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Listening to catalysis—a real time parallel method for high throughput product analysis

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Abstract

In this paper, we describe the development of two parallel real time detection systems for the analysis of the products of a heterogeneously catalyzed gas phase reaction based on the photoacoustic effect. We developed a process addressing the problem of automated catalyst preparation and prepared bulk metal oxides with high surface areas by an automated, parallelized synthesis based on activated carbon. To evaluate analytical systems and catalytic activity of our materials we performed catalytical tests in CO oxidation and ODH of ethane.

Keywords: Catalysis; Photoacoustic; High surface areas

1. Introduction

Ten years ago, research methods changed dramatically with the upcoming of combinatorial principles [1,2]. In catalysis, and especially in heterogeneous catalysis, the theoretical knowledge about the type of surface reactions is at present not sufficient to design an active catalyst ab initio. Although rational design of catalysts has reached an impressive level, many breakthrough discoveries are still serendipitous. The problem of real time parallel product analysis still prevails. In addition, also the parallel preparation of catalysts is a problem, complicated by the solid-handling procedures during synthesis. Combinatorial chemistry methods are increasingly applied to material sciences, which includes homogeneous and heterogeneous catalysis. Basic elements of high throughput experimentation (HTE) are parallelized synthesis, rapid parallel testing of as many catalysts as possible with equally fast analytical methods for real time parallel monitoring of reaction products [3–5] and an adapted informatics environment. Several parallel analytical methods are known, including REMPI [6], IR-thermography [5], and LIF [7]. However, since all methods have their limitations, mostly with respect to selectivity, there is still a need for alternative parallel detection methods. Parallel photoacoustic analysis is such a method which is very fast, in many cases selective and easily parallelized.

For synthesis of solids, some methods from the pharmaceutical industry like pipetting robots and titer plates may also be useful in materials science, but there is still a lack of methods for the preparation of solids for heterogeneous catalysis. Several methods have

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already been described, relying mostly on impregnation [8], hydrothermal synthesis [9], washcoating [10] or precipitation and coprecipitation [4]. However, especially for the preparation of bulk oxide catalysts these techniques have their limitations, since not all oxides can be precipitated easily in an automated fashion from solution [11]. The route via the impregnation of activated carbon and subsequent combustion of the carbon [12] has proven to be easily parallelizable and is thus a very suitable method to form high surface area binary or multinary oxides in an automated fashion.

We have reported the basics of the photoacoustic analysis and the parallelization of the activated carbon route for oxide synthesis in a short communication [13]. Here, we report in more detail the implementation of these techniques in a concerted high throughput approach for the discovery of novel catalytic materials.

2. Analytical developments

To reliably compare different catalysts, an effective testing has to be real time parallel to accumulate information about activity of all catalysts at the same time. Since this can be very difficult for complex reactions, in the past catalysts often have been evaluated sequentially by switching of multiport valves or movement of sampling capillaries, with the exception of the references cited in Section 1. To overcome this problem, we have developed a parallel detection system which is based on the photoacoustic effect. It relies on the detection of pressure pulses, which are generated by exciting a selected type of molecule with a laser pulse. The wavelength of the laser determines which molecules are excited, because they must have an absorption band at this frequency. The molecule absorbs energy and produces a pressure pulse (if the laser is pulsed or modulated) by internal radiationless conversion of the energy into molecular translation. The intensity of the pressure pulse is correlated to the concentration of the product. In order to demonstrate the versatility of this system, we evaluated this method in a first set of experiments in oxidative dehydrogenation of ethane and subsequently in a low temperature CO oxidation process. These two reactions are model systems which provide product molecules with high (ethene) and low (CO_2) extinction coefficients for the wavelength of the applied laser source (modulated CO_2 laser at 943–949 cm^{-1}) which was used in the initial studies. Furthermore, side products of these reactions are well known and investigated. For the parallel testing of our solid catalysts, several reactors have been developed which are described elsewhere [4]. There are a number of different analytical techniques for analysis in high throughput screening [14–16]. Especially the REMPI technique [6] and the photothermal deflection method [17], both of which are based on laser techniques should be mentioned here. Our method solves two problems associated with these methods. While thermal deflection is a sequential method which relies on two crossed laser beams, the parallel REMPI technique uses an array of electrodes directly exposed to the gas stream, which could cause problems in long time measurements by drift of the electrode response. Shortcomings of the photoacoustic detection are possible overlap of absorption bands of different molecules and the fact that in the IR, which is the most convenient frequency range to use, since many specific, relatively narrow absorption bands are present, high power laser sources are limited. However, with solid state lasers, the whole frequency range in the mid IR can be covered, albeit at reduced intensity and a high price level.

