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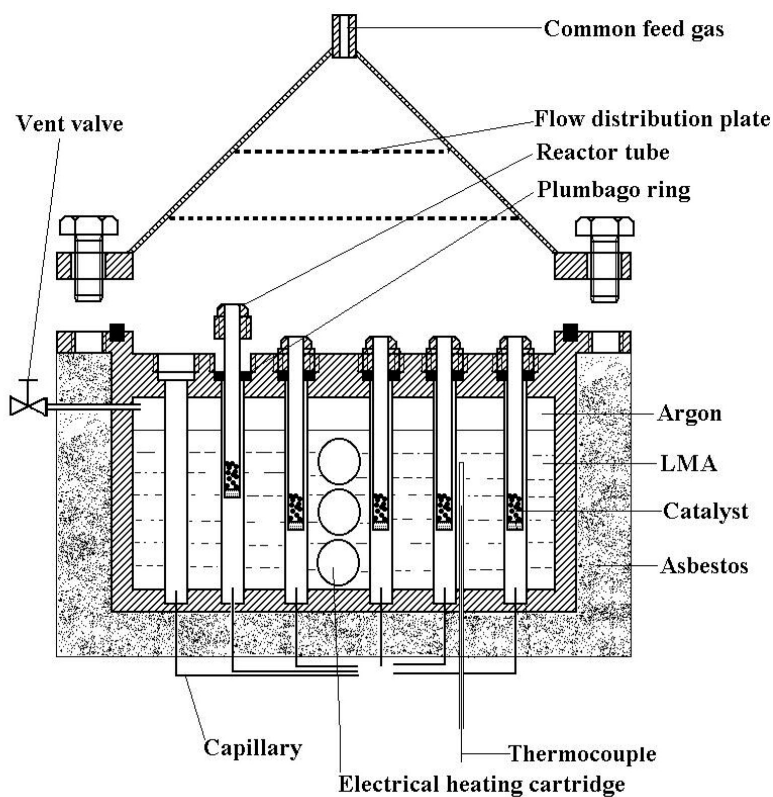# Quantified MS Analysis Applied to Combinatorial Heterogeneous Catalyst Libraries

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Quantified MS Analysis Applied to Combinatorial Heterogeneous Catalyst Libraries

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A high-throughput screening system for secondary catalyst libraries has been developed by incorporation of an 80-pass reactor and a quantified multistream mass spectrometer screening (MSMSS) technique. With a low-melting alloy as the heating medium, a uniform reaction temperature could be obtained in the multistream reactor (maximum temperature differences are less than 1 K at 673 K). Quantification of the results was realized by combination of a gas chromatogram with the MSMSS, which could provide the product selectivities of each catalyst in a heterogeneous catalyst library. Because the catalyst loading of each reaction tube is comparable to that of the conventional microreaction system and because the parallel reactions could be operated under identical conditions (homogeneous temperature, same pressure and WHSV), the reaction results of a promising catalyst selected from the library could be reasonably applied to the further scale-up of the system. The aldol condensation of acetone, with obvious differences in the product distribution over different kind of catalysts, was selected as a model reaction to validate the screening system.

Introduction

Combinatorial chemistry, by which a large diversity of chemical compounds are prepared, processed, and tested in a high-throughput fashion, has created a revolution in pharmaceutical and biotechnology development. Now, this method has been extended to the discovery of heterogeneous catalysts.[1−8] In analogy to the development of new drugs, the major problems in combinatorial heterogeneous catalysis are centered not on the synthesis of new libraries, but on the effective method for high-throughput detection of the desired properties of the library components,[4] as the synthesis of 25 000 different components on a few square centimeters has been realized.[9]

There have been several examples of the high-throughput screening of heterogeneous catalyst libraries. The infrared (IR) thermography method has been relatively widely used to screen the activities of libraries by monitoring the temperature changes of the catalyst sites in gas-phase reactions,[10] as well as the heat changes of homogeneously catalyzed reaction systems,[11] although it cannot provide any information on the identity of the products formed in a reaction. Recently, Hendershot et al.[12] developed Fourier transform infrared imaging[13] for parallel analysis of transients in catalytic reactions. The acid−base fluorescence indicator method,[14] laser-induced fluorescence imaging (LIFI),[15,16] and resonance-enhanced multiphoton ionization (REMPI)[17,18] techniques are also developed for high-throughput experimentation. Mass spectrometry (MS)[19−23] is a mature and widely used detection technology for rapidly analyzing gaseous mixtures in a sequential manner. However, the quantified analysis of a mixed gas by MS is very complex and difficult.

