Real-Time Photoacoustic Parallel Detection of Products from Catalyst Libraries**

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Over the last few years, high-throughput experimentation has found increasing acceptance as a powerful methodology to accelerate the discovery of solid catalysts. Although interesting developments in product analysis have been reported,[1–4] there is an urgent need for fast and truly parallel techniques for analysis. Moreover, versatile automated procedures for catalyst synthesis are not easy to implement. Herein we report developments which address both problems: 1) Detection of a pressure pulse after laser excitation of the target molecules (photoacoustic detection) is used to monitor catalytic activity in a real-time, parallel fashion. 2) Automated libraries of high surface area multinary oxides are synthesized by using activated carbon as an "exotemplate" for the generation of small particles. Using the synthesis approach and the detection method, novel low-temperature CO-oxidation catalysts have been discovered.

The high-throughput search for novel catalytic materials is hampered by two conflicting targets: On the one hand, catalysts should be measured under plug–flow conditions at a defined residence time, which requires reactors such as those described by Hoffmann et al.[5,6] On the other hand, the parallel techniques for product analysis described so far are difficult to adapt to such reactor systems. The system we have developed to reconcile these conflicting objectives relies on the photoacoustic effect, which has been used for nonparallel gas analysis in the past.[7] To convert it into a parallel-detection technique we developed the setup which is shown schematically in Figure 1. The exit streams from the different channels of a parallel reactor are directed into an array of tubes (eight in our case), arranged in line with each other. A laser tuned to an absorption frequency of the target molecule is passed through the free-flowing exhaust plumes of all catalysts. We used a pulsed CO_2 laser (10 Hz or 100 Hz modulated 25 W laser with a pulse length of 35 μs or 25 μs), emitting at 943–950 cm^{-1}, because ethene (one of the target products) has a strong absorption band in this range. In addition, CO_2 lasers are cheap, readily available, high-power light sources. However, other lasers can also be used for target molecules with absorption bands in other ranges of the spectrum. A microphone (Brüel & Kjaer condenser microphone) with a fast response time and decay is used to record the pressure pulse generated after energy absorption of the target molecules. The time lag between laser pulse and different pressure pulses can be used to localize the origin of the pulse with a resolution of about 3 cm. Shorter pulses will improve the spatial resolution because they lead to sharper signals which could ideally be slightly longer than the time the pressure pulse needs to propagate a distance equal to the diameter of the gas exhaust. This, however, would also require the use of a microphone with better damping characteristics.

In Figure 1, the voltage signal from the microphone after a laser pulse at $t = 0$ s is also shown. The minima correspond to pressure pulses from subsequent gas outlets, the decrease of intensity with increasing time is caused by the increasing distance to the microphone. The signal-to-noise ratio can be improved by summing signals from several laser pulses which, in the present setup, increased the time for a complete set of data to 2.5 s. Automated on-line calibration of the signal uses substrate gas (0% ethene) and product gas, typically 2% ethene. Despite the fact that absorption of laser light could be nonlinear in terms of laser power, a linearity of concentration and measured signal intensity between 0 and 2% was shown in calibration experiments. Deviations from linearity were not detectable within the error margin (about 1% of the maximum for 2.5 s signal averaging). Because of the higher signal, precision of the measurements is better for the

