

Accelerated Articles

Laser-Activated Membrane Introduction Mass Spectrometry for High-Throughput Evaluation of Bulk Heterogeneous Catalysts

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Laser-activated membrane introduction mass spectrometry (LAMIMS), a high-throughput screening method, evaluates heterogeneous catalysts under realistic reactor conditions. It is a precise, versatile system requiring no moving parts. The catalyst array is supported on carbon paper overlaid upon a silicone rubber membrane configured in a variation of membrane introduction mass spectrometry as introduced by Cooks. The carbon paper serves as a heat-dissipating gas diffusion layer that permits laser heating of catalyst samples far above the decomposition temperature of the polymer membrane that separates the array from the mass spectrometer vacuum chamber. A computer-controlled CO₂ bar code writing laser is used for fine-tune heating of the catalyst spots above the base temperature of the LAMIMS reactor. The detailed design and performance of LAMIMS is demonstrated on arrays of “real world” bulk water–gas shift catalysts using natural and isotopically labeled reactor feed streams. A bulk catalyst array spot can be evaluated for activity and selectivity in as little as 1.5 min. All array screening results were confirmed by industrial microreactor evaluations.

Traditional heterogeneous catalyst discovery methods are labor intensive and involve time-consuming trial-and-error procedures. Combinatorial synthetic methods are being developed to process large libraries that, if combined with high-throughput screening integrated with data mining and predictive modeling, are expected to accelerate the catalyst discovery process. Our comprehensive discovery program includes combinatorial subsystems that include

at least two levels of resolution. A discovery subsystem would evaluate thousands of unique compositions per week (most likely a parallel screening method) with sufficient resolution to identify promising hits (10%). A focus subsystem, capable of evaluating up to 100 catalysts/week could be a parallel or serial system. The focus subsystem data would generate several strong leads for further development and provide guidance for direct scale-up studies. The data acquired from all subsystems would be leveraged by advanced informatics to increase the probability of successful discoveries.

The most commonly used methods in catalyst screening are optical and mass spectrometric (MS) methods because of their broad applicability and dynamics. An optical screening method for electrocatalysts, whereby ions generated in an electrochemical half-cell reaction are converted to a fluorescence signal, has been reported.¹ Although this method identifies the most active catalysts on the array, commercial fuel cell electrocatalysts have not yet been realized because this method finds activity maximums that are localized by the synthetic methods available for the catalyst array preparation. Maier and co-workers demonstrated IR thermography as a heterogeneous catalyst-screening tool by taking into account different emissivities of catalyst clusters.² IR thermography is a fast and localized method, but it does not provide substantial information on the products formed in the reaction. Scanning mass spectrometry has emerged as a versatile method of analysis. Claus stated that there are two basic concepts for the application of scanning mass spectrometry including transient modes and continuously operated reactor arrays, as discussed below.³

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(1) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E.; Mallouk, T. *Science* **1998**, 280, 1735–1737.

(2) Holzwarth, A.; Schmidt, P. W.; Maier, W. E. *Angew. Chem.* **1998**, 110, 2788; *Angew. Chem., Int. Ed.* **1998**, 37, 2644.

Cong⁴ reported sequential MS screening where a carbon dioxide laser sequentially heats catalyst sites. Reactant gases are delivered to the catalyst site through the annular section of a double concentric probe in a stagnation–flow manner. Orschel⁵ described catalyst libraries prepared by a sol–gel method, placed in a spatially addressable configuration on an open-air heated substrate. Sequentially flowing the feed gas over the catalyst spot surface through a capillary feed line and then withdrawing the products through another capillary is the basis of the method. The above screening systems do not address time-dependent behavior of catalytic materials because they were designed to provide reactant–catalyst contact only for a short period of time (i.e., ~1 min).⁶ They suffer from the inability to establish realistic catalyst exposure histories.

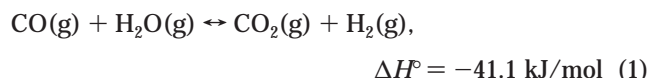
The second concept involves high-throughput screening with parallel channel reactors.³ These systems accommodate both fixed-bed catalysts and catalytic coatings applied to reactor microchannels. The latter requires that new catalyst candidates be adapted for adhesion to surfaces. Parallel channel reactors use a scanning mass spectrometer to spatially probe continuously operating parallel gas-phase reactions.⁷ Multichannel reactors screen under nearly industrial conditions but are susceptible to interference from adjacent channel outputs. The above concepts require moving parts (e.g., robotics, sampling devices, or moving libraries).