The techniques mentioned above are certainly very valuable in the initial stage (primary screening) of catalytic materials development, but the promising candidates that are selected from primary libraries have to be analyzed in more detail in the next step (secondary screening). Secondary screening targets the optimization of already-existing formulations and tests the catalytic materials under conditions as realistic as possible. Hoffmann and co-workers[24] developed a 16-pass reactor equipped with a nondispersive IR analyzer to screen secondary libraries. However, the IR screening technique could not provide enough information about reaction selectivity for secondary screening. Subsequently, they developed a 49-channel parallel reactor with on-line GC for product analysis.[25,26] However, the temperature difference between catalyst beds was about 5 K, which results in less comparability of the results from different streams. Moreover, given that the use of GC to analyze products is obviously time-consuming, this technique cannot easily address issues related to the time-dependent behavior of catalytic materials. In the examples described by Schüth et al.,[24−26] normal-scale catalysts were used to validate the developed methods under nearly conventional testing conditions, which is a great improvement for the parallel tests; the results could also be used for further scale-up.

We therefore report studies on the application of an 80-pass reactor with homogeneous temperature together with a multistream mass spectrometer screening (MSMSS) technique for parallel testing and fast screening of secondary heterogeneous catalyst libraries under conventional testing conditions. Moreover, by combining a GC with MSMSS, this approach could realize high-throughput screening of the

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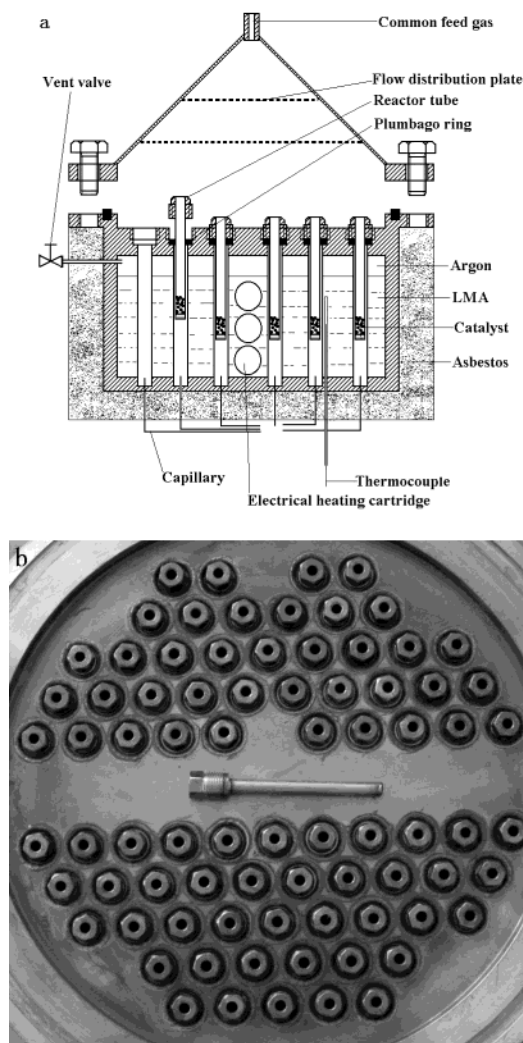
Figure 1. (a) Schematic drawing of the 80-pass reactor and (b) planform photograph of the reactor.

selectivity of each compound in a mixed gas over all of the catalysts. This technique not only offers a method for the screening of secondary heterogeneous catalyst libraries, but also provides a possible means for the rapid quantification of MS data.

Methodology

A schematic drawing of the reactor is shown in Figure 1a, and a planform photograph is displayed in Figure 1b. It consists of 80 tubes (1 cm diameter each) welded in a vessel in which low-melting alloy (LMA, melting point is about 100 °C) was filled as a heating medium to ensure temperature uniformity, and argon was sealed in the vessel to prevent oxidation of the alloy. The pressure of the argon in the vessel can be controlled by regulating the vent valve. Three electrical heating cartridges were placed in the vessel. At the bottom end of each tube, a stainless steel capillary (2 m in length and 0.25 mm in internal diameter) was connected to draw off the outflow of the reaction. In each tube, a smaller reactor tube that had one open end with screw thread and one flow-permeable end was sealed against the reactor with a graphite ring to ensure that the feed gas passed completely through the catalyst bed. For this design, the filling of the reactor tube is simple and rapid, with only 20 min required

