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

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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 Chinchen 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, 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 CuZnO/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