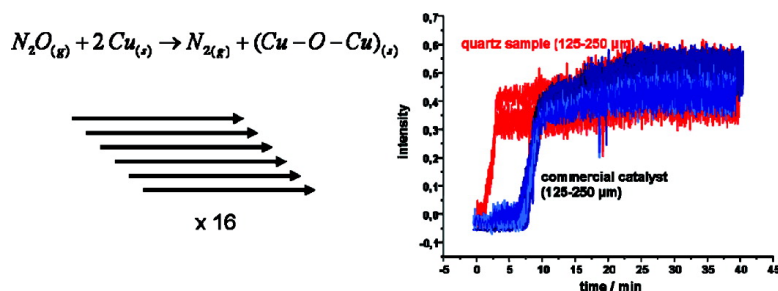


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J. Comb. Chem., **2008**, 10 (3), 387-390 • DOI: 10.1021/cc700144y • Publication Date (Web): 07 February 2008

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Parallelized N₂O Frontal Chromatography for the Fast Determination of Copper Surface Areas

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Received August 28, 2007

A parallel reactor setup in combination with a spatially resolving Fourier transform infrared focal plane array detector (FTIR-FPA) system in rapid scan mode has been developed which is capable of analyzing simultaneously the specific surface area of 15 copper catalysts. The system allows the reliable determination of copper surface areas with an error of about ± 1 m²/g. Problems are encountered with very fluffy catalyst powders, since this leads to excessive pressure drop over the catalyst bed. The error brought about by this effect can be eliminated by taking into account the flow deviations between channels in such cases.

Introduction

High-throughput methods in heterogeneous catalysis are by now well-established, and many publications deal with both the synthesis and the catalytic evaluation of solid samples.^{1–4} However, in order to establish synthesis–property–activity relationships, which is crucial for a basic understanding of the catalytic reaction, also techniques for the high-throughput analysis of solid catalysts would be required. Some efforts have been reported in this field,^{5–16} but high-throughput analytical methods are certainly much less developed than catalytic testing.

Especially interesting are methods for the determination of metal surface areas, such as CO or H₂ adsorption, since such measurements are typically very time-consuming, on the order of several hours up to one day, due to the need of extensive pretreatment, often involving heating and cooling cycles in different gas atmosphere. Since we are interested in copper based catalysts for different processes, such as methanol synthesis and methanol steam reforming, for which the specific copper surface area is crucial, we have developed an efficient and parallelized method for the determination of these data in copper containing catalysts. The technique is based on N₂O reactive frontal chromatography (RFC), which was introduced in 1987 by Chinchin et al.,¹⁷ and is now a standard method for the sequential determination of copper surface areas in copper containing catalysts.¹⁸ It relies on the fact that N₂O can selectively oxidize only the surface atoms of copper in a temperature window between 333 and 363 K at a stoichiometry of one oxygen atom per two copper surface atoms (for a discussion of the limitations of the technique, see refs 17 and 18). N₂ is released as the reaction product. In the conventional setup, the gas phase leaving the RFC reactor is analyzed for N₂ and N₂O, typically with a

mass spectrometer which allows continuous analysis. The appearance of N₂ in the gas phase indicates the onset of the surface oxidation; the breakthrough of N₂O indicates its completion. The copper surface areas can be determined from the amount of N₂O decomposed.

Since typically a tubular reactor is used in such a setup, this type of analysis seemed in principle parallelizable by using a parallel reactor. However, sequential mass spectrometric analysis is then not very suitable due to the time needed for moving the MS inlet capillary from channel to channel and flushing, which results in an insufficient time resolution of the analysis, although such a method has been used for parallel temperature programmed reduction of 10 samples with a cycle time of 80 s. A truly parallelized analytical method for the gas phase was therefore needed. One of the few parallel methods is FPA-FTIR (focal plane array detector Fourier transform infrared) spectroscopy, which was introduced in high-throughput experimentation in heterogeneous catalysis by the group of Lauterbach.⁸ Such systems are normally operated in step-scan mode, but for high temporal resolution, this is much too slow. Lauterbach and co-workers have also modified the system to allow rapid scan analysis,^{19,20} and with this modification, FPA-FTIR spectroscopy should in principle become a suitable method for the analysis of the gas phase in N₂O RFC. We therefore decided to implement this method in the high-throughput mode, using a parallelized reactor setup, a parallelized gas cuvette, and FPA-FTIR spectroscopy in rapid scan mode as analytical method.