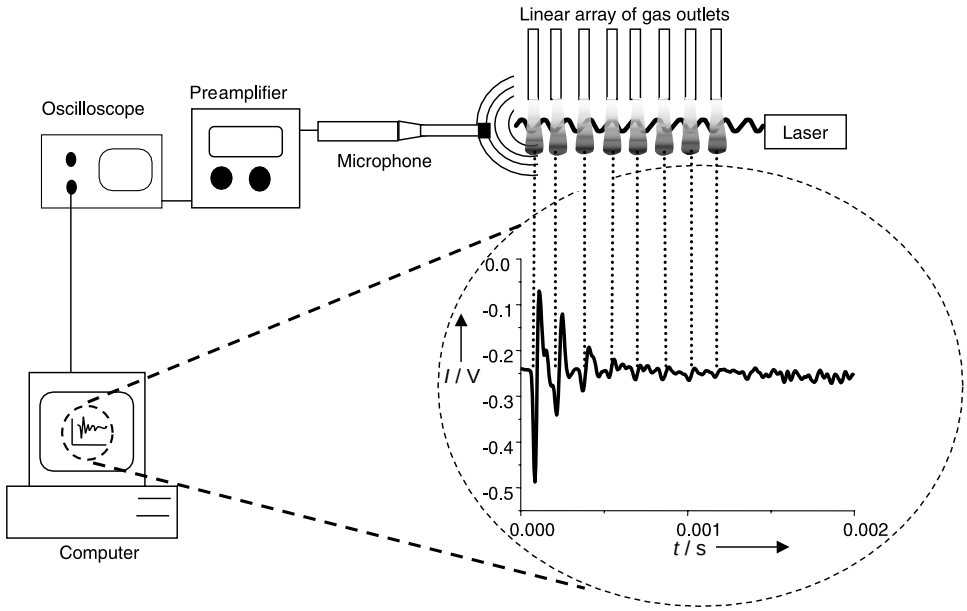

Figure 1. Setup of the photoacoustic free-field measurement. The diagram shows a real signal of voltage versus time, with $t = 0$ being the moment of the laser pulse. 2% ethene flowed through all channels. The minima correspond to the subsequent reagent outlets, additional minima result from residual echos.

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channels close to the microphone, but even for the most distant channels, 0.3 % ethene could be reliably measured. By using several microphones suitably placed, it will be possible to analyze a two-dimensional sound field from an array of gas outlets, which allows a much higher degree of parallelization than described in this initial study.

One can even use the technique for the analysis of molecules with very low extinction coefficients, such as CO_2. The CO_2 laser relies on transitions between excited vibrational states of the CO_2 molecule. CO_2 has thus a very low extinction coefficient at the emission wavelength of the laser. In this case, analysis in the free-flowing gas decribed above is not possible, but the signal can be amplified by resonance. The gas from each reactor channel is directed to a metal pipe that acts as a resonance tube, which is equipped with a separate microphone (cheap electrete microphone for about 1 €). The laser is modulated on a resonance frequency of the tubes. The microphone signal is detected with a lock-in amplifier and a multiplexer, which switches between the different microphones. A setup with 16 parallel channels has been realized. Analysis speed is essentially determined by the electronics of the system. In the present setup, the single channels can be read in times below 1 s. For a molecule such as CO_2, a detection limit of 100 ppm was achieved, the detection limit for ethene can be estimated to be in the ppb range with the resonance setup.

There are two other laser-based techniques which have been used to analyze the products of a catalytic reaction, resonance-enhanced multiphoton ionization (REMPI)[8] and photothermal deflection.[9] The new development reported here solves two problems associated with these methods. While thermal-deflection spectroscopy is not a parallel but a sequential method, the REMPI setup makes it necessary to expose an electrode array to the product stream, which can lead to severe contamination and disturbance of the electrode array. In addition, more absorption frequencies and combinations of frequencies could be used than in REMPI, which can make this method more selective. Suitable absorption frequencies can be selected based on the known IR spectra of substrates and possible products. The only limitation is the availability of commercial laser sources that emit in the selected range of the electromagnetic spectrum.

Both detection techniques described above, the resonant method and the free-field method, were used to evaluate libraries of high surface-area metal oxides. The automated synthesis of this class of important catalysts has so far not been possible using automated procedures.[10] We have now developed a synthesis route to solve this problem. There are scattered reports that impregnation of a micro- or mesoporous mold and subsequent removal of the mold can lead to highly porous solids.[11,12] If activated carbon is impregnated with a highly concentrated metal-salt solution (nitrates have been best in most cases) and then dried and calcined, a highly disperse oxide remains. Random libraries of such mixed oxides were generated by random selection of components from a pool of ten. The desired compositions were then automatically recalculated to volumes of solution for impregnation, and the resulting file of pipetting data transferred to an automated dispenser, where a library of 77 catalysts was prepared in one go by impregnating the activated carbon. The whole library was then calcined simultaneously and the catalysts transferred to the reactor for testing.