2.1. Free field set-up

For molecules with high extinction coefficient and therefore strong light matter interactions we developed a cell for parallel on-line detection of up to eight gas flows, which is in principle expandable to more channels (Fig. 1). Information on the concentration is obtained from the intensity of the pressure pulse, information on the position of the channel is obtained from measuring the time delay between laser pulse and pressure pulse detected at the microphone. Spatial resolution of the set-up depends on the damping of the microphone and the length of the excitation pulse. With our set-up a spatial resolution in the centimeter-range can be achieved. In our model system, the oxidative dehydrogenation of ethane, we could easily detect ethene in an ethane/air/water background because of the strong, non-overlapping band of ethene at around 950 cm^{-1}. Additional side products which would result in a strong absorption in the same regime as ethene, such as acrolein, are usually not observed or only in very low amounts compared to

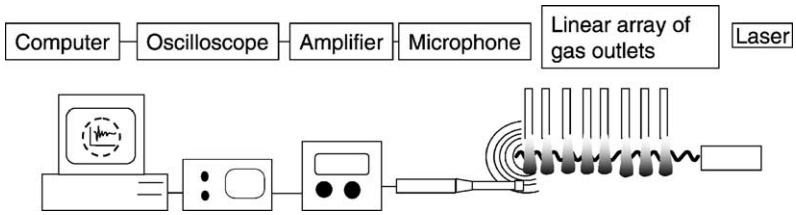

Fig. 1. Set-up of free field measurement. Single laser pulses are guided through the effluents of eight gas outlets. The generated pressure pulses are detected by a Brüel & Kjaer condenser microphone. The amplified signals are automatically added and averaged by a Tektronix TDS 380 oscilloscope. The overall signal is automatically integrated on the interesting time sections by a LabView routine on a PC.

ethene. The gas is excited by a modulated DEOS 25 W CO_2 laser which was operated at 10 or 100 Hz and 35 μs pulse length. Other repetition frequencies and pulse lengths can also be used, but these values turn out to be most suitable for the damping characteristics of the condenser microphone used and the distances of the different gas outlets in terms of signal separation. The generated pressure wave, which contains the information about the position and the concentration of ethene in all gas flows at the same time, is detected by a commercial condenser microphone (Brüel & Kjaer Falcon 1/4 zoll condenser microphone type 4938). The time difference of the different signals gives a maximum spatial resolution of less than 3 cm, which could be improved by further reduction of the pulse length of the laser to reduce the propagating pressure pulse to a minimum while increasing the sensitivity of the microphone and its damping characteristics. However, for our purpose of evaluating the possibility of the free field measurement, this was sufficient, since the outlets were arranged in a line with equal spacing of 5.3 cm between subsequent gas channels. For best spatial resolution, the damping of the microphone has to be strong enough to reduce the oscillation to the offset level within the time the pressure pulse of the next channel is detected, which is especially important for the channels close to the microphone where typically high pressure intensities are recorded. For the channels which are further away from the microphone, the damping should be low enough to still detect the pulse which is reduced by $1/r^2$. In our experiments, different filters have been used and for detection of all pulses a filter with low level of 20 Hz and upper level of 30 or 100 kHz turned out to be best. The signal from the microphone was recorded on an oscilloscope (Tektronix TDS 380 digital real time oscilloscope) and then read out by a PC. For the free field set-up, a linear correlation of product concentration and signal intensity was proven experimentally (Fig. 2). The concentration of ethene is correlated to the integrated section of the pressure wave which corresponds to a specific channel (Fig. 3). As can be seen in Fig. 3, there are further signals which correspond to residual echoes generated in the set-up. We covered the exposed inner surface of our system with a damping material (cloth), but also this could not fully eliminate the echoes which were

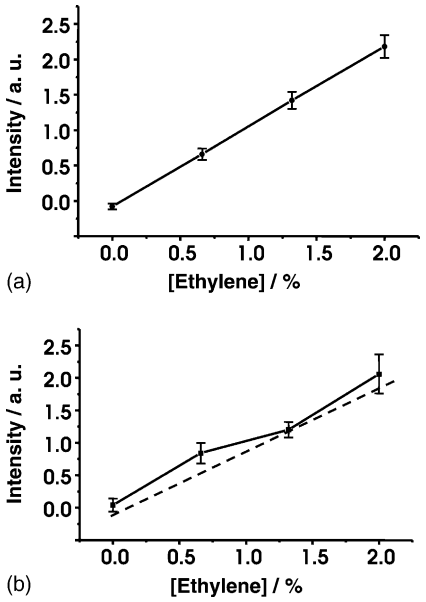

Fig. 2. Calibration curve of free field set-up: (a) channel close to microphone; (b) channel with a distance of 30 cm to microphone. Intensity of the measured signal is directly proportional to the concentration of ethene in the gas mixture. One can see that deviations from linearity are not observed considering the error bars.