Results and Discussion

First, the breakthrough curves for a blank sample (fused silica powder) and a Cu/ZnO/Al₂O₃ reference catalyst were recorded in order to evaluate the characteristics of the setup (Figure 1), where also the principle of the surface area determination is explained. One example for the breakthrough in the spectral range of interest for one channel is

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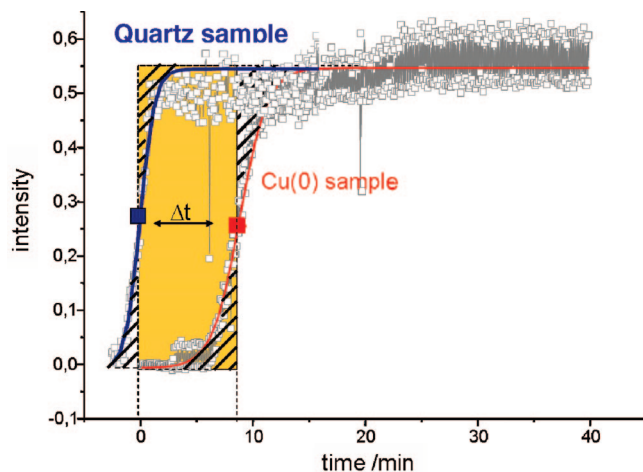


Figure 1. N_2O -breakthrough curves for the blank sample and a commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ sample. Both curves were fitted with a Boltzmann function, as drawn through the data points. The N_2O amount consumed is approximated by multiplying the molar flow of N_2O with the time difference between the breakthrough of the blank sample (t_0) and the catalyst sample ($t_{\text{breakthrough}}$). This method gives essentially identical results as numerical integration of the curves.

given in the Supporting Information Figure S1, which also allows to judge the signal-to-noise ratio of the spectra. The N_2O concentration increases from a baseline signal after a delay time in a sigmoidal curve to the final value, both for the silica blank and the copper catalyst. The delay for the channel filled with fused silica powder is due to the purging of the reactor, tubes, and the cuvette which is necessary before the IR signal increases. The tailing of the breakthrough curves is probably due to traces of nitrogen which are only slowly completely flushed from the system. The breakthrough of the N_2O from the channel filled with the blank sample defines the zero point for the analyses of the copper containing samples. The delay for the copper samples is substantially longer, due to the surface oxidation of the copper by the N_2O . Both curves can be numerically integrated and the integrals subtracted from each other, which gives, with known flows and concentration of N_2O , the amount of N_2O consumed. In practice, it has been found that simply approximating the breakthrough curves by fitting with Boltzmann functions, as shown in the figure, and multiplying the time difference between the symmetry point of the Boltzmann functions for the blank and the catalyst with the flow and the concentration of N_2O gives virtually identical results. For the catalyst sample shown here, a specific copper surface area of $20 \text{ m}^2/\text{g}$ has been determined, in good agreement with the analysis carried out with the dedicated single channel setup at Bochum University which gave $19.2 \text{ m}^2/\text{g}$.

In a subsequent set of experiments, the reproducibility and dependence of the system performance on various parameters were determined. Figure 2 shows the breakthrough curves for 6 channels which were filled with the reference silica and 10 channels which were filled each with 200 mg of the same copper catalyst. As can be seen from the figure, the breakthrough times are very reproducible and the surface area determined for this catalyst is $20.5 \text{ m}^2/\text{g}$ with a standard deviation of $1.1 \text{ m}^2/\text{g}$.

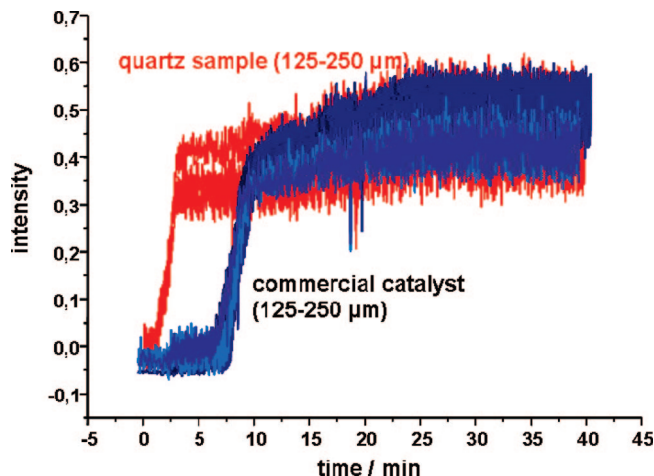


Figure 2. Superimposed N_2O -breakthrough curves for 6 quartz samples and 10 samples of the same commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst, demonstrating the reproducibility of results for different reactor channels.

The shape of the breakthrough curve is dependent on the particle size fraction used for the experiment (Figure 3). For proper hydrodynamic conditions in the reactor, the particle size fraction from 125 to $250 \mu\text{m}$ is the most suitable. At larger particle sizes, some channeling may occur which leads to a broadened breakthrough curve. The most ill-defined breakthrough is obtained with unclassified catalyst material, which contains fines and also larger grains, leading to an ill-defined flow pattern in the bed. However, independent of the sharpness of the breakthrough front, the integrals over the curves are almost unchanged, resulting in surface areas of 14, 14.3, and $15.9 \text{ m}^2/\text{g}$ for this sample, which is only slightly higher than the error margins for repeated experiments with the same catalyst fraction. Similar differences had also been observed with the dedicated setup at Bochum University for different sieve fractions of the same catalyst.

