Analysis of Catalytic Reactions

High-Throughput Catalytic Science: Parallel Analysis of Transients in Catalytic Reactions**

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In the field of heterogeneous catalysis, variations in temperature, pressure, or reactant concentration are commonly encountered under real operating conditions. Experiments to identify transients, such as the titration of adsorbed species, exchange of isotopically labeled reactants, and step changes in the reaction conditions are invaluable tools in understanding the synergy between the catalyst nanostructure and the kinetics of a catalytic reaction.[1] When deciding between competing kinetic models, often the key distinguishing feature is their ability to model transient as well as steady-state behavior. Furthermore, the analysis of oscillations in kinetics and spatio-temporal pattern formation on catalysts can greatly increase our understanding of dynamic processes and interactions on catalyst particles.[2]

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Historically, catalysis studies have been performed by testing a single catalyst formulation at a time. However, catalysts are very complex systems with compositional heterogeneity on both the nano- and mesoscales. Using a single reactor to study hundreds or even thousands of catalyst formulations systematically in order to understand reaction behavior as a function of composition would entail a prohibitive amount of time. Combinatorial catalysis, or high-throughput screening, has created significant excitement in the past few years, opening new possibilities for catalyst discovery and optimization.[3] Several analytical approaches to high-throughput experimentation (HTE) have emerged for the rapid screening of catalyst activity. The true power of the combinatorial approach, however, can only be realized with the ability to perform quantitative studies in parallel. This methodology, in combination with microkinetic modeling of the quantitative data, can take our understanding of heterogeneously catalyzed reactions to a higher level, accelerate discovery of novel catalyst formulations, and ultimately lead to rational catalyst design.[4] Novel high-throughput approaches are therefore needed to study catalytic reactions quantitatively, in parallel, and under both transient and steady-state conditions. To answer this need, we have developed Fourier transform infrared (FTIR) imaging for the study of multiple catalytic reactors simultaneously with a time resolution below 2 s.[3i,j,5]

To demonstrate the power of parallel transient studies, we present results on a library of NO_x storage and reduction (NSR) catalysts supported on γ-alumina (Table 1). As government and consumer demands for automotive fuel economy and emission controls become more stringent, new catalysts are needed for exhaust aftertreatment.[6] These emission regulations include controls on pollutants such as nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HC), and carbon dioxide (CO_2). To increase fuel economy, automobile manufacturers are introducing lean-burn engines in which combustion occurs in an excess of air, as opposed to a stoichiometric mixture of fuel to air. Current three-way catalytic converters cannot reduce NO_x emissions to acceptable levels under these conditions. The NSR catalysts are designed to reduce NO_x from automotive exhaust in the presence of excess oxygen by cycling the automobile engine between a fuel-lean phase (FLP), in which NO_x is stored on the catalyst surface, and a fuel-rich phase (FRP), in which the NO_x is released and reduced to N_2.[7] The complexity of the formulation of these catalysts—which typically contain noble metals (for oxidation and reduction), alkaline earth metals (for NO_x storage), and transition metals or other additives (for improved sulfur tolerance)[8]—clearly displays the necessity of a combinatorial approach for the successful discovery of optimum formulations. Since these catalysts are designed to operate under transient conditions, a HTE system that can monitor effluent compositions rapidly and in parallel is essential for a systematic study of NSR catalysts.

Table 1: The catalysts tested with Fourier transform infrared (FTIR) imaging.

Catalyst	Loading [wt%]			Preparation method
	Ba	Pt	Fe	
1	26.3	1.5	0	four-step sequential impregnation: Ba (3×) then Pt
2[a]	30	1.5	0	one-step wet impregnation
3	30	1.3	9	four-step coimpregnation
4[a]	15	0	10	three-step sequential impregnation: Ba (2×) then Fe
5	28	1.5	11	five-step sequential impregnation: Ba (3×), Fe then Pt
6	14.2	0	0	two-step impregnation
7[a]	5	1	3	one-step coimpregnation
8	0	1.7	0	one-step impregnation
9[a]	15	1.5	10	four-step sequential impregnation: Ba (2×), Fe then Pt
10[a]	30	1.5	0	one-step slurry impregnation
11	0	0	0	
12[a]	30	1.5	10	one-step slurry impregnation
13[a,b]	0	1.5	0	one-step impregnation
14[a]	30	1.5	10	one-step slurry impregnation
15	25.7	0	0	three-step impregnation
16	–	–	–	no catalyst

[a] Nominal weight loading. [b] Titania support was used instead of alumina.

The transient responses of a library of NSR catalysts were monitored during step changes between the FRP and the FLP at six different temperatures.[9] During the transition, spectral images were collected every three seconds of the effluents from 16 reactors simultaneously. Figure 1 presents representative IR spectra of the effluent stream from one of the 16 reactors during a portion of the switch from the FRP to the FLP. The concentrations of NO, NO_2, NO_x, and N_2O calculated from the IR spectra during this switch are shown in Figure 2.

