[15] Compound **6**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_8]$xylene, 50 °C, H_3PO_4): $\delta = 36.6$ (d, $^2J(P,P) = 25.4$ Hz), 0.6 (d, $^2J(P,P) = 25.4$ Hz). ^1H NMR (300 MHz, $[D_8]$xylene, 50 °C, TMS): $\delta = 0.71$(d, $^3J(P,H) = 21$ Hz, 3H; $PCCH_3$), 0.73(d, $^3J(P,H) = 23$ Hz, 3H; $PCCH_3$), 4.12 (d, $^2J(P,H) = 15.4$ Hz, 1H; NH), 4.50 (br, 2H; NH), 7.18 (d, $^4J(H,H) = 2.3$ Hz, 1H; Aryl-H), 7.29 (d, $^4J(H,H) = 2.0$ Hz, 1H; Aryl-H), 7.32 (d, $^4J(H,H) = 2.0$ Hz, 1H; Aryl-H), 7.44 (d, $^4J(H,H) = 2.3$ Hz, 1H; Aryl-H). Signal assignments were aided by 2D $^1H\{^{31}P\}$-HMQC spectra; the remaining resonance signals could not be unequivocally assigned.

[16] See: J. Böske, E. Niecke, B. Krebs, M. Läge, G. Henkel, *Chem. Ber.* **1992**, *125*, 2631.

Parallel Analysis of the Reaction Products from Combinatorial Catalyst Libraries**

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The combinatorial approach has great potential in many disciplines to optimize systems that have large parameter spaces. Recently, this concept has been introduced to the field of materials science.[1] The ultimate goal of the combinatorial approach is to efficiently optimize and discover new formulations, be they pharmaceutical products, catalysts, or other materials. Practically, this is accomplished by a systematic and efficient exploration of the parameter space that controls the properties of the final product. The two key components to a successful combinatorial approach are the controlled synthesis of a collection of materials with systematic variations in properties and the subsequent high-throughput analysis of libraries of these materials. Speed, through parallel synthesis and characterization, consequently becomes critical for the success of the combinatorial discovery process. Herein, we report the first analytical technique for truly parallel high-throughput screening of the reaction products from libraries of heterogeneous supported catalysts.

A number of experimental approaches have been reported for screening catalyst libraries. These are based on conventional serial techniques, which have been automated to decrease the screening time. Scanning mass spectrometry is based on rapidly analyzing the gases from one sample in a combinatorial library at a time, in a sequential manner. One approach uses a single probe composed of coaxial gas delivery and gas analysis tubes.[2] Libraries are analyzed by sequentially placing the tube over each element of the library, feeding reactant gases, and analyzing product gases. This approach is applicable to the initial screening of libraries deposited onto flat, solid substrates due to its gas delivery design. A second approach uses array microreactors with supported catalysts, coupled with capillary microprobe sampling.[3] Reactants, products, and carrier gas are withdrawn from each microreactor channel using a capillary sampling probe. By repeating this approach for each microreactor, the entire library can be screened. Another experimental method is based on photoionization of reaction products using tunable UV lasers.[4] The resulting photoions are detected by a microelectrode in close proximity to the sample. One disadvantage of this technique is that a suitable laser frequency for each species of interest must be known and accessible. In general, all of these techniques have the shortcoming that the screening time is proportional to the library size.

In contrast, truly parallel screening techniques gather information simultaneously from all the elements in a library. This category so far only includes heat-sensing techniques. Infrared thermography and thermistor arrays detect heat evolved from active library members and have been used to detect activity for exothermic reactions in combinatorial libraries.[5] These techniques, however, cannot chemically resolve product composition, which is often the most important issue when studying catalytic reactions, and therefore cannot determine the selectivity of a catalyst. Also, the assumption is made that the exothermicity is derived solely from the desired reaction, and not from any unforeseen side reactions, limiting these techniques to the study of well-known, simple reactions.

FT-IR imaging has the ability to gather chemically sensitive information from all library elements simultaneously. This approach has been demonstrated in recent work, where our group has pioneered infrared spectral imaging for the rapid analysis of reactions on solid bead materials.[6] IR spectroscopy is a well-established tool for the analysis of the composition of gas mixtures. The lower detection limit depends on several factors, such as the absorptivity of the absorption bands of the specific gas, the path length of the cell, the concentration of the species of interest, the spectral noise level, and the strength and structure of the bands of interfering gases. The true power of FTIR imaging for high-throughput analysis lies in its capability for parallel examination of product streams from multiple reactors. For this purpose, we have developed a novel gas-phase array attached to a multiple sample reactor, which currently allows us to perform parallel screening of the product stream of 16 supported catalyst samples.

To demonstrate the applicability of gas-phase IR imaging to parallel reaction product analysis, we present results, in which the parallel FTIR analysis was used to determine conversion during temperature-programmed complete oxidation of propene. This reaction is important for the automotive three-way catalyst and, in general, hydrocarbon oxidation is mainly catalyzed by platinum group metals.[7]

The samples examined in this study were commercial catalyst monoliths as well as custom-synthesized supported catalyst powders. Additionally, some channels of the reactor were filled with blank support material. After approximately 0.2 g of each catalyst sample was loaded into the 16-catalyst parallel reactor; all samples were pretreated simultaneously by alternate oxidation and reduction cycles. After the reactant gases were introduced, a temperature ramp of 10 K min^{-1} was

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[**] This work was supported by the National Science Foundation (grant CTS-0071020).