We now report a third concept for high-speed screening, laser-activated membrane introduction mass spectrometry (LAMIMS).⁸ LAMIMS is a discovery subsystem “compromise”. It is a very rapid serial technique with no moving parts that is versatile and screens under realistic conditions. Cooks developed membrane introduction mass spectrometry (MIMS).⁹ MIMS involves the use of a semipermeable membrane as an interface between a gaseous or liquid analyte stream and the vacuum of a quadrupole mass analyzer (QMA). The thermal stability of the polymer membranes limits the operational temperatures of MIMS systems.

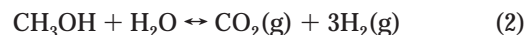
We extensively modified MIMS for high-throughput screening of catalysts under realistic conditions. Our innovation is the protection of the membrane with a heat dissipater that also serves as the support for the catalyst library. This permits laser heating or activation of the catalysts far above the decomposition temperature of the membrane. The use of laser heating in combination with MIMS obviates the need for moving parts of any kind and enables analysis without compromising catalyst conditioning/exposure history. Organic membrane inlets have high selectivity toward organic compounds relative to water. Thus, aqueous solutions can be examined on-line by MIMS to monitor dynamic chemical environments.¹⁰ The introduction of analyte into the

(QMA) vacuum is a result of transport through a polymer membrane involving absorption into the membrane, diffusion through the membrane, and evaporation from the membrane surface into the vacuum.¹¹ Each step depends on the properties of the analyte and the membrane material. Large molecules such as ferrocene, molybdenum hexacarbonyl, naphthalene, methyl salicylate, and chlorinated hydrocarbons have been analyzed by MIMS using membranes ranging in thickness from 25 to 430 μm .^{12–15} Recent utilization of microporous membranes permits the analysis of even larger molecules.¹⁶ The most successful membrane material for the detection of organic compounds in aqueous solutions is silicone,¹⁷ which has the characteristics of allowing passage of relatively nonpolar, organic compounds into the mass spectrometer while excluding the water matrix to a very high degree. This enrichment allows the attainment of detection limits in the parts per trillion ranges for most volatile organics without preconcentration or any other sample treatment.¹⁸

We exemplify LAMIMS using low-temperature water–gas shift (LTWGS) catalysts. WGS reactors are components of fuel processor systems delivering reformat H_2 to fuel cells.¹⁹ Equation 1 is the WGS reaction:



Commercial LTWGS catalysts have poor kinetics at the low temperatures required to reduce the water load to the reactor and CO output from the WGS reactor. The steam reforming of methanol can be represented as methanol cracking followed by the WGS reaction:



The typical reformer product distribution has a stoichiometric H_2/CO_2 ratio of 3 with CO levels of 2–3 mol %.^{20,21} We refer to this as “standard reformer feed” hereafter. The H_2 partial pressures in reactant and product streams of the WGS reactor are similar. Thus, H_2 detection in the QMA is not viable for screening of WGS catalysts. However, the WGS CO conversion is substantial (2–3% to below 1%). Mass spectrometric detection of CO conversion to CO_2 affords the greatest sensitivity with negligible background interference.

(3) Claus, P.; Honicke, D.; Zech, T. *Catal. Today* **2001**, 67, 319–339.

(4) Cong, P.; Doolean, R. D.; Fan, Q.; Giaquinta, D. M.; Guan, S.; McFarland, E. W.; Poojary, D. M.; Self, K.; Turner, H. W.; Weinberg, W. H. *Angew. Chem.* **1999**, 111, 508; *Angew. Chem., Int. Ed.* **1999**, 38, 484.

(5) Orschel, M.; Klein, J.; Schmidt, H. W.; Maier, W. F. *Angew. Chem.* **1999**, 111, 2961; *Angew. Chem., Int. Ed.* **1999**, 38, 2791.

(6) Senkan, S. *Angew. Chem., Int. Ed.* **2001**, 40, 312–329.

(7) Zech, T.; Lohf, A.; Golbig, K.; Richter, T.; Honicke, D. *Industrial Prospects, Proceedings of the Third International Conference On Microreaction Technology*; Springer: Berlin, 2000; pp 260–266.

(8) Nayar, A.; Liu, R.; Willis, R. R.; Smotkin, E. S. Apparatus and Method for Laser Activated Membrane Introduction Mass Spectrometry. U.S. Patent Pending, 2001.

(9) Johnson, R. C.; Cooks, R. G.; Allen, T. M.; Cisper, M. E.; Hemberger, P. H. *Mass Spectrom. Rev.* **2000**, 19, 1–37.

(10) Kotiaho, T.; Lauritsen, F. R.; Choudhary, T. K.; Cooks, R. G. *Anal. Chem.* **1991**, 63, 875.

(11) Wong, P. S. H.; Cooks, R. G.; Cisper, M. E.; Hemberger, P. H. *Environ. Sci. Technol.* **1995**, 29, 215.