A key characteristic of NSR catalysts is their ability to store NO_x during the FLP. A steady concentration of NO_x after switching from the FRP to the FLP signifies that the

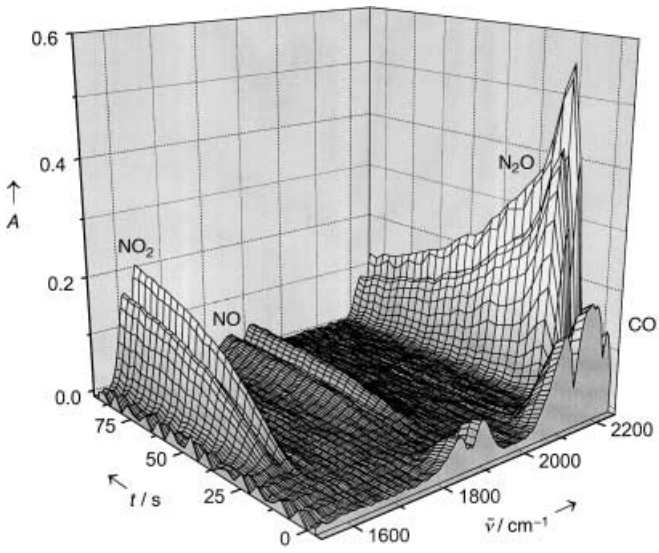

Figure 1. Transient IR spectra after the switch from the FRP to the FLP at 300°C for catalyst 1. During the FRP the CO and NO are not fully oxidized or reduced at this temperature. When the reaction conditions were switched to the FLP at $t = 0$ s, the CO was completely oxidized to CO_2, the N_2O band grows and decays, and later ($t \approx 25$ s) the NO_2 and NO bands appear. A = absorption.

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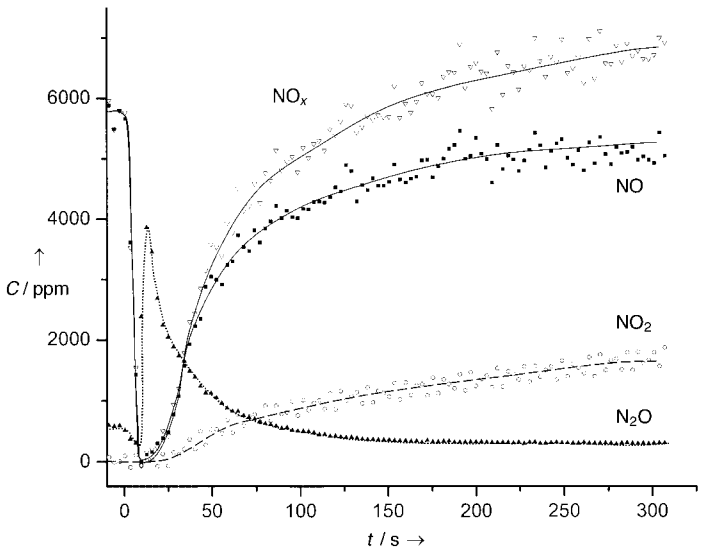

Figure 2. Concentration C for NO, NO_2, NO_x, and N_2O for the same catalyst and conditions as in Figure 1.

NO_x storage sites on a catalyst are saturated. Figure 3 is a plot of the NO_x concentration for five selected catalysts as a function of moles of NO_x introduced into each reactor. The difference in the number of moles of NO_x necessary to observe saturation is a consequence of differing NO_x storage capacities. The storage capacity of all 16 reactors under these conditions as a function of temperature are given in Table 2.

The results corroborate previously published data for storage capacities determined in single reactors and show the maximum in NO_x storage capacity between 350 and 400 °C.[10] The differences in the reported NO_x storage capacities can be attributed to different operating conditions and catalyst amount, type, and preparation. Our findings are also consistent with other results indicating that increasing the amount of alkaline earth metal increases the NO_x storage capacity (compare catalysts 5 and 9).[10b] In addition, these results indicate that the catalyst preparation technique affects the performance of the catalysts (compare catalysts 1 and 2 and catalysts 3 and 5).

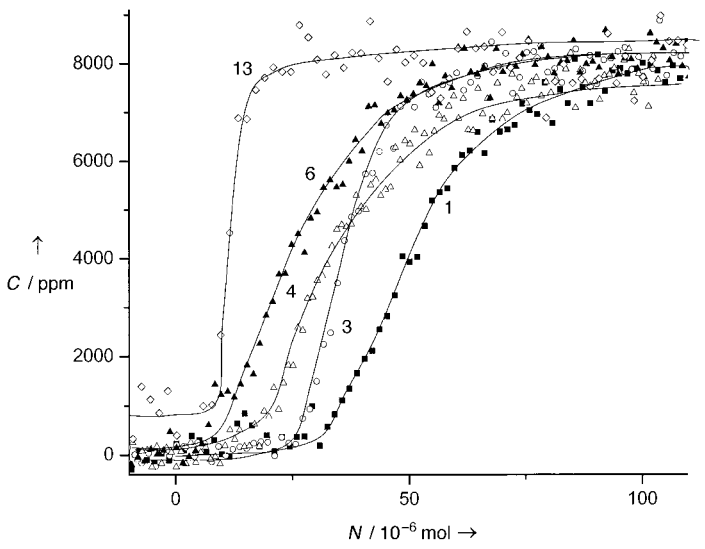

Figure 3. Concentration C of NO_x for catalysts 1, 3, 4, 6, and 13 as a function of moles N of NO_x passed through the catalyst at 400 °C during the switch from the FRP to the FLP.