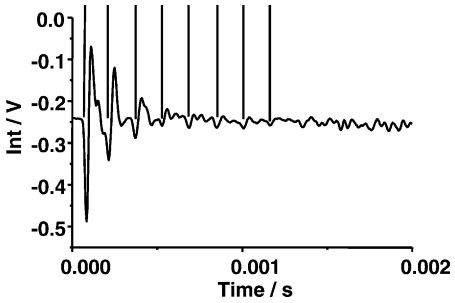

Fig. 3. Picture of 256 averaged spectra from eight different gas outlets. Shown is a real signal intensity (voltage) vs. time. The minima in the spectra correspond to single channels. The distance to the microphone can be calculated by the time the pulse needs to reach the microphone. $t = 0$ is equivalent to the time of the laser pulse. The vertical lines are located at the time corresponding to the distance of a single gas outlet. Additional peaks derive from residual echoes generated by the cell. A concentration of 2% ethene in air was flowed through all the tubes.

still detectable at low level. However, the echoes were reproducibly always at the same position of the time axis and can thus be taken into account in the analysis. To improve signal to noise ratio, the oscilloscope was operated in an averaging mode with adding the response of 256 single laser pulses. The averaged curve was transferred to a PC and evaluated in a LabView program. An automatic peak detection and integration routine gave directly the conversion to ethane on-line on screen. We attached this detection cell to one of our 16-channel parallel reactors and were able to accumulate the complete data set of concentrations of ethene in eight gas flows within a few seconds. The long measurement time is due to the averaging of 256 spectra for one measurement and the communication of the amplifier with our computer. Physically, one measurement only takes a few milliseconds. At 10 Hz measurement repetition frequency, averaging is the time limiting step. In this mode, data collection could be optimized by reducing the residual echoes, e.g. by operating the analytical unit in an anechoic chamber. This would provide an increased signal to noise ratio and would make averaging redundant. At 100 Hz, data transfer is time limiting which could easily be overcome by using faster data transfer methods. When operating the system in an averaging mode, the lower detection limit is below 0.015% for the channels close to the microphone and even for the remote channels, which provide an intensity decreased by $1/r^2$, 0.3% of ethane can reliably be measured. Several small libraries of mixed oxide catalysts were analyzed, and the analysis by the photoacoustic detection was checked in experiments in a single channel reactor equipped with GC analytics [13]. The agreement was excellent, which proves that the method can be used to reliably analyze strongly absorbing molecules in a truly parallelized fashion in the free field set-up. It should be mentioned, that no special requirements with respect to noise reduction in the environment are necessary. Only the echoes generated immediately during the measurement and described above proved to be a possible source of error.

2.2. Resonance set-up

For molecules with low extinction coefficients this set-up cannot be used due to the low intensity of the pressure pulses. Such low intensity pulses cannot be detected by microphones with a good damping characteristics which would allow the necessary time resolution. These very fast microphones usually have low detection limits. But with increasing the diameter of the microphone membrane one can easily optimize the sensitivity on the expense of decreased time resolution. For CO oxidation processes with a very low extinction coefficient of CO_2 we therefore had to change the detection method and gave up the spatial resolution and truly parallel detection, which requires good time resolution. We instead amplified the signals from each channel by the use of resonance tubes integrated at the end of each channel in the gas outlet (Fig. 4). For several reasons, we decided to build cylindrical resonance chambers. These can be arranged parallel in one line and are therefore suitable for quasi-parallel operation without complex guidance and alignment of the laser beam. Due to 7.3 mrad widening of the beam, we had an optical path length of about 0.5 m for the resonance tubes of the dimensions used. If one wants to build bigger systems which is in principle possible, additional focusing optical elements are needed. For the same reason the tubes were arranged perpendicular to the beam. With this geometry we could build a system containing up to 16 tubes next to each other within 50 cm. To increase the length of the absorption path, short additional horizontal tubes were attached to the resonance tube which were equipped with ZnSe windows on one side to avoid cross-contamination between the different