to fill all 80 tubes. The maximum temperature differences between the tubes, especially the temperature deviations from the tubes in the center to the tubes at the outer rim of the reactor, measured under flowing air with thermocouples inserted into the catalyst bed in previous testing experiments, were less than 1 K at 400 °C. During a test, the reaction temperature was monitored by four thermocouples in the guide tubes near the catalyst sites at different distances from the heating cartridges (see Figure 1). The preheated reactant feed could be introduced from the top of the reactor into all 80 tubes simultaneously. Flow distribution plates were used to establish a uniform gas composition through each tube. The whole reactor was heat-insulated using asbestos on the external surface. After making contact with the catalyst, the gases passed through the flow-permeable ends of the reactor tubes and then entered into the MSMSS via the capillaries.

The MSMSS system consists of an 80-way valve (Hiden Analytical) and a mass spectrometer (Hiden Analytical). Figure 2 shows the schematic representation of the quantified MS analysis system. Each path of the 80-way valve was connected to a reaction stream by a capillary from the reactor. The valve could be warmed to 120 °C and evacuated to a minus pressure condition by a vacuum pump (P1) to ensure that all of the components were gaseous. Any stream could be automatically selected to pass through the sample transfer tube and partly enter into quadrupole mass spectrometer (QMS) after further decompression by another vacuum pump (P2) through a warmed quartz inert capillary (QIC). The amount of gas entering into the QMS can be controlled by adjusting a bypass valve setting between the QIC and P2 (Figure 2). All other streams, including part of the selected stream, could be released by a common exhaust pipe. The time for sample selection and for data collection, depending on the number of mass ions monitored, could be within 1−10 s. The MSMSS could sequentially analyze all 80 streams in 80 s to 13.3 min and then start another cycle of analysis according to a predefined program.

To obtain quantitative results, a GC equipped with a six-way valve was combined with the MSMSS (Figure 2). During a reaction test, one of the gas streams from the 80-pass reactor was analyzed online either by GC or by MS simultaneously. The outlet pipelines and the six-way valve were kept at a constant temperature higher than 250 °C to prevent the condensation and strong adsorption of heavy products.