  1433-7851/01/4016-3028 $ 17.50+.50/0

established, and absorbance images of the exit stream of all 16 samples were taken every 30 s over a temperature range from 300 K to 670 K. Figure 1 shows a representative FTIR spectrum of the exhaust stream at 300 K. The spectrum is dominated by the absorption bands of propene. This spectrum was taken from one pixel in the detector array using one scan, that is, no coaddition or averaging of spectra was performed. This demonstrates the excellent spectral quality that can be achieved with this instrumental setup.

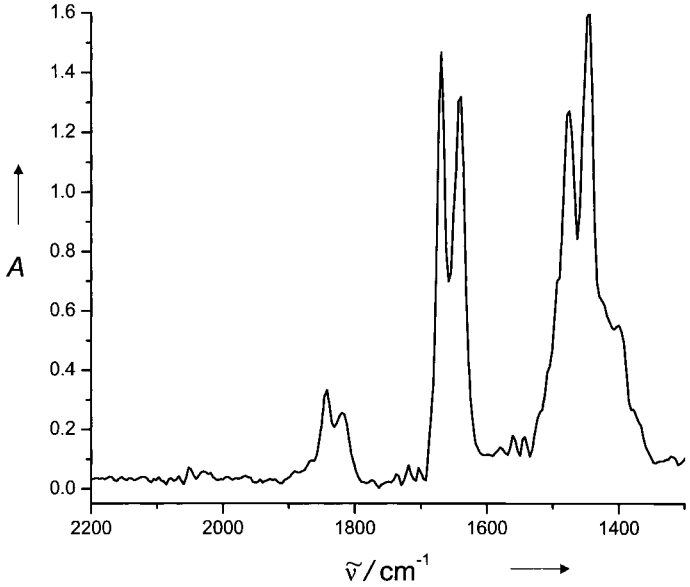

Figure 1. Representative gas-phase spectrum of propylene recorded with the FTIR imaging spectrometer equipped with the gas-phase sampling array.

Figure 2 shows absorbance images for the gas-phase CO_2 vibration band for catalyst temperatures of 440 K and 650 K. Plotting absorbance intensities for a specific reaction product for the entire array reveals the position of the active catalysts. High intensity in the image indicates an active catalyst converting propene to CO_2. Each pixel in the image contains a full IR spectrum from 2600 to 1300 cm^{-1}. At 440 K, seven catalysts are active for total oxidation of propene, while at 650 K 12 catalysts produce CO_2. All of the inactive array elements are those containing the silica and alumina support materials, which are expected to show no reactivity. Notably, one entire data set (i.e., 4096 IR spectra with 8 cm^{-1} spectral resolution) takes less than 20 s to collect and process.

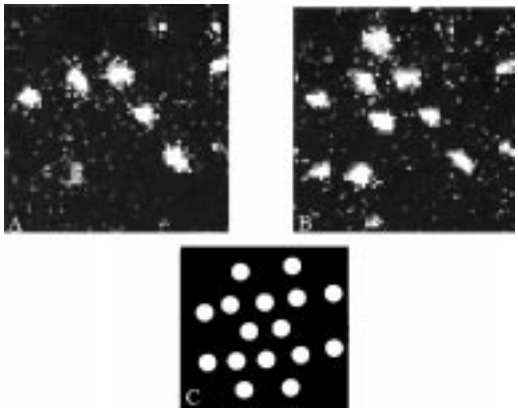

Figure 2. Spectral images of CO_2 concentration (2360 cm^{-1}) measured by FTIR imaging at 440 K (A) and at 650 K (B). Light-off between these two temperatures can be seen for several elements of the array. C) Schematic representation of the location of the individual cells in images A and B.

Integration of the IR bands belonging to the desired reaction products from each array element in the image allows quantitative analysis of the product stream. Data for the amount of CO_2 produced as a function of reactor temperature are shown in Figure 3 for seven selected catalysts from the array. The pure support shows no measurable reactivity, as expected. The dashed line shows the decrease of propene in the reactor effluent for the 5 wt % Pt on γ-Al_2O_3 catalyst. This line follows very closely the CO_2 production and the material balance closes within an error of less than 5 %. The reproducibility of the method is demonstrated by comparing two identical catalysts (commercial samples; Figure 3).