We prepared several such libraries for various catalytic applications. About 150 different compositions were tested in total with the photoacoustic setups described above. For the oxidative dehydrogenation (ODH) of ethane, activity has been detected in some of the compositions, and the results of the photoacoustic parallel detection correspond very well to separate measurements in a conventional reactor with GC analysis (Figure 2). It is noteworthy that, because of the fast analysis, systems could also be identified which had very good performance over the first 20 min of the reaction, but then deactivated rapidly.

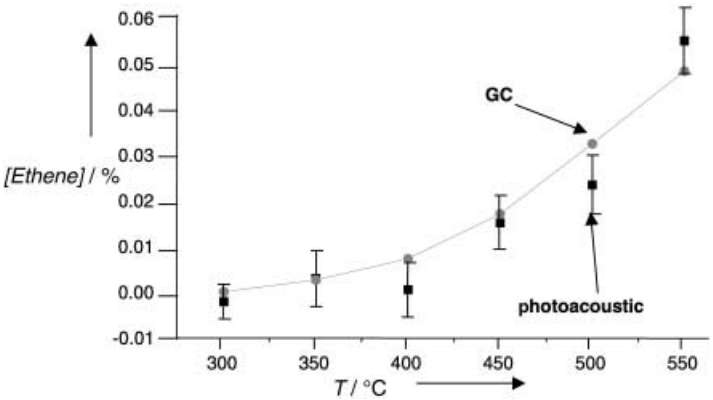

Figure 2. Measurement of ethene concentration in the oxidative dehydrogenation of ethane; comparison between novel free-field photoacoustic setup and conventional GC analysis. The composition of the catalyst was 12 % La, 2 % Ba, 9 % Pb, 7 % Th, 27 % Mn, 24 % Ni, and 19 % Cu as oxides, synthesized by the activated-carbon route described in the text.

In the CO oxidation, novel low-temperature CO-oxidation catalysts that are free of noble metals have been identified. The best catalyst is much better than most noble-metal-based systems, with the exception of the Sn-promoted Pt catalysts. Only Haruta-type gold catalysts[13] and some other formulations, such as the Co_3O_4-based systems[14] and the hopcalite-related (Cu-Mn-O) systems,[15] show better activity than the materials discovered. Figure 3 shows the conversion versus temperature curves for different catalysts analyzed in parallel during a dynamic heating/cooling experiment. The agreement is excellent, which demonstrates that photoacoustic detection can be used as a quantitative tool under optimized conditions. Figure 4 shows the powder diffraction pattern and the sorption isotherm of the best CO-oxidation catalyst discovered in the screening of the samples. Because the best systems contain Cu and Mn, these materials are probably related to the hopcalite system. The diffraction pattern corresponds to a spinel phase or a mixture of several similar spinel phases, the exact nature of which is not yet known, and amorphous by-products. The sorption isotherm shows a Brunauer–Emmett–Teller (BET) surface area of 60 $m^2 g^{-1}$, both the phase and the sorption behavior is also rather typical for other members of the libraries investigated here.

In summary, we have introduced: 1) a real-time, parallel, and fast detection technique for the analysis of products from

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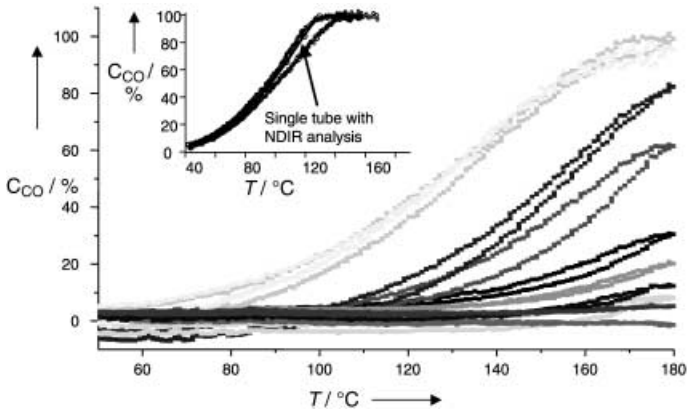

Figure 3. CO-conversion curves measured simultaneously with the resonance setup. Out of the 16 curves only 10 are shown, to increase readability. The inset shows the comparison of the results for the best catalyst ($Fe_{17}Ni_{25}Mn_{27}Cu_{30}$) measured with the resonance photoacoustic setup and in a conventional reactor with a nondispersive IR system (URAS 3E).