The use of capillaries, which provides an additional flow resistance of the system, dampens the effect of different pressure drops over the catalyst beds. However, there is some variance (less than 10%) in the flow delivered by the capillaries used because of fabrication errors, which would cause some differences in the flow rate in the reactor tubes. To maintain identical reaction conditions, the amount of catalyst in each reactor tube was adjusted in a narrow range according to the flow rate in the corresponding capillary. The flow rates were initially measured before each reaction experiment. During testing and screening processes, all catalysts could be operated for an identical contact time that is a basis for comparing the results from different streams and also comparing with the results of fixed-bed reactions.
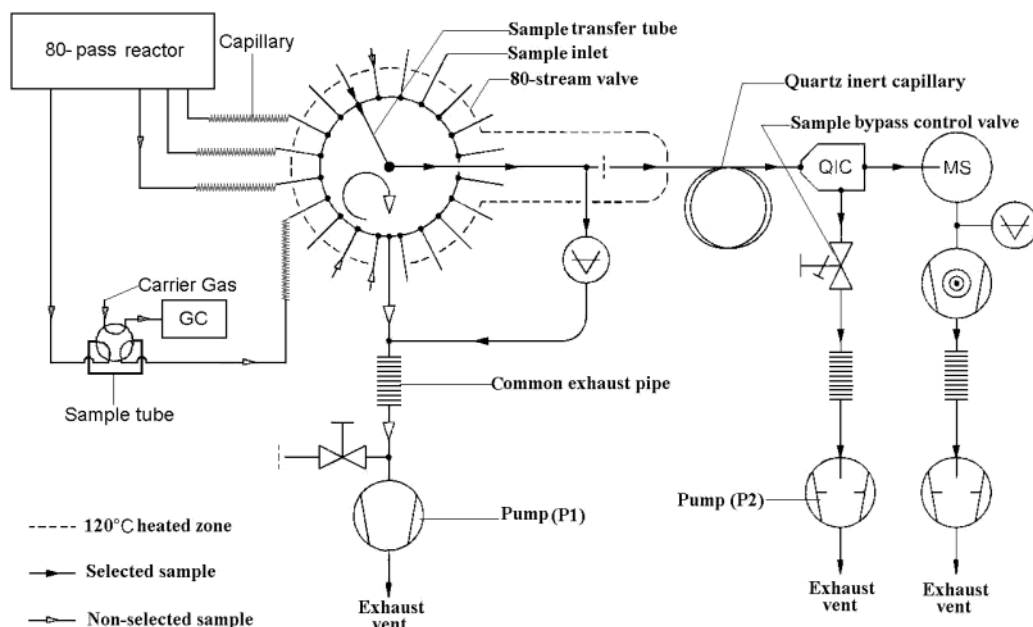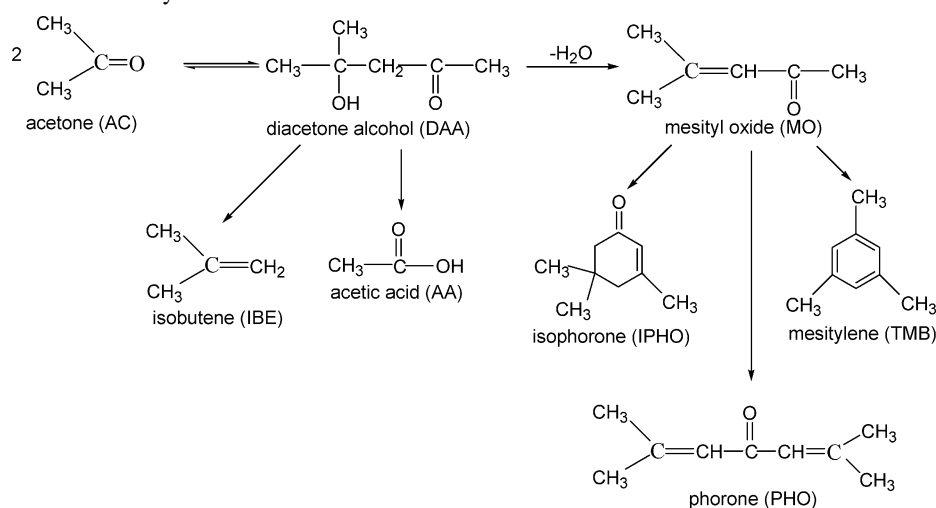
Figure 2. Schematic representation of the quantified MS analysis system.

Scheme 1. Main Reaction Pathways for the Acetone Condensation Reaction

Experimental Section

ZSM-5 zeolite with a Si/Al ratio of 60, Y-type zeolite, Beta, 13X, dealuminated HM molecular sieves, SiO_2, and γ-Al_2O_3 were supplied by Fushun Petrochemical Corp., PetroChina. ZSM-5 samples with Si/Al ratios of 25, 38, and 50 were obtained from Nankai University. SAPO-34 and SAPO-5 molecular sieves were synthesized in our laboratory by the reported methods.[27,28] The supported catalysts were prepared by impregnating HZSM-5 (Si/Al = 60) grains (40−60 mesh) with precursor solutions prepared by a computer-controlled sample preparation system (model SPS-5, Varian). A solution of metal nitrates or H_3PO_4 was added to a tube (100 mL) containing 20 g of fresh HZSM-5 zeolite. After impregnation for 24 h at room temperature, the solutions were removed from the tubes, and the zeolite grains were dried for 12 h at 120 °C. The catalysts subsequently were calcined for 4 h at 550 °C under air.

The compositions of the molecular sieve catalysts were determined by X-ray fluorescence spectroscopy using a Philips Magix 601 apparatus. X-ray power diffraction patterns were recorded on a Rigaku D/max-rb instrument using Cu Kα radiation with a nickel filter to ensure that the zeolite samples were of high crystallinity.

The aldol condensation of acetone, which is known to be catalyzed by both acid and base catalysts, was selected as a model reaction of technical interest because of the obviously different product distributions obtained over different kinds of catalysts. The reaction produces diacetone alcohol (DAA) as the initial product. The formation of numerous products is then possible through a complex reaction network that involves self- and cross-condensations between DAA with itself or with acetone. Several of these products, such as DAA, mesityl oxide (MO), isophorone (IPHO), and phorone (PHO), find many industrial applications. A scheme of the main pathways for acetone condensation is depicted in Scheme 1, although the reaction itself is evidently more complex in detail.

