the support so that catalysts supported on mixed oxides, which have higher oxygen ion mobility and are more readily reducible, required significantly longer induction time than the catalysts supported on the pure oxides. However, the mecha-

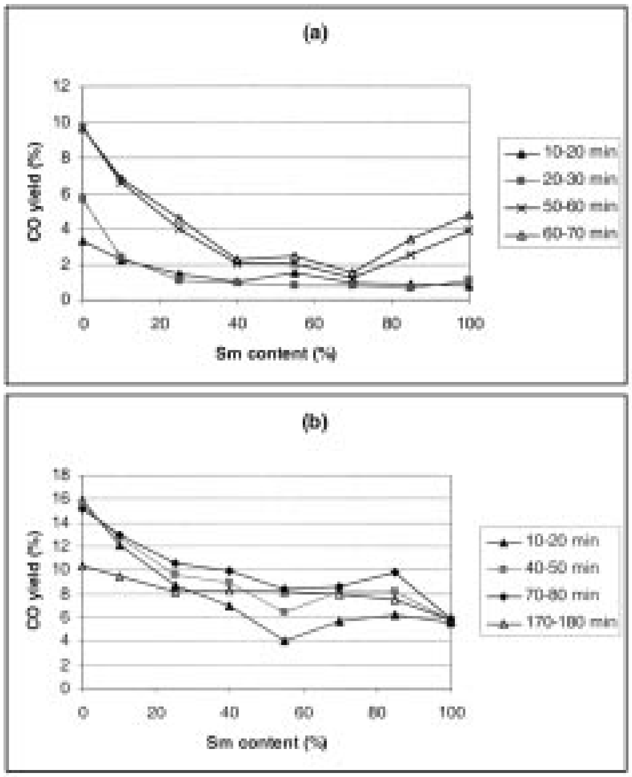

Figure 3. CO yield from CH_4 reforming with CO_2 on $Pt/Ce_{1-x}Sm_xO_{2-0.5x}$ at (a) 650°C and (b) 700°C at different times onstream.

nism of this activation could not be inferred from these limited experiments. Long induction periods for the same reaction were observed for rhodium supported on cerium or zirconium oxides, as reported by Wang and Ruckenstein (2000). These authors suggested that the long induction time could be due to reconstruction of metal particles and migration of partially reduced support oxides.

Replicate runs showed reproducible trends of catalytic activities for the $Pt/Ce_{1-x}Gd_xO_{2-0.5x}$ and $Pt/Ce_{1-x}Sm_xO_{2-0.5x}$ catalysts, although the absolute values of the CO yield varied from run to run with standard error about 20% of the measurement. The different measurements among replicate runs could be due to small changes of catalyst mass caused by small differences in the rod lengths. Another possible source of error is variation of the time taken to activate the catalyst due to slightly different temperatures from run to run.

Extensions

The loading of rare earth and other oxide catalysts can be significantly increased, if desired, by using porous α-Al_2O_3 rods instead of glass rods, and by applying the solution by impregnation instead of dip-coating. Rods of porous alumina can also be used as metal supports using conventional impregnation. Another way to vary the catalyst loading is by changing the viscosity and/or concentration of coating solutions or the coating withdrawal speed. For example, using 8 wt. % poly (vinyl butyral) instead of ethyl cellulose (increasing the viscosity of the coating solution from 30 cps to 180 cps), the catalyst loading on each rod was increased to 120 μg.

A reactor accommodating only five to ten samples as described here only offers a very modest parallel processing capability. However, the basic design appears capable of significant extension. Increasing the diameter of the surrounding cylinder (see Figure 1) from 2.5 to 7.5 cm will allow as many as 100 microreactor tubes to be accommodated. A combination of multiport valves will permit sequential sampling of all microreactors. Alternatively, the valve can be eliminated and product sampling can be carried out using a movable capillary probe inserted sequentially in each of the microreactors. Sealing in this case is not necessary, because intrusion of gases from the surrounding atmosphere by diffusion is suppressed by the flow. With this alternative mode of sampling, the flow rate differences will be eliminated, provided that the microreactor tubes are of uniform ID. Temperature rather than flow rate uniformity will be the critical issue. One possible means of achieving uniform temperature is preheating the feed gas before introduction into the surrounding cylinder. For highly exothermic reactions, even small temperature nonuniformities may be a problem near the lightoff temperature.

Conclusions

A system of nine parallel microreactors was constructed that permits convenient catalyst preparation and loading in the form of thin films coated on quartz rods. Uniform catalyst loading can be achieved by maintaining uniform viscosity in all coating solutions, with the aid of a suitable polymer. The solution viscosity and other parameters of coating can be varied to change the catalyst loading. A ten-port valve served to conduct the product streams sequentially to a mass spectrometer for analysis. There was some variation of the flow rates through the different microreactors, possibly due to different valve internal channels. Achieving uniform flow rate through the individual microreactors requires additional attention. The number of individual microreactors can be increased by a factor of 5 or 10 by using a larger number of multiport valves or by changing the mode of sampling. Preheating the feed is a possible means of maintaining uniform temperature for a larger number of reactors.

The multireactor system was tested with carbon dioxide reforming of methane on a series of $Pt/Ce_{1-x}Gd_xO_{2-0.5x}$ and $Pt/Ce_{1-x}Sm_xO_{2-0.5x}$ catalysts. The coated catalysts showed similar properties to bulk catalysts and gave consistent and adequate activities for comparison purposes. The results showed that the Pt/CeO_2 catalyst had higher activity than the catalysts supported over the mixed oxides. However, mixed samarium-cerium oxide maintained better its catalytic activity.

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