While most catalyst samples could be processed in the parallel setup easily and reliably, one specific class of copper based catalysts caused problems in some cases. These were materials based on ordered mesoporous carbons, which had been impregnated with different amounts of copper by different methods. Carbons are very difficult to pelletize due to the elastic properties of the material and thus could not be pressed and sieved. Since the primary particle size of these materials is rather low, very fine, sometimes fluffy catalyst powder had to be filled in the reactor channels. This led to very high pressure drops over the channels filled with this powder, and if some channels contain carbon-based catalysts, while the others are filled with catalysts based on oxide supports, a maldistribution of the flow results. This maldistribution could amount to flow differences up to a factor of 3 in unfavorable cases. It is therefore advisable to measure the flows through each channel using a bubble meter or some other means for flow measurement and correct the results for the different flows through the channels, both with respect to t_0 and $t_{\text{breakthrough}}$. This eliminates the error brought about by maldistribution of the flows. The time required for this is only about 30 min which does not substantially increase the overall time required for the determination of 15 copper surface areas.

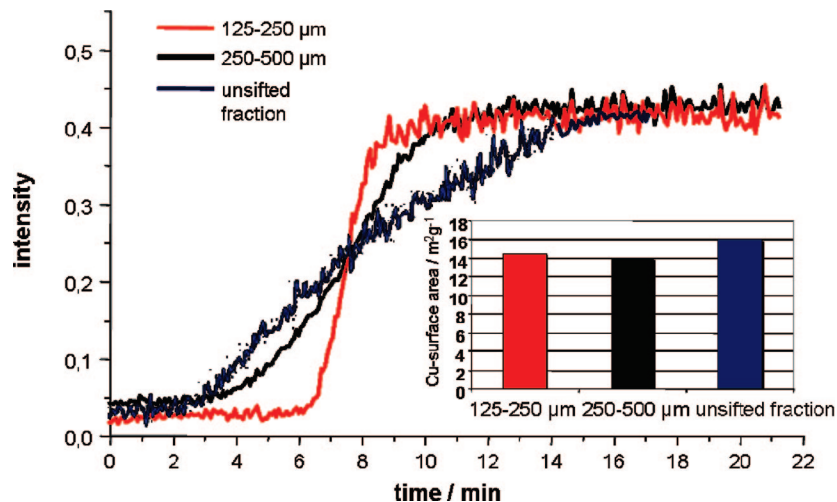


Figure 3. N₂O-breakthrough curves for different fractions of a Cu/ZnO/Al₂O₃ catalyst and surface areas calculated from the breakthrough curves (insert).

Some points should be taken into account when using such a setup for the parallel determination of copper surface areas. It has already been mentioned that maldistribution of flow can severely distort the results if it is not taken into account, and thus, we are now routinely checking the flows in the channels during each measurement. Another problem arises for low copper surface area materials. Since in such cases the difference between t_0 and $t_{\text{breakthrough}}$ becomes rather small, the relative error increases strongly. In such cases, it is advisable to decrease the N₂O concentration in the reaction gas in order to prolong the breakthrough for the copper containing samples. The sensitivity of the IR system (the detection limit with the setup is below 0.1%) is still sufficient in these cases for reliable analysis. It is obvious that the same precautions as in catalytic high-throughput experiments have to be taken to avoid leaks, bypassing, or crosstalk between reactor channels, but this is no problem with properly designed reactors.

We are now using this system in routine operation to analyze big collections of copper containing catalysts with respect to surface area and to correlate these data with activity in methanol synthesis and methanol steam reforming. Figure 4 gives one example for a correlation between copper surface area and methanol synthesis activity for a set of Cu/ZnO/Al₂O₃ catalysts with nearly identical composition, but precipitated under different conditions (pH and temperature were varied in this case). Several of the catalysts have been analyzed two or more times, where again typical deviations on the order of 1 m²/g were found. The essentially linear correlation between surface area and catalytic activity, which is known from the literature, was observed also in our experiments, and a detailed analysis of these and related results will be reported in a forthcoming publication.²¹

Summary

A method for the parallel determination of copper surface areas in a high-throughput reactor with an attached multi-channel gas cuvette in combination with a FPA IR detector has been introduced. This method allows the acceleration of the analysis of copper surface area in catalysts by a factor of 15, while maintaining an acceptable error level of about