In the catalyst screening test for the reaction, all 80 fresh catalyst samples (about 0.3 g in each tube, 40−60 mesh), including duplicates and blanks (quartz grains), were placed
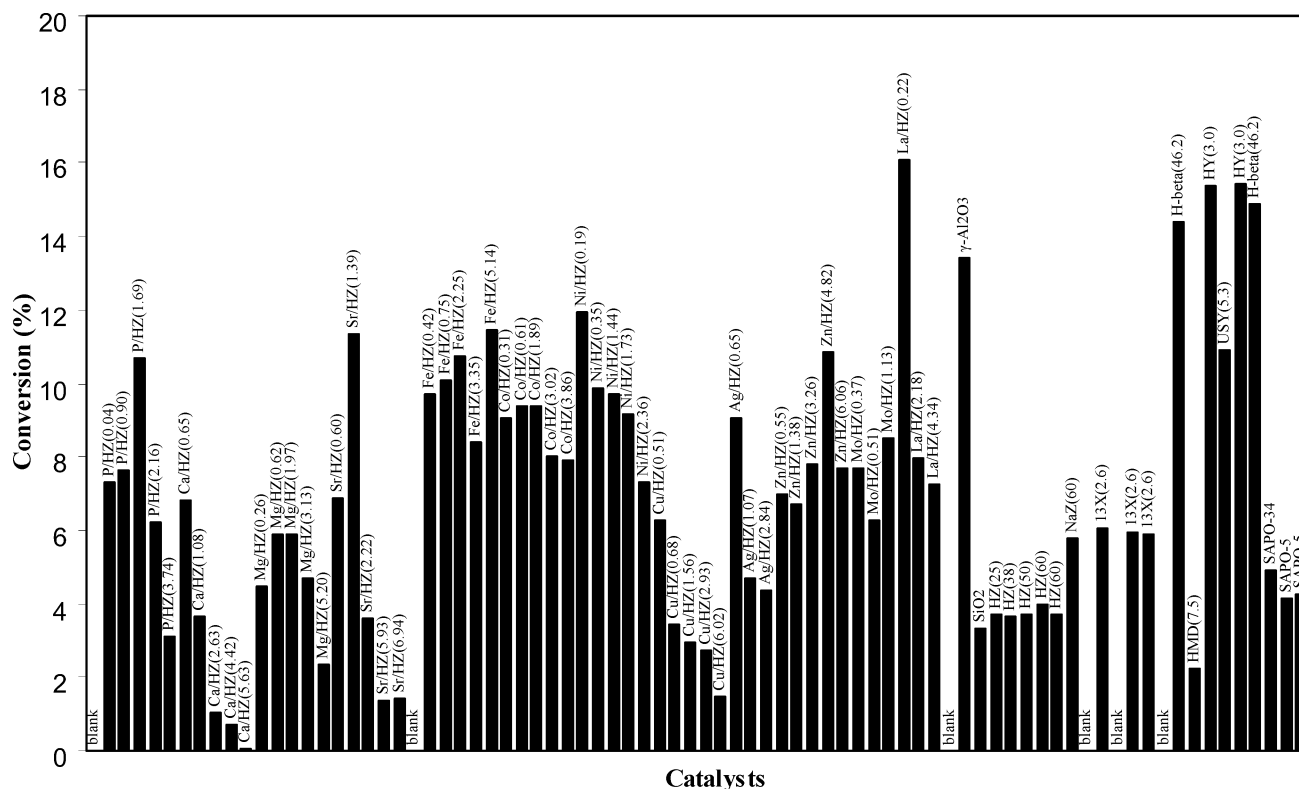
Figure 3. Relative signal intensity of products of acetone condensation over solid catalysts at 250 °C after 1 h on stream (HZ = HZSM-5 zeolite with Si/Al of 60; for supported catalysts, the number in parentheses refers to the amount of supported oxide; for pure molecular sieve catalysts, the number in parentheses refers to the Si/Al ratio. The mole composition of SAPO-34 is $Al_{0.55}P_{0.21}Si_{0.24}O_2$, and that of SAPO-5 is $Al_{0.50}P_{0.44}Si_{0.06}O_2$).

into the reactor tubes. The catalyst samples were then pretreated at 550 °C for 2 h in argon flow. After activation, the temperature was lowered to the desired test temperature (250 °C for the acetone condensation reaction). Acetone, together with argon (about 60% acetone in argon), was then introduced into the reaction system. Under the experimental conditions, the nominal weight hour space velocity (WHSV) of acetone was about 3.0 h^{-1}.