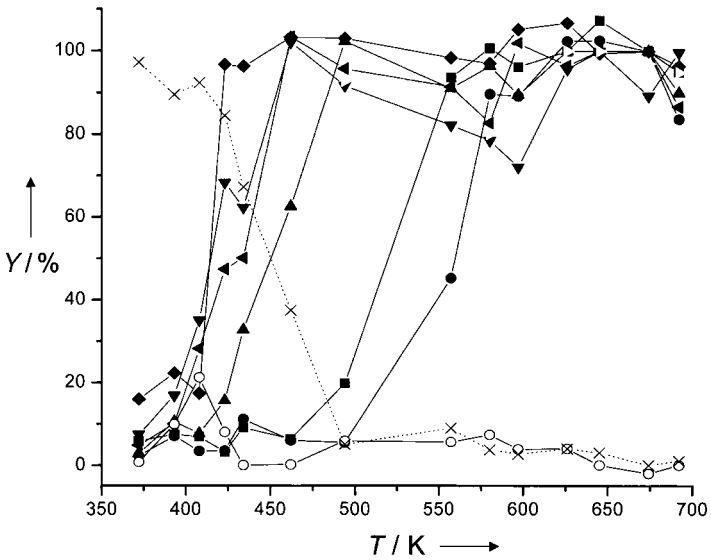

Figure 3. Results for the production of CO_2 during the oxidation of propene for four γ-Al_2O_3 catalysts with 1 wt % Pd (■, 520 K), 1 wt % Pt (●, 560 K), 5 wt % Pt (◆, 450 K), 5 wt % Ru (◇, 420–435 K), a SiO_2 catalyst with 2.67 wt % Pd (▲), pure SiO_2 support (○), and two commercial catalyst samples (◀, 420–435 K). The temperature or temperature range given in parentheses indicates the light-off temperature of the catalyst. (×) propene signal for the 5 wt % Pt on γ-Al_2O_3 catalyst. Y = conversion [%].

With the temporal resolution of our analytical technique, it becomes possible to monitor the effect of changing control parameters of the reaction (i.e., temperature, gas composition) on a time scale of seconds. Additionally, this allows the high-throughput evaluation of the light-off characteristics of catalysts. For example, it took only around 30 min to assess the light-off characteristics and reactivity of an array of 16 supported catalyst samples over a temperature range of 350 K.

It has been demonstrated that rapid-scan FTIR spectral imaging is the first technique that is capable of monitoring gas-phase reaction products from multiple members of a supported catalyst library in a truly parallel fashion. This experimental methodology is fully scalable, and with the coming availability of larger FPA detectors, this approach will

  1433-7851/01/4016-3029 $ 17.50+.50/0

be capable of screening 100 s to 1000 s of supported catalyst samples on a time scale of seconds. In addition, rapid-scan FTIR imaging is a flexible technique, which can be used for analysis of many combinatorial systems, that is, the technique is independent of the specifics of the reactor setup.

Experimental Section

The optical setup consists of a Nicolet Magna 860 FTIR spectrometer, barium fluoride (BaF_2) optics, a long pass optical filter, a KBr diffuser, and a 64×64 pixel mercury cadmium telluride (MCT) focal plane array (FPA) detector. A more detailed description of the rapid-scan imaging setup can be found in reference [8]. The reactor has 16 individual channels that each hold one powdered catalyst sample. The individual gas outlets are connected to the gas sampling array constructed from 16 stainless steel tubes, each with a separate gas inlet and outlet. The ends of the cells are equipped with IR transparent windows sealed by gaskets. The cells are arranged in an array fashion, so that all 16 can be studied simultaneously using our FTIR imaging system. The entire path that the reactant and product gases travel through is composed of stainless steel, teflon, buna rubber, and calcium fluoride, all of which are not catalytically active at the temperatures used in the experiments. Currently, each cell has a path length of 15 cm. However, due to the fact that a parallel IR beam travels through the array, it is possible to extend the cells. This might become necessary, for example, to study gas concentrations below the current detection limit, which was determined to be around 1000 ppm for the case of propene. This may also become necessary when studying mixtures of gases with similar IR signatures, where weak vibrational bands have to be followed to distinguish various components of the gas mixture. Also, due to the inherent nature of IR vibrational spectra, this technique is not suited for the detection of homonuclear diatomic gases, such as O_2 and N_2.

The catalyst samples used were 1.33 % Pt and 2.67 % Pd co-impregnated on silica support, 1.33 % Pd and 2.67 % Pt co-impregnated on silica support, 1 % Pt on γ-Al_2O_3, and 1 % Pd on γ-Al_2O_3 (all synthesized in house), and 5 % Pt on γ-Al_2O_3, (from Alfa Æsar), 5 % Pd on γ-Al_2O_3 (from Alfa Æsar), 5 % Ru on γ-Al_2O_3 (from Alfa Æsar), pure silica support powder, and a commercial automotive monolith catalyst. The synthesized catalysts were prepared by using the incipient wetness technique, calcined in air at 573 K for 6 h, and reduced at 473 K in 20 % H_2/He for 12 h. All catalysts were pretreated simultaneously in situ by flowing oxygen in nitrogen at 625 K for 90 min. Reaction conditions were established with flow ratios of propene:O_2:N_2 of 0.1:0.57:1 with a total flow of 210 sccm. The reactor was heated to the desired temperature, allowed to equilibrate, and infrared spectral imaging data of the gas-phase array were collected.

Received: February 28, 2001 [Z16698]

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