(12) Baumgardner, J. E.; Neufeld, G. R. *Ann. Biomed. Eng.* **1997**, 25, 858–869.

(13) Cisper, M. E.; Hemberger, P. H. *Rapid Commun. Mass Spectrom.* **1997**, 11, 1454–1456.

(14) Allen, T. M.; Cisper, M. E.; Wilkerson, C. W.; Hemberger, P. H. *Waste Manage. Conf. Proc.* **1999**.

(15) Ketola, R. A.; Mansikka, T.; Ojala, M.; Kotiaho, T.; Kostianen, R. *Anal. Chem.* **1997**, 69, 4536–4539.

(16) Choudhary, T. K.; Kotiaho, T.; Cooks, R. G. *Talanta* **1992**, 39, 573.

(17) Bauer, S. J.; Cooks, R. G. *Am. Lab.* **1993**, 25 (16), 37–51.

(18) Soni, M.; Bauer, S.; Amy, J. W.; Wong, P.; Cooks, R. G. *Anal. Chem.* **1995**, 67, 1409.

(19) Ovesen, C. V.; Stoltze, P.; Norskov, J. K.; Campbell, C. T. *J. Catal.* **1992**, 134, 445.

(20) Idem, O. R.; Bakshi, N. N. *Ind. Eng. Chem. Res.* **1995**, 34, 1548.

(21) Jiang, C. J.; Trimm, D. L.; Wainwright, M. S. *Appl. Catal. A* **1993**, 93, 245.

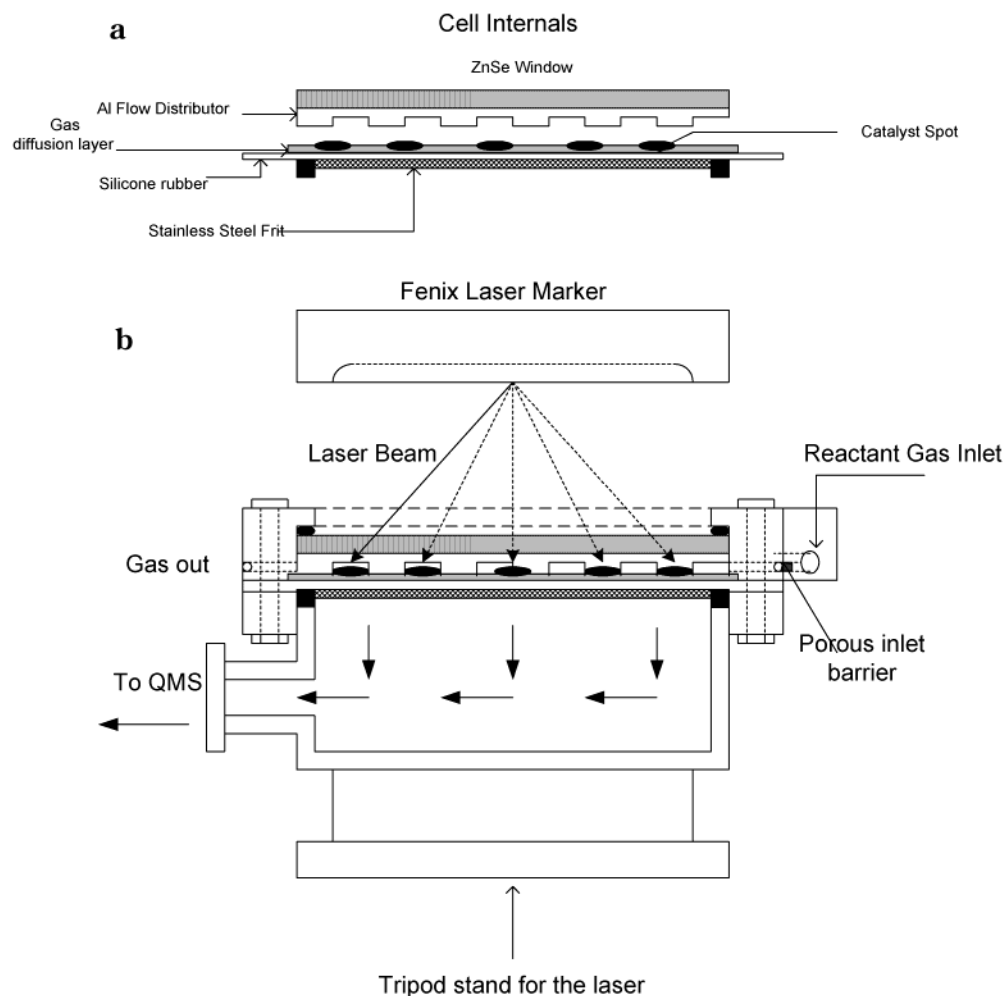


Figure 1. Schematic of the LAMIMS system.