To ensure that no residue from the previous sample remained in the sample transfer tube or in the QIC, a 5-s flushing time was set before acquisition of data for each stream, and the sampling time was 3 s. This time period was adequate to acquire three or four sets of data, which was deemed sufficient for the present work. We were able to screen 80 samples in about 10 min. Further acceleration of the data acquisition process is clearly possible by shortening the flushing (and/or sampling) time or by decreasing the numbers of mass ions monitored.

Results and Discussion

To accelerate the data acquisition process and to minimize the volume of the data acquired, only selected mass ions, determined earlier in the scooping experiments, were monitored during the testing process. These m/e mass numbers were as follows: 20 (Ar, internal standard), 56 (isobutene, IBE), 58 (acetone, AC), 60 (acetic acid, AA), 82 (isophorone, IPHO), 83 (mesityl oxide, MO), 105 (mesitylene, TMB), and 123 (phorone, PHO). The possibility of other species contributing to these mass signals was also considered but determined to be insignificant under the conditions investigated.

The relative signal intensities of the products of acetone condensation over different catalysts after 1 h on stream are shown in Figure 3. To avoid congestion, the data for PHO are omitted, as only trace PHO was observed over most of the catalysts and the ratios of I_{PHO}/I_{Ar} were very small. The conversions of acetone over different catalysts are shown in

Figure 4; these values were calculated from the equation

$$\text{conversion} = 100 \times \frac{I_{\text{blank}} - I_{\text{catalyst}}}{I_{\text{blank}}}$$

where I indicates the intensity of the signals and I_{blank} and I_{catalyst} represent the MS signal intensities of the reactant from a blank tube and from a catalyst tube, respectively. It is evident from Figures 3 and 4 that the developed measurement technique allows for easy discrimination of the individual ports. No "crosstalk" between the neighbor ports was observed, which could be clearly confirmed by comparing the data from the catalytic and blank ports. The relative activities of the different catalyst ports are readily discernible, illustrating the utility of the system as a high-throughput screening tool.

From Figure 3, the selectivity of each product over the different catalysts can easily be qualitatively compared. For example, the selectivity of MO over 13X catalyst is much higher than that over the other catalysts, given that the relative signal intensity of MO on 13X is stronger than on the others. This indicates that the developed technique could be used for the selection of catalysts in terms of activity and selectivity. However, there is no means to compare the signal intensities of different compounds over the same catalyst, because different compounds have different decomposition rates under the same MS operating conditions, and the signal intensity of the selected fragment ion cannot indicate the actual percentage of the corresponding compound in the mixed gases.

We understand that the relative MS signal intensity of a selected ion ($I_{\text{product}}/I_{\text{Ar}}$) of a given compound is proportional to the mole ratio of the compound to Ar in the mixture. By simultaneously analyzing the same stream of gas with MS and a GC equipped with a thermal conductivity detector (TCD), a correction coefficient relating $I_{\text{product}}/I_{\text{Ar}}$ to the relative mole ratio of a product (product/Ar) corresponding to GC analysis can be obtained. This coefficient should be suitable for the selected ion over any catalysts. In this way,

Figure 4. Conversions of acetone over solid catalysts at 250 °C after 1 h on stream.

all of the compounds in the mixed gases can be corrected by the corresponding correction coefficients, and a "bridge" between the MS data and the GC results can be established. This provides a possible aprroach to the quantified analysis of combinatorial heterogeneous catalyst libraries.

In our experiments, 13X, γ-Al$_2$O$_3$, HY, and La/HZSM-5 (0.22) were selected as the catalysts examined by GC and MS to calculate the correction coefficients and to validate the method for obtaining quantitative analytical information. The selectivities of some products over 80 catalysts are shown in Figure 5; these value were obtained by multiplying the MS relative intensities shown in Figure 3 by the corresponding correction coefficients. The reliability of the acetone conversions calculated from the equation

$$\text{conversion} = 100 \times \frac{I_{\text{blank}} - I_{\text{catalyst}}}{I_{\text{blank}}}$$

was also validated by the GC analysis results.