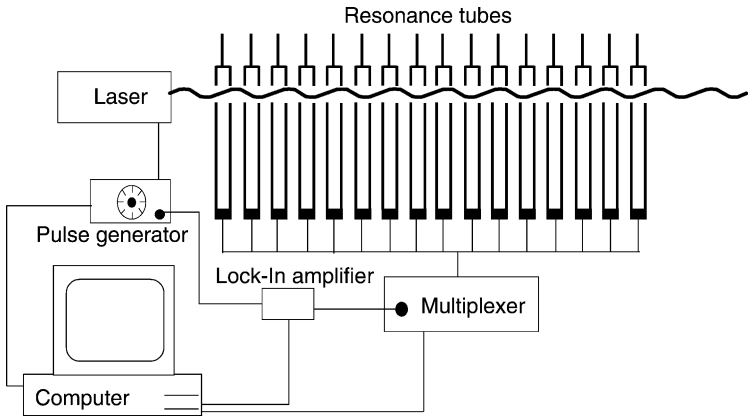

Fig. 4. Set-up of resonance measurement. In each gas outlet integrated is an adjustable resonance tube through which a modulated laser beam is guided. The modulation frequency of the laser fulfills the resonance conditions of the tubes. The amplified standing wave is detected by cheap electret microphones and amplified by lock-in technique operated in phase dependent mode. A multiplexer is switched sequentially within the single channels to ensure the lock-in amplifier only amplifies the signal of one channel at a time. Signal evaluation is done by LabView on a PC which also controlled pulse generation, lock-in amplifier and process conditions.

channels which could result from diffusion out of open tubes. Due to the geometry of the chamber and the laser beam perpendicular to the tube, the modulation frequency of the laser was tuned to a longitudinal resonance of a tube. The excitation area was adjusted to be $\lambda_{mod}/2$ from the top (Fig. 5). Resonance conditions for the different tubes are not exactly identical, due to the different conditions, i.e. beam divergence and different gas mixtures. Therefore, we developed an array of resonance tubes with adjustable length of the cylinder to exactly tune the resonance frequency

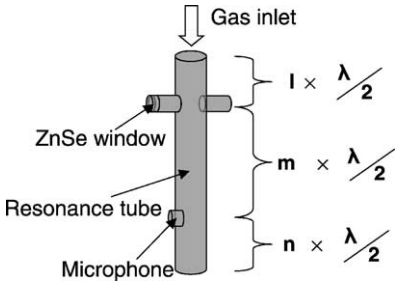

Fig. 5. Schematic picture of a resonance tube. To get optimal resonance conditions, the distance between excitation point to top of the tube should be a multiple of $\lambda/2$ of the modulation frequency. The same conditions for the distance of the microphone to the end of the tube and between microphone and point of excitation gave best results. We operated our system at modulations of 6 kHz which corresponds to 2.8 cm for $\lambda/2$.

of each tube to the modulation frequency of the laser. Each tube was equipped with one microphone, and the whole array was connected to one lock-in amplifier, which was sequentially switched from channel to channel. While operating the amplifier in a magnifying mode we found an unexpected decrease of signal intensity up to a CO_2 concentration of 0.3% in the exit gas. For higher concentrations up to 3%, a linear correlation of signal intensity to CO_2 concentration was found. The decrease of the signal at low concentrations is due to a superimposing constant wave generated by absorption of the tubes or trace gas effects as reported by other groups [18]. By operating the amplifier in a phase angle-dependent mode, we could suppress the phase of the second wave and only detect the signal generated by the product molecules. The problem of phase shifting due to fluctuations of e.g. temperature, to which a phase angle dependent measurement is very sensitive, could be solved by operating the unit with constant temperature and adjusting the length of the tubes to operate all tubes on top of a resonance peak with phase angle 0°. This leads to low sensitivity for fluctuations of e.g. temperature or other parameters which could cause changes in the velocity of sound and therefore phase stability. With this system attached to a 16-fold parallel reactor, we were able to monitor 16 CO_2 concentrations in less than 1 min. The time limiting factor for

this measurements is the dead times of the switching process due to the lock-in amplifier, not the analysis itself which is completed in less than 1 s.

On first sight it might appear that the 16 microphones are a drawback compared to the free field set-up, but since the resonance does not require time resolution, cheap electret microphones (less than 1 €) can be used instead of the expensive time resolving microphone (1500 €).

Also the reliability of this resonance detection method was checked against results from a single channel reactor equipped with non-dispersive IR-analysis (URAS 3E, Hartmann & Braun) and found to be in excellent agreement [13].

Both of our detection systems, the free field set-up as well as the resonance system, are fully automated and have a self-calibration routine, which runs automatically before the actual test is started, to avoid differences due to drifts of the gas flow and misadjustment of the laser. Therefore, we are very flexible concerning the environmental conditions in which the system can be operated. This could be very interesting, especially for industrial applications.