EXPERIMENTAL SECTION

Figure 1 schematizes the LAMIMS analysis system. The heart of LAMIMS is the semipermeable composite barrier (gas diffusion layer (GDL)/membrane) that also serves as a separator between the reaction zone (Figure 1a) and the low-pressure analysis zone of a QMA. A porous carbon paper is overlaid upon a 127- μm -thick class VI medical-grade silicone membrane (SF Medical, Hudson, MA) and serves as both a support for the catalyst library and a heat dissipater minimizing membrane temperature variations as the catalyst spots are heated by a computer-controlled carbon dioxide laser (Synrad, Inc., Mukilteo, WA). The carbon paper has a high void volume and thus also serves as a GDL. The catalyst library, (e.g., array of 4-mm diameter, 4-mg spots) is supported upon the GDL. The membrane/GDL/catalyst array is referred to as the membrane array assembly (MAA). The MAA is positioned beneath a ZnSe window in an atmospherically closed upper housing with heater cartridges to establish the reactor baseline temperature (T_B), which cannot exceed the decomposition temperature (T_D) (204 $^{\circ}\text{C}$) of the silicone membrane. The array is positioned under the laser source away from the focal point such that the beam size is matched to the catalyst spot size. Since the spot temperature is linearly related to the laser power, the final reaction temperature (T_R) is fine-tuned by adjusting the laser power output (Figure 2). Thus, $T_B < T_D < T_R$, and the heat-dissipating gas diffusion layer allows T_R to be hundreds of degrees

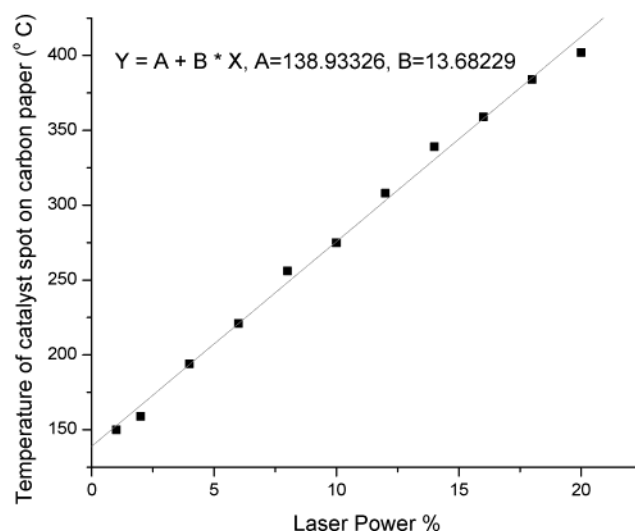


Figure 2. Temperature of catalyst spot on carbon paper in the reaction zone (150 $^{\circ}\text{C}$) vs laser power %.

above the T_D . A toothed aluminum flow distributor supports the ZnSe window above the MAA. The reaction zone is bolted to the lower vacuum system with the oversized silicone membrane serving as a sealing gasket (Figure 1b).

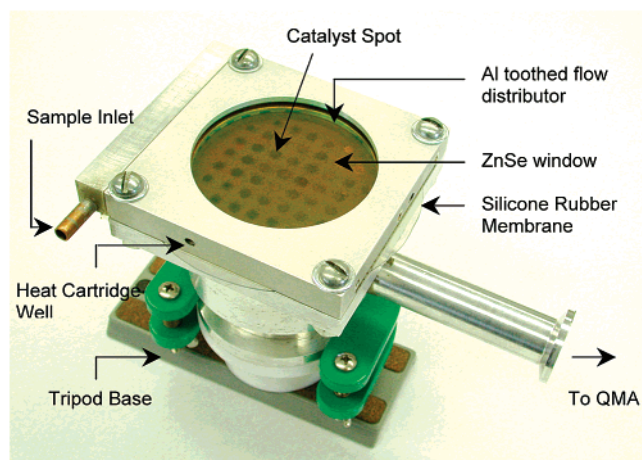


Figure 3. The LAMIMS reactor.

Table 1. Nominal CuO/ZnO/Al₂O₃ Catalyst Precursor Compositions and Calcination Conditions^a

catalyst precursor	concentration (wt %)			calcination conditions	
	CuO	ZnO	Al ₂ O ₃	temp (°C)	time (h)
1	33	54	13	400	3
2	33	54	13	300	6
3	12	80	8	300	6

^a Note that copper oxide is reduced prior to catalyst evaluation.

