Innovative use of a Gas Chromatograph for heterogeneous catalytic studies

Alexey Ignatchenko, Jennifer Hill, James Gray, Don Nealon, Roy Dushane

Eastman Chemical, Longview, TX 75607-7444 (alexey@eastman.com)

Introduction

A variety of designs for a simple micro reactor have been used for heterogeneous catalytic studies in research laboratories over the past years. Yet, the simplest one is suggested in this work. Usually, products from the reactor outlet are delivered by different means to a GC for analysis. We have converted an ordinary Gas Chromatograph into a Pulse Micro Reactor by placing a small amount of a catalyst inside an inlet tube, where normally a sample for the GC analysis is injected. The GC inlet is designed to vaporize the sample by a carrier gas, the vapors being carried through the GC column to the GC detector. In our case, we are injecting starting materials, which are vaporized, passed through the catalyst bed, and converted to products. These are the reaction products, which move to the GC column, are separated there, and then registered by the GC detector.

The benefits of the micro reactor being arranged inside a GC are summarized below. The sample collection step is now eliminated from the product analysis, which saves time and improves accuracy. All products can be analyzed, without lose of volatile and unstable ones. The material balance of the reaction is accurately accounted for. The simplicity of the micro reactor and the availability of GCs in any modern lab allow anyone to have a quick “test tube” screening for vapor phase catalyzed reactions. Catalyst loading and unloading now becomes a very simple procedure. Faster screening of new catalysts for existing processes can be done more efficiently. Using the new technique, we have found several applications of existing catalysts for new processes in fine chemicals business for which the reaction conditions were optimized without having any equipment other than a GC. Addition of the ChemStation software and an auto sampler allows automation in processing and analysis of the data from the micro reactor.

Results and Discussion

Process conditions for the micro reactor inside GC are flexible. The temperature range of the inlet tube in a modern GC can be anywhere from RT to 400°C and the pressure range from 0 to 4 atm in excess to atmospheric. In order to control vapor residence time by the rate of a carrier gas flow, injections have to be made with the GC running in a split mode. The split mode of analysis is illustrated in Figure 1. When the total flow is 104 ml/min, and the septum purge flow is 3 ml/min, the split flow, which is the flow through the catalyst bed, is 101 ml/min. From 101 ml/min flow only 1 ml/min goes to the GC column, and 100 ml/min goes to the vent. This corresponds to the split ratio 100:1. When the split ratio is set to 50:1, the total flow changes to 54 ml/min, with 51 ml/min flow through the catalyst bed and still the same 1 ml/min flow through the GC column. As the result, the residence time should
increase 1.98 times. Since the column flow remains constant, changing the residence time has no effect on the retention time of components on GC column.

Retention time is shifted sometimes due to the chromatographic effect of the catalyst bed, but this shift is very small and does not cause problems in compounds identification. A number of different catalytic reactions were tested, including acid-base catalyzed reactions, and oxidations-reductions. Hydrogenation was studied with hydrogen as a carrier gas, and oxidation reactions by simultaneous injection of substrate together with oxygen.

The described micro reactor was also conveniently used for a pulse chemisorption analysis, instead of expensive commercial instrument, to find concentration of catalytically active sites.

For a bimolecular reaction, we have saturated surface with one component and started pulse injections of another component. This method allowed conversion and selectivity study depending on concentration of both components on surface. Analysis of the conversion rate as a function of surface concentration gave reaction constant, and the temperature dependence of the reaction constant allowed us in one specific example to estimate Arrhenius activation energy.

We have also placed a catalyst inside GCMS to study mechanisms of catalytic reactions with isotopically labeled compounds. Finally, pulse injections with a catalyst inside GCMS were used for isotopic switch method to determine concentration of active sites during catalysis. After saturation of a catalyst surface with unlabeled compound, pulses of a labeled compound were added. A fraction of labeled molecules adsorbed on a sample, after \( i \) injections in this case is \( \theta^i = S^i / N_o \), where \( S^i \) is a number of labeled molecules adsorbed on a sample, after \( i \) injections, \( N_o \) is a number of all molecules adsorbed on a sample (adsorption capacity of a sample at full coverage). After each equilibration, a fraction of labeled molecules on the surface is equal to the fraction of labeled molecules in the gas and can be expressed as \( \theta^{i+1} = (S^i + G^{i+1}) / (N_o + G^{i+1}) \), where \( G^{i+1} \) is a number of labeled molecules added into the gas phase with the injection \( i+1 \). After combining both equations, the adsorption capacity can be calculated as \( N_o = G^{i+1} \cdot (1 - \theta^{i+1}) / (\theta^{i+1} - \theta^i) \), or \( N_o = G^{i+1} \cdot \Phi / \Delta \Phi^i \), where \( \Phi = 1 - \theta^i \) is the fraction of unlabeled molecule.

In summary, a convenient and readily available approach to study heterogeneous catalytic reactions was developed by placing catalyst sample inside GC or GCMS.

References
1. Distributed by Agilent Technologies.