The parallel photoacoustic method can only be used for reactions with known products. If there is one product which provides a characteristic absorption band in a frequency range which is accessible by laser sources, this method is a fast alternative to other methods like GC or MS. Of course, photoacoustic detection allows to obtain information only about the absorbing species, while with GC or MS the whole product spectrum can be analyzed. For applications one has to decide whether a fast real time detection is needed (typically in the stage I or discovery mode) or rather a method which gives information about the complete product distribution, which is more typical for the stage II or optimization mode. One should mention that if the energy is absorbed by more than one species in the gas mixture the only measurable signal is a superposition of all the absorbing species. In some cases, this may disfavor an analysis based on this technique. However, a great advantage of real time parallel detection of all the catalysts at the same time is the possibility of comparing different catalysts at identical time-on-stream. Fast processes which may occur during certain phases of the reaction are therefore detected and a more detailed picture of catalyst activation or deactivation is obtained.

3. Parallel oxide synthesis and catalytic results

The time limiting step of the high throughput process with the photoacoustic detection set-up is the preparation of the catalysts. To increase the number of possible catalytic tests we therefore developed a versatile route, with which a great variety of bulk metal oxides can be prepared in a simple and very straightforward manner, and which avoids filtering steps and handling of suspensions or different solids. The route consists of two steps: the impregnation of a suitable activated carbon with a metal oxide precursor solution of high concentration, and subsequent thermal treatment of the impregnated carbon in oxidizing atmosphere which ultimately leads to full combustion of the carbon matrix [12]. A related technique was used to prepare ZrO_2 and $Zr_2Nd_2O_7$ and zeolite particles in the past [19,20]. Analytical and physical data of selected materials we prepared by this method can be found elsewhere [12].

For the fast random library design a computer program was written, which combined 1–10 catalyst components in random relative compositions. A synthesis robot then automatically prepared 77 different materials in one go.

With the free field set-up in ODH, no catalyst going beyond the state of the art was discovered so far. In our experiments, the feed was 2% ethane in air at 45,000 ml/g h. The most active composition was 12% La, 2% Ba, 9% Pb, 7% Th, 27% Mn, 24% Ni, 19% Cu, which, however, only produced 0.06% of ethene absolute at a 30% conversion of ethane at 550 °C. The product stream basically consisted of carbon dioxide which was produced due to the excess of oxygen.

By using the resonance set-up in CO oxidation, the best materials found so far proved to be complex mixtures (Table 1). Using a feed of 3% CO in air and a flow of 20,000 ml/g h, the lowest temperature for 50% conversion (102 °C) was measured for a catalyst with the rounded molar composition (as oxides) 17% Fe, 25% Ni, 27% Mn, 30% Cu. Phase analysis of this catalyst and other relatively active materials revealed that they consist of spinel-related phases, with admixtures of other, still unknown phases. Surface areas were in the range of 50–100 m^2/g. The best catalysts all contained nickel, manganese, and copper. One possibility for the composition of the active phase in our catalyst could be the hopcalite system, which is a Cu-Mn-O material.

Table 1
Relative metal composition of the best catalysts which were found during initial studies of catalyst libraries in CO oxidation

Relative metal composition	$T_{50\%}$ (°C)
17% Fe, 25% Ni, 27% Mn, 30% Cu	102 ± 5
11% Fe, 11% Cr, 16% Ni, 21% Mn, 7% Al, 13% Co, 21% Cu	108 ± 5
11% Fe, 12% Cr, 20% Ni, 21% Mn, 14% Co, 22% Cu	112 ± 5
33% Ni, 32% Mn, 35% Cu	115 ± 5
17% Fe, 17% Cr, 22% Zn, 22% Mn, 22% Cu	115 ± 5
13% Fe, 11% Cr, 18% Ni, 17% Mn, 10% Al, 12% Co, 19% Cu	122 ± 5

The table only shows the metal composition. The materials basically consist of oxides and oxide mixtures which are assumed to have spinel structures. The second column shows the temperature with a CO conversion of 50%.

However, the method described allows to easily explore different additives for such catalysts by creating focused libraries around the initial successful composition. This work is in progress in our laboratory.

Summarizing our results we developed two different analytical systems for high throughput product analysis. One of the techniques is suitable for molecules with high absorption coefficients and the second one is for products with very low absorption. The speed of these new analytical systems brought up new time limiting steps which are due to slow manual preparation procedures. Therefore, a preparation procedure was developed which can provide high surface area metal oxides in amounts which are equal to the capacities of our high throughput testing facilities. In low temperature CO oxidation new materials were found which show full CO to CO_2 conversions at lower temperatures than noble metal compounds.

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