For a clear assessment of the reproducibility of the duplicates, the selectivities over the duplicate samples are shown in Figure 6. There are some differences in selectivity over most of the duplicates, and the highest deviation is about 40% (AA over HZ), which seems to imply that the developed method is not sufficiently reliable enough. However, considering the low conversion of acetone over these samples (about 5% over HZ), the yield of AA is about 0.4%, and the actual percentage of AA in the mixtures (about 40% Ar in the stream) is even lower (about 0.24%). Accurate quantification of such a low percentage in a mixture is not easy by this method, as the signal fluctuations of a MS with a Faraday detector and a GC with a TCD detector would significantly affect the accuracy of the analysis results. Using

more precise detectors, such as an electron multiplier for MS and an FID for GC, can certainly improve the accuracy, and in such a case, an inert organic gas (such as methane) that can generate an FID signal must be used to replace Ar as the internal standard. Now, we can realize less than 5% deviation of conversion and selectivity over duplicate catalysts for some reactions, such as the decomposition of NH$_3$, by replacing the Faraday detector with an electron multiplier detector. For the very low conversion of acetone over some supported catalysts, such as Ca/HZSM-5 (5.63), Cu/HZSM-5 (6.02), Sr/HZSM-5 (5.93), and Sr/HZSM-5 (6.94), the percentages of the products in the mixtures are very small. In these cases, the fluctuations of the MS signal would significantly influence the accuracy of the analysis results. Therefore, we consider only the data in Figure 5 with more than 1% actual percentage in the mixture to be reliable by our experience.

The data in Figure 5 indicate that, although the formation of diacetone alcohol (DAA) initially occurs over both acidic and basic catalysts during the reaction, the product distributions are evidently different over the different kinds of catalysts. The acidic catalysts favor the formation of isobutene and acetic acid by the cracking of DAA, whereas the dehydration of DAA to mesityl oxide and secondary reaction products is favored over basic catalysts (13X), which is in complete agreement with the previous measurements reported by other investigators.[29,30] The selectivity of acetic acid is usually lower than that of isobutene or even under detection limits over some catalysts because of its rapid cleavage into methane and carbon dioxide. This is also in line with previous work[31] and has been validated by the detection of *m/e* 16
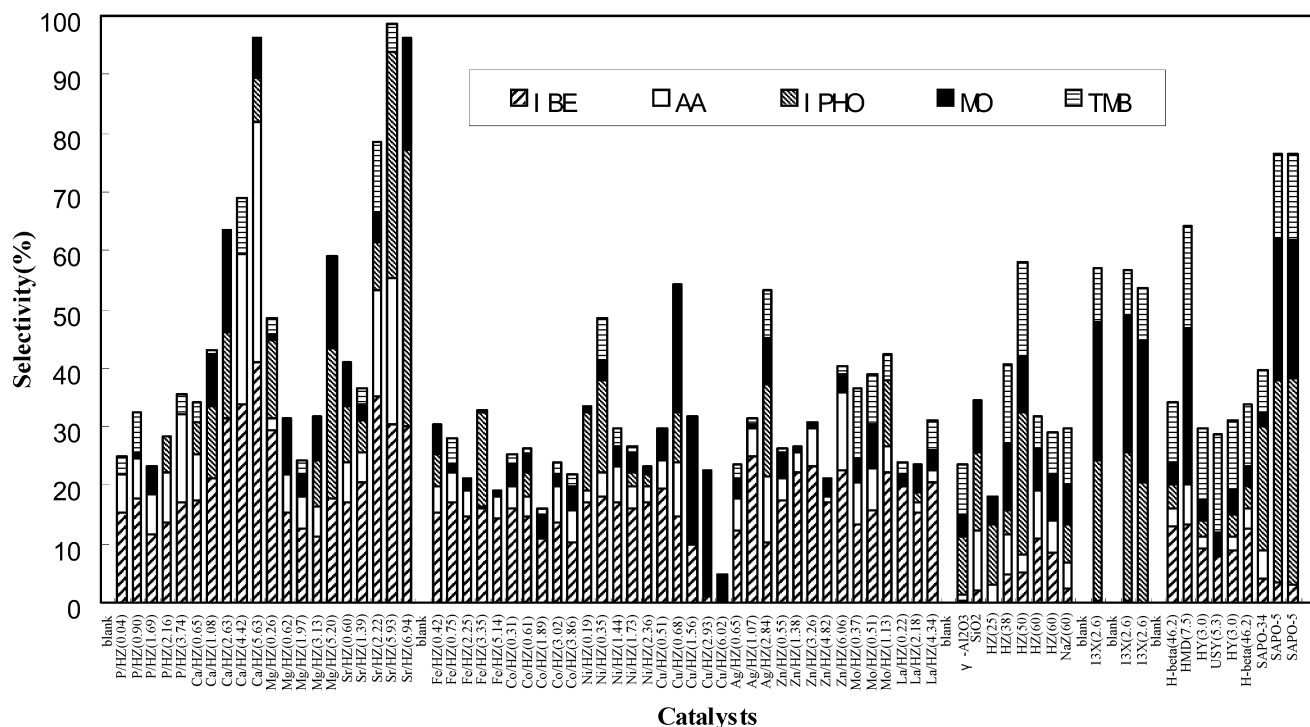
Figure 5. Product distributions of acetone condensation over solid catalysts at 250 °C after 1 h on stream.
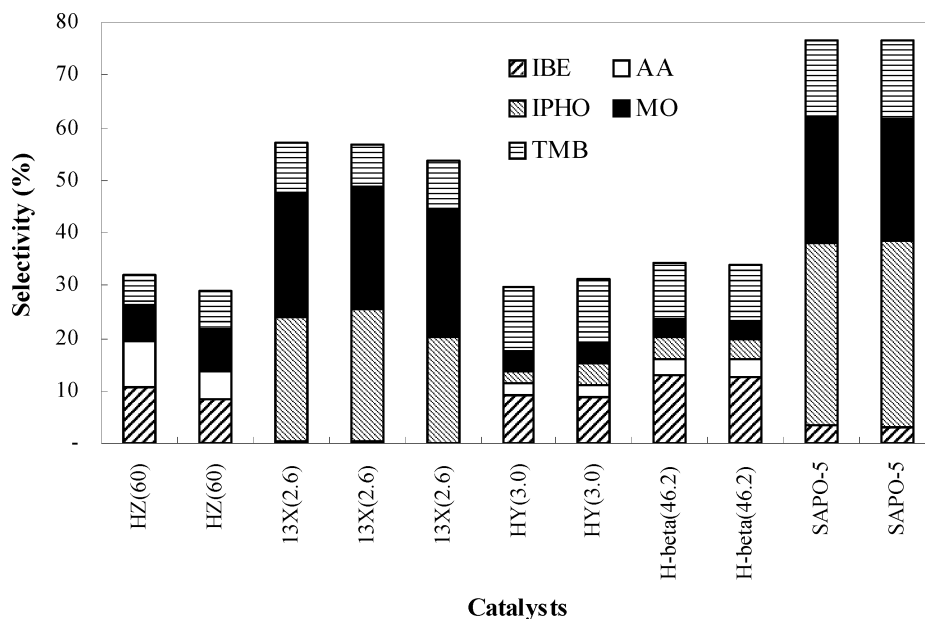