A photograph of the LAMIMS system (Figure 3) shows three pressure zones. In Figure 1b, the reactant gas inlet is separated from the MAA housing by a porous barrier having a length equal to the reactor width. The reactant gases diffuse from the high-pressure zone to the lower pressure (above or below ambient) MAA housing. The array performance is evaluated under steady-state reactant flow by rapid serial laser heating of the array spots to a predetermined reaction temperature above the baseline temperature. The products rapidly diffuse through the composite membrane into the QMA vacuum system.

RESULTS AND DISCUSSION

Three CuO/ZnO/Al₂O₃ catalyst precursors (compositions of 1–3 are in Table 1) were evaluated by LAMIMS. Precursor 1 was prepared by calcining the hydrous mixed metal oxide at 400 °C for 3 h, and precursors 2 and 3 were prepared by calcining the respective oxides at 300 °C for 6 h.²² The in situ reduction process is required for activation of the LTWGS catalysts.

Ceria-supported precious metals are also excellent LTWGS catalyst candidates.^{23,24} Mixed oxides of ceria and zirconia are more stable supports for precious metals.²⁵ Six experimental platinum/ceria–zirconia catalyst precursor samples (4–9; see Table 2) were also screened by LAMIMS. The catalyst supports (25–50 mol % zirconia) were prepared by coprecipitation at pH 10. Platinum was added as tetraamineplatinum(II) hydroxide via typical laboratory evaporative impregnation methodology. The

Table 2. Platinum on Ceria Zirconia Catalyst Properties, LAMIMS Catalyst Rankings, and Microreactor Testing Ranking/Results

catalyst ^a	wt % Pt	LAMIMS rank (from Figure 5b)	microreactor rank (% CO conversion at 250 °C)
4*	0.68	1	1 (27)
5	0.5	4	6 (2)
6	0.48	6	4 (6)
7*	0.62	3	3 (8)
8*	1.24	2	2 (10)
9	0.75	5	4 (6)

^a The asterisk indicates the top three ranked catalysts.

LAMIMS results for the above two classes of catalysts were conducted in the range of 220–250 °C. A LAMIMS study of high-temperature WGS catalysts (e.g., Fe₂O₃/Cr₂O₃) demonstrated that catalyst library heating to 450 °C has no adverse effect on the membrane.

A manifold with mass flow controllers is used to blend a reactant stream for delivery to the LAMIMS system. A controlled-temperature water sparger is used to humidify the reactant stream prior to delivery to the high-pressure zone of the LAMIMS system. As in actual reactors,^{26,27} the WGS catalysts evaluated by LAMIMS are prereduced under H₂ within the closed LAMIMS system with base heating complemented by spot-by-spot laser heating. After the prereduction process, the H₂ is replaced with the reactant stream (humidified H₂ and CO). The reactant stream causes the baseline pressure to increase as CO₂ is formed. Prior to sequential laser heating of the catalyst library, a steady-state baseline of CO₂ (44 amu) is established (~1 h), after which a fresh dynamic scan is initiated. Two minutes after the start of the dynamic scan, the programmable laser heating is initiated. The dynamic scan monitors the CO₂ partial pressure with time as each catalyst spot is sequentially heated (~20 s). The end of the spot heating period corresponds to a peak in the mass 44 partial pressure. The peak-to-peak dwell time in this study is ~5 min. Dwell times of 1.5 min have been established with higher flow rates. The signal-to-noise ratio is high enough to permit the use of even smaller catalysts spots, which would reduce the dwell time even further.

To examine possible effects due to flow nonuniformities, multiple array configurations were evaluated. Three configurations for the CuO/ZnO/Al₂O₃ catalyst series are designated by the vectors (1 2 3) (Figure 4a), (3 1 2) (Figure 4b), and (2 3 1) (Figure 4c) where the first vector element is closest to the porous inlet barrier and the last vector element is furthest away. Figure 4 shows that the catalyst ranking (2 > 1 > 3) is independent of the vector element order. This ranking was consistent with the microreactor ranking obtained at UOP LLC. Multiple array configurations is a form of signal averaging that permits the attainment of high precision rankings by reducing the standard deviation to below that of the spot-to-spot standard deviation.

Catalyst precursors 4–9 were supported on the MAA in two different library arrangements. Figure 5a is a single-row configuration with results shown in Figure 5b. Figure 6a is a two-row

(22) Sekizawa, K.; Yano, S.; Eguchi, K.; Arai, H. *Appl. Catal. A* **1998**, 169, 291.

(23) Whittington, B. I.; Jiang, C. J.; Trimm, D. L. *Catal. Today* **1995**, 26, 41.

(24) Shido, T.; Iwasawa, Y. *J. Catal.* **1993**, 141, 71.