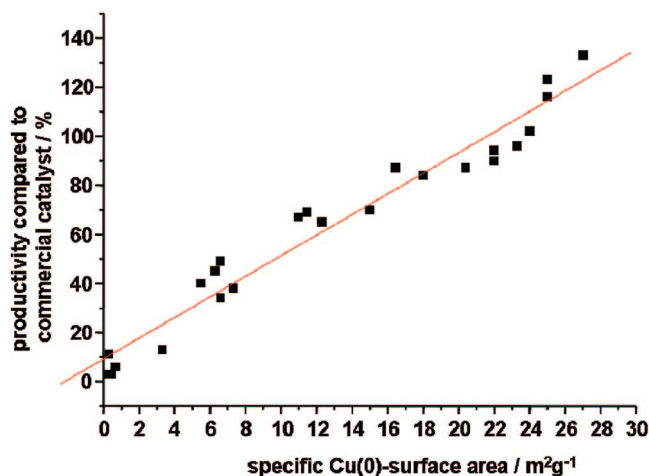


Figure 4. Correlation between copper surface areas and methanol synthesis activity of different Cu/ZnO/Al₂O₃ catalysts compared to a commercial benchmark catalyst. The catalysts were precipitated from identical solutions at different pH and temperature values. For most catalysts, Cu/Zn/Al molar ratios of around 1/0.47/0.3 were obtained, with the exception of samples precipitated at low pH and low temperature values which had copper contents up to 10% higher. Activity of the commercial catalyst is 30 mol_{MeOH}/(kg_{Cu} h) at a temperature of 245 °C and at 45 bar syngas pressure.

1 m²/g. The absolute error could be reduced further with N₂O at a lower concentration level for low surface area catalysts, but in order to cover a wide range of different surface areas, the conditions given above have been found to be a good compromise.

In principle, the setup can be used to parallelize also adsorption techniques for other IR active probe molecules, such as CO, as long as the stoichiometry of the surface reaction is well-defined and the surface area is sufficiently high. Also temperature programmed methods in heterogeneous catalysis, such as temperature programmed reduction or temperature programmed reaction, can be parallelized using this technique, as long as characteristic educt or product molecules can be detected by IR spectroscopy. We are presently exploring temperature programmed reduction using D₂ as the reducing agent, since the D₂O can much more

reliably be analyzed compared to H₂O, which is difficult to quantify due to overlap with water present in the IR-optical setup.

Experimental Section

Setup. The experimental setup consists of an Equinox 55 FTIR spectrometer (Bruker) which was operated in the continuous scan mode, and allowed to record about 14 spectra per minute with a spectral resolution of 32 cm⁻¹. This time resolution is more than sufficient for reliable analysis. The external port of the spectrometer is used to pass the IR beam via imaging optics through the gas cuvette which has been described elsewhere²² onto the FPA detector which consists of an array of 64 × 64 pixels.

The samples to be analyzed are placed in the sample cartridges of a 16-channel parallel reactor made from brass, the principle of which has been described elsewhere.²³ Inlet gas is fed into the reactor via a common inlet; the outlet of each channel is passed through 1/16 in. capillaries with a length of approximately 150 cm to the inlets of the channels of the 16-channel gas cuvette. An overview of the setup and details of the setup and the reactor can be seen in the photographs and schematic drawings in the Supporting Information Figures S2 and S3.

Procedure. The procedure for the analysis is closely related to the one used in conventional N₂O RFC determination of copper surface area.¹⁸ 200 mg of each sample is placed in the sample cartridges of 15 channels, the remaining channel is filled with the same amount of fused silica powder (125–250 μm) as *t* = 0 reference. After closing the reactor lid, the catalysts are first reduced by passing 200 mL/min of a gas mixture containing 5% H₂ in nitrogen at 573 K for 3 h. The final temperature is reached with a ramp of 5 K/min. After 3 h at reduction temperature, the gas is switched to pure nitrogen and the reactor is cooled down to 313 K. Then, the gas is switched to 1% N₂O in helium at a flow of 40 mL/min in each channel. At the same time, recording of IR spectra is started. All spectra are calculated against a background corresponding to the cuvette filled with nitrogen.

Data Processing. During one run, a datafile of about 1.5 GB size is created. In order to analyze the data in a reasonable time frame, the size of the data file has to be reduced. This is done by averaging all pixels of the FPA detector which belong to one channel of the gas cuvette (about 100 pixels). Then, the band intensity of the band corresponding to N₂O at 2200 cm⁻¹ is determined and plotted against time for each of the cuvette channels. This gives the breakthrough of N₂O for each channel. After subtraction of the breakthrough determined for the reactor channel filled with silica, the copper surface area can be calculated from the amount of N₂O consumed by each catalyst.

Acknowledgment. Financial support by the DFG (SFB 558), in addition to the basic funding provided by the Max-Planck-Society, is gratefully acknowledged.

Supporting Information Available. Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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