Figure 6. Selectivities of products in duplicate tests of catalysts.

(monitored methane) and 44 (monitored carbon dioxide) in a sequential screening test of some ports.

As for all previous techniques, there are still some problems for which suitable solutions are lacking and where more work is needed: (1) Although the 80-pass reactor allows for the screening catalysts at uniform temperature, it can be used only at temperatures lower than 600 °C. An improved reactor that can be used for high pressure is under design in our laboratory. (2) The MS detector itself has some limitations in the analysis of complex isomeric mixtures of hydrocarbons. (3) The analysis is still done sequentially, although it can analyze 80 catalysts in about 10 min, and it is difficult to detect rapid deactivation processes. (4) The multivalve system is limited in temperature, so this system

is impossible for use with reactions in which high-boiling products or reactants are formed.

Conclusion

In summary, a high-throughput quantitative screening system for secondary catalyst libraries has been developed by the combination of a multistream mass spectrometer screening (MSMSS) system with an 80-pass reactor and an on-line GC. The multireactor proved to be of uniform temperature and to allow the selection of heterogeneous catalysts under conventional fixed-bed reaction conditions. Moreover, it provides a possible route to quantitative analysis of MS data by calibrating the MS data by GC results, by which information on the activity, selectivity, and even yield

of each product can be obtained in just one run for all 80 catalysts. By using this technique, it is possible to test catalysts under identical conditions with a throughput of 400 catalysts per week. A combination of this secondary screening technique with primary screening techniques such as IR spectroscopy, REMPI, and LIFI has been proposed to be most effective, because new materials discovered by primary screening can next be optimized by this secondary screening technique.

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