(25) Putna, E. S.; Bunluesin, T.; Fan, X. L.; Gorte, R. J.; Vohs, J. M.; Lakis, R. E.; Egami, T. *Catal. Today* **1999**, 50, 343.

(26) Mellor, J. R.; Coville, N. J.; Sofianos, A. C.; Copperwaite, R. G. *Appl. Catal. A* **1997**, 164, 171–183.

(27) Lima, A. A. G.; Nele, M.; Moreno, E. L.; Andrade, H. M. C. *Appl. Catal. A* **1998**, 171, 31–43.

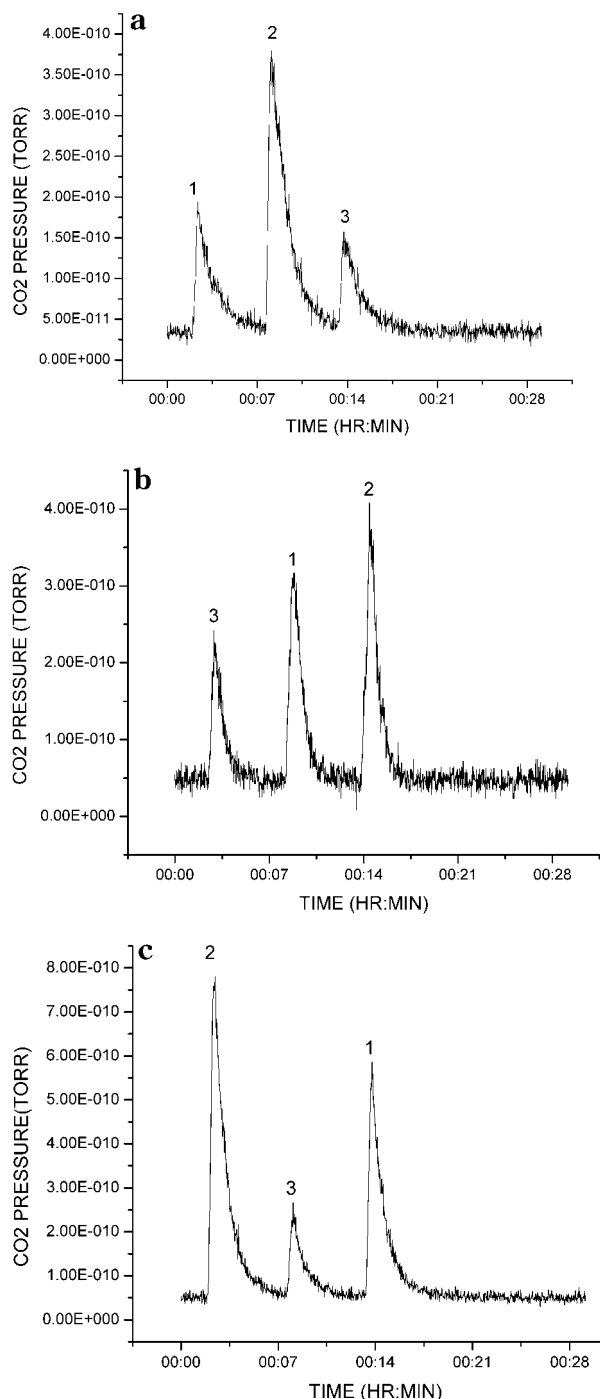


Figure 4. Catalysts 1, 2, and 3 arranged in three different patterns. Catalyst activity ranked consistently as $2 > 1 > 3$.

configuration with the results shown in Figure 6b. The aggregate of the data confirms a LAMIMS ranking of the three most active catalysts as $4 > 8 > 7$. These catalysts were tested in a microreactor at UOP LLC, and those results are shown in Table 2. The microreactor feed was 8% hydrogen, 4% water, 1% CO, 2% CO₂ balanced with inert gas. The reaction temperature in the microreactor ranged from 180 to 280 °C. The space velocity was between 15 000 and 70 000 h⁻¹. Catalysts were prereduced in the microreactor in 5% hydrogen in nitrogen at 220 °C. The relative standard error on this microreactor is +5% and LAMIMS is +10%.