Table 2: Amount of NO_x stored during the FLP until saturation.

Catalyst[a]	Amount of NO_x stored [$\times 10^{-6}$ mol]					
	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
1	8	29	48	47	44	38
2	9	25	38	41	39	24
3	4	28	38	37	29	17
4	20	19	24	33	29	24
5	25	15	13	30	41	34
6	5	15	24	27	20	17
7	1	8	20	26	27	25
8	1	22	24	25	22	16
9	3	14	21	25	19	16
10	7	15	20	22	22	20
11	23	28	28	22	12	12
12	0	10	12	13	10	9
13	9	7	10	8	4	6
14	6	1	1	3	4	10
15	12	16	0	1	6	18
16	2	1	2	1	0	1

[a] See Table 1.

Our technique is not only capable of comparing catalysts, but also provides insight into the elementary reaction steps. For example, the rate at which the NO_x concentration increases varies (Figure 3), thus indicating differences in the kinetics of the underlying elementary reactions. Likewise, the concentration of NO increases before NO_2 (Figure 2), which indicates the oxidation of surface nitrite species to surface nitrate as the stored NO_x first exists on the BaO surface as nitrite. Nitrogen dioxide is able to adsorb onto the surface and oxidize nitrite to nitrate, resulting in the release of NO to the gas phase.[10a,11] As the BaO surface becomes saturated with nitrate, NO_2 begins to appear in the gas phase. At complete saturation, the concentrations of NO and NO_2 reach a steady-state value determined by the rate of NO oxidation over the catalyst.

By comparing transient responses, we also noticed a maximum in the N_2O concentration before saturation of the NO_x storage sites for some of the catalysts. This effect is most prominent at temperatures below 400 °C. This magnitude in the N_2O concentration has not been previously reported, even in single-reactor experiments.[10,12] The difference can be attributed to several factors, including enhanced time resolution and chemical sensitivity of our analytical technique and slight differences in reaction conditions or catalyst preparation methods between the two studies. In a previous investigation, the time resolution of approximately 40 s between data points was not fine enough to resolve the brief N_2O maxima clearly observed in our experiments.[12] In another study by mass spectrometry, a similar response was reported for an unspecified mass to charge ratio (m/e) assigned to be CO_2 by the authors.[11b] It is unclear what m/e was used, but the species could be N_2O since the resolution of the mass spectrometers employed in these studies is most likely

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sufficiently low such that both N_2O and CO_2 would appear at an *m*/*e* of 44.

This work provides the first example of an analytical approach capable of truly parallel, quantitative analysis with a temporal resolution applicable to transient experiments. FTIR imaging is a flexible technique capable of studying a large number of catalytic reactions and unambiguously identifying various components. The speed of data acquisition and the quantitative capability of this new technique marks the dawn of a new field of scientific endeavor: high-throughput catalytic science. We now have the ability to study rapidly many formulations of catalytic materials at a level that allows successful kinetic modeling. This enables us to rise above simple screening to the level of fundamental understanding of reaction mechanisms, which will lead us to rational catalyst design.

Experimental Section

The catalysts were tested simultaneously in a 16-channel vertical microreactor developed in-house.[13] The effluents from the 16 channels were analyzed simultaneously using an FTIR imaging system slightly modified from the one described in references [3i] and [5]. The optical setup consists of a Bruker Equinox 55 FTIR spectrometer, barium fluoride optics, a long pass optical filter (3750 nm), and a 64×64 mercury cadmium telluride focal plane array detector (Santa Barbara Focalplane) collecting at a frame rate of 315 Hz. Data processing is automated by software written in-house and run on a standard Pentium 4 2.4 GHz desktop computer. The raw data files, consisting of 4096 interferograms for each spectral image, serve as input to our program and a series of data-processing steps (Fourier Transform, absorbance calculation, baseline correction, peak integration, and conversion to concentration from previously performed calibrations) are then performed in a batch mode. The program produces a text file consisting of concentrations as a function of time combined from the different data spectral images. For example, a data set consisting of 672 MB and 140 spectral images (or 573 440 interferograms and a collection time of about 7 min) can be processed and the concentration evolution for five different species for all 16 reactors written to a 285 kB text file in less than 10 min. The entire process is automated and requires less than 20 s of input from the user before starting the analysis. A graph can be generated from the data with Microsoft Excel by using a macro written with Microsoft Visual Basic for Applications.

Each channel in the microreactor holds 150 mg of catalyst. The catalysts were pretreated before testing with two successive cycles of 15 min of 17 % O_2 in He followed by 15 min of 9 % H_2 in He at 773 K. The catalysts were then exposed to five cycles of switching between the FLP followed by the FRP at 250 °C to age the catalysts before testing. At subsequent temperatures, two cycles of switching between the FLP followed by the FRP were completed before testing.

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