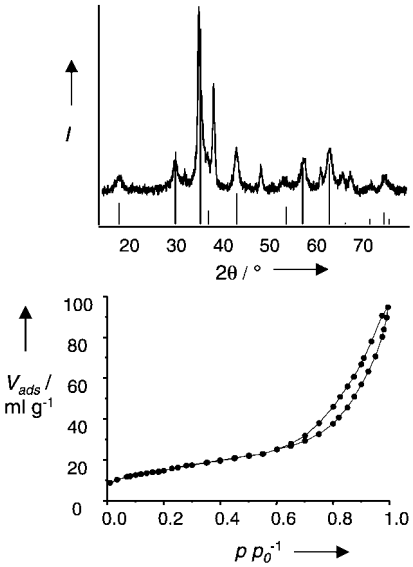

Figure 4. Nitrogen-sorption isotherm (bottom) and X-ray diffraction pattern (top) of the $Fe_{17}Ni_{25}Mn_{27}Cu_{30}$ catalyst. The material has a surface area of 60 $m^2 g^{-1}$, the lines in the diffraction pattern correspond to $CuNi_{0.5}Mn_{1.5}O_4$, which suggests that the crystalline part of the catalyst—in addition to the amorphous material present—is a spinel phase.

catalytic reactions, 2) a method to synthesize libraries of complex mixed oxides automatically, and 3) applied the setup to investigate ethane ODH and low-temperature CO oxidation, for which several novel noble-metal-free catalysts were discovered. These components will form the basis for a new technology platform for high-throughput screening in catalysis research.

Experimental Section

Fluka 05120 and Darco KB-B, supplied by Aldrich, were used as activated carbon. Metal compounds were hydrates of nitrate salts supplied by Fluka. All precursor solutions were saturated.

Catalyst impregnation was performed using a commercial pipette system (Gilson XL 232). The carbon was transferred into vials in a 77-well plate by using fixed volumes which were equal to 230 mg (± 10 mg) in weight. We used a total amount of 450 μL of mixed precursor solution which corresponds to incipient-wetness conditions. The composition of the precursor solution was determined by a random algorithm which first determines whether a precursor is chosen as an ingredient or not, and afterwards which quantity of the chosen precursor contributes to the total composition. The impregnated samples were then calcined on a 77-well plate covered with gauze to prevent oxide particles being expelled during carbon combustion. Samples were dried at 90 °C overnight and slowly heated to 500 °C within 3 h. After remaining at 500 °C for 2 h, which led to full combustion of the carbon, the samples were allowed to cool down.

For the free-field measurements, we used a DEOS 25 W radio-frequency-excited CO_2 laser, modulated by a (TTL) signal that was generated by an external pulse generator. The same pulse triggered the Tektronix TDS 380 digital real-time oscilloscope. The generated pressure wave was detected by a condenser microphone (Brüel & Kjaer, Falcon $\frac{1}{4}$ zoll, type 4938). A conventional Nexus two-channel conditioning amplifier was used to produce the signal for the Oscilloscope. The signals were accumulated (up to 100 per second) to reduce the signal-to-noise ratio. The software, which is based on LabVIEW, functioned as a controlling unit for the reaction parameters and as an evaluating system of the data produced. Every 10 seconds, the pressure curve, averaged over 2.5 s, was transferred to the PC and automatically integrated in the interesting time domains, which are directly correlated to the position of the sound origin and the concentration. For the resonance setup we used the same laser as for the free-field setup. For data collection we used self-built amplifiers and small electrete microphones. The amplification was automatically done by a commercial Lock-In amplifier (model 5105 EG&G) with the TTL signal of the laser as a reference. Data collection and process conditions were controlled by LabVIEW. GC experiments were performed on two HP 6940 GCs operated in series.

ODH experiments were carried out under a constant flow of 37.5 mL min^{-1} of 2% ethane in air with 50 mg of catalyst. The temperature was increased in steps of 50 °C and maintained for 30 min at each temperature. CO oxidations were carried out in a flow of 12.5 mL min^{-1} of 3% CO in air. Temperature was constantly raised by 1 °C min^{-1}.

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