The microreactor ranking of the three most active catalysts was $4 > 8 > 7$ (marked with * in Table 2). The ranking for

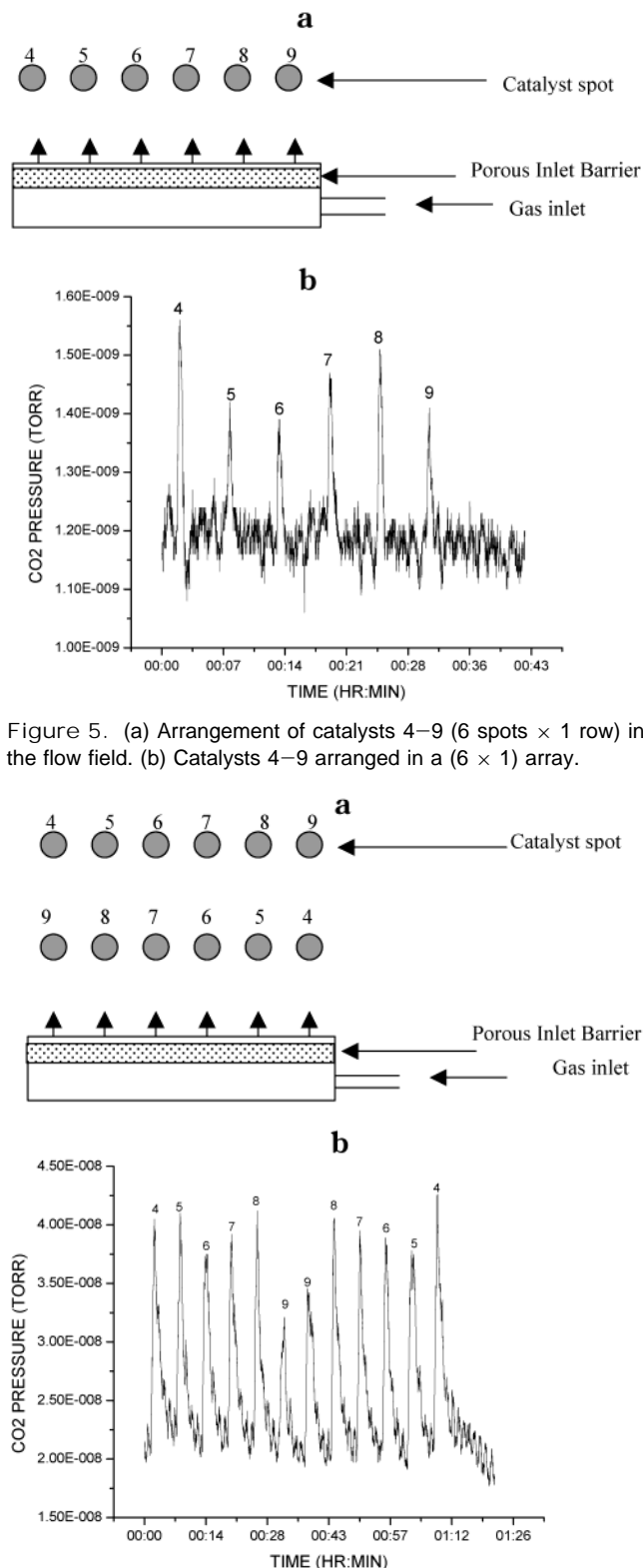


Figure 6. (a) Arrangement of catalysts 4–9 (6 spots \times 2 row) in the flow field. (b) Catalysts 4–9 arranged in a (6 \times 2) array.

catalysts 5, 6, and 9 were ambiguous, and their performances in the microreactor were inferior. More recently, we studied arrays of catalysts for dehydrogenation of methylcyclohexane. These data further exemplify flow uniformity over the arrays and show that spot-to-spot evaluation can be done at intervals less than 1.5 min/spot.²⁸

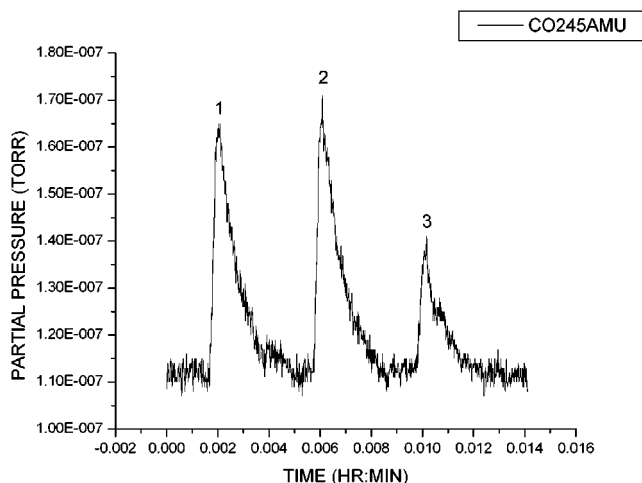


Figure 7. Monitoring CO₂ (45 amu) in the forward WGS reaction in the reformer feed-isotope experiment.

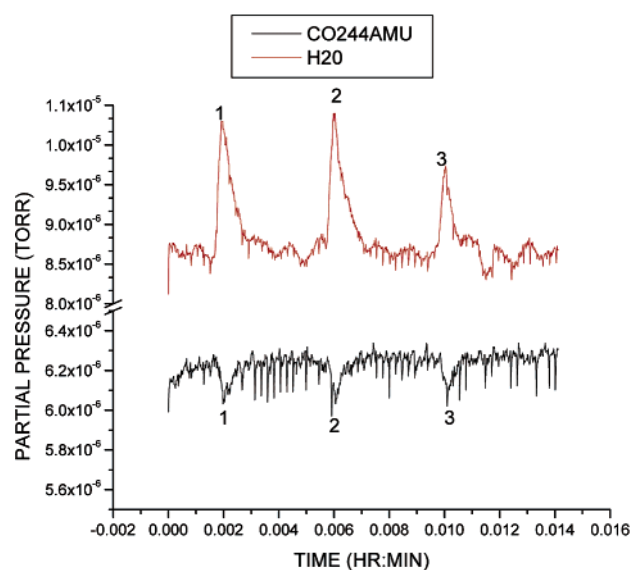


Figure 8. Monitoring CO₂ (44 amu) and H₂O (18 amu) in the reverse water-gas shift reaction in the reformer feed-isotope experiment.

Isotopic Reformer Feed Analysis. Standard reformer feed was used for the WGS catalyst screening. The standard reformer feed, modified by substitution of the CO with ¹³CO, was used along with previously ranked catalysts (1, 2, 3) for the isotope experiments. The masses analyzed were CO₂ (45 amu), CO₂ (44 amu), and H₂O (18 amu). The experimental results are summarized in Figures 7 and 8. The forward WGS reaction on catalysts 1, 2, and 3 were monitored by the formation of ¹³CO₂ peaks, which were used for catalyst ranking. The rankings were 2 > 1 > 3, which was identical with previous rankings done with naturally abundant CO (Figure 4). Inverted CO₂ (44 amu) peaks and positive H₂O (18 amu) peaks resulting from the reverse WGS reaction (Figure 8) appear coincident in time where peaks for CO₂ (45 amu) appear for the forward reaction (Figure 7). Although the reverse WGS reaction yields CO (28 amu), this signal cannot be monitored with reliability because of interference due to atmospheric nitrogen

that can be introduced at comparable levels via back pressure from mass spectrometer roughing pumps.

The rankings of the catalysts by evaluation of the reverse reaction are identical to rankings based on the forward reaction. This is consistent with the principle of microscopic reversibility formulated by Tolman.²⁹ For reversible reactions, the principle of microscopic reversibility indicates that a material that accelerates the forward reaction will also catalyze the reverse reaction.³⁰ The ability to measure products from the reverse and forward reactions, enabled by the use of isotopes, opens the door to the evaluation of a variety of Arrhenius parameters related to the screening reactions.³¹

CONCLUSION

LAMIMS is a fast, environmentally closed, screening method that has been substantiated by microreactor evaluation. The method is based on the use of a composite membrane system consisting of a heat-dissipating gas diffusion layer supported on a semipermeable polymeric membrane, which serves as both a support for catalyst library and a separator between the catalyst reaction chamber and the vacuum of a QMA. LAMIMS can be used over a very broad range of temperatures (e.g., 220–450 °C) because the catalyst array support includes a high-void-volume carbon paper, which acts as a heat dissipater protecting the membrane separator. The membrane array assembly is housed in a ZnSe-windowed heated reactor that permits the fine-tuning of the temperature by laser heating. LAMIMS requires no moving parts, and the closed environment permits establishment of catalyst exposure histories and reactor environments that are relevant to reaction engineers. The closed environment permits the establishment of true baselines absent of artifacts due to sudden introduction of reaction feed in the absence of realistic histories. The system is adaptable to array-prepared catalysts or bulk catalysts deposited as an array using a volumetric array dry catalyst-depositing device. The use of isotopic substitution in reaction feed streams permits the study of both forward and reverse reactions enabling detailed kinetic studies. This, combined with the ability of the QMS to monitor multiple reactants and products, enables determination of selectivity of catalysts along with highly reliable rankings. A typical single catalyst microreactor evaluation takes ~10 h, while an array of 12 catalysts evaluated by LAMIMS took less than 1 h, representing a timesaving factor of greater than 2 orders of magnitude.

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(28) Nayar, A.; Kim, Y. T.; Galloway, D. B.; Willis, R. R.; Smotkin, E. S., manuscript in preparation.

(29) Laidler, K. J. *Chemical Kinetics*; Harper & Row Publishers: New York, 1987.

(30) Charles, J. H. *An Introduction to Chemical Engineering Kinetics & Reactor Design*; John Wiley & Sons: New York, 1977.

(31) Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman and Co.: New York, 1994.