

High-throughput characterization of heterogeneous catalysts by temperature-programmed analysis method

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Abstract

A multistream reactor for high-throughput examining the surface acidity by NH_3 -TPD method by application of multistream mass spectrometer screening (MSMSS) technique has been developed. This method allows for examining the surface acidity of 10 catalyst samples in about 6 h, which is an improvement over the traditional process. The demonstration of the feasibility of high-throughput TPD can be significant in convincing the hardened traditionalists in the heterogeneous catalysis community that, combinatorial methods indeed should have an important place in scientific catalyst research and development. The developed method could also be used for almost all the temperature-programmed analysis theoretically with careful designed multistream reactors.

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1. Introduction

Temperature-programmed analysis method, in which both the temperature and the surface coverage of heterogeneous catalyst vary with time, has been widely applied to characterizing heterogeneous catalysts, primarily because it possesses the advantage of providing information which is not available from steady-state kinetic. This technique, which was first used by Cvetanovic and Amenomiya [1], has been developed further and applied in an ever-wide range of temperature-programmed applications: desorption (TPD), reduction (TPR), oxidation (TPO) and surface reactions (TPSRs). Among these applications, NH_3 -TPD has been most commonly used to probe the surface acidity of heterogeneous catalysts, for the acid sites in solid catalysts, especially in zeolite catalysts, play an important role in various industrial processes. However, this technique is deemed to be tedious and time-consuming for the repeated operation of characterizing samples one by one.

With the application of combinatorial technique in the discovery of new solid-state materials [2], several high-throughput screening techniques have been developed to screen heterogeneous catalyst libraries. Infrared (IR) thermography as a detection tool in combinatorial catalysis allows parallel analysis of libraries by monitoring the temperature change of the catalyst sites in gas-phase reaction [3] as well as the heat change of homogeneously catalyzed reaction in the liquid phase [4], although it could not provide any information on the chemical identity of the products formed in a reaction. The laser-induced fluorescence imaging (LIFI) technique [5,6] exploits the alteration of the fluorescence properties of molecules as a consequence of the creation or destruction of chemical bonds. Senkan has used resonance-enhanced multiphoton ionization (REMPI) technique [7,8] which based on in situ ionization of reaction products by UV lasers and detecting of the photo-ions or electrons by microelectrodes placed in the vicinity of the catalyst site to detect benzene as the dehydrogenation product of cyclohexane. High-throughput screening mass spectrometry (MS) [9–12] is a mature and widely used detection technology for rapid analyzing gaseous mixtures from one sample of a

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combinatorial library at a time to all samples in a sequential manner. Recently, a method based on coupling a GC with multistream mass spectrometer screening (MSMSS) has been used to select catalysts by quantified analysis [13].

In contrast to the concentration of studies on screening technique for the selecting novel catalyst formulations, there are still no studies on the high-throughput characterization of heterogeneous catalysts.

We therefore report the first example on the application of multistream mass spectrometer screening (MSMSS) technique [13] together with a multistream reactor similar to that developed by Hoffmann and Schüth [14,15] for high-throughput characterization of heterogeneous catalysts by NH_3 -TPD method. This technique allows examining the surface acidity of 10 catalyst samples in about 6 h, which is an improvement over the traditional operation. Moreover, the reduction of some metal oxides and the decomposition of NH_3 over supported catalysts have been observed, which proves that the NH_3 -TPD method is not appropriate for some supported catalysts.

2. Experimental

A schematic drawing of the multistream reactor is shown in Fig. 1. It consists of a steel block with 10 wells of 8 mm diameter each, equipped with five heating cartridges inserted into the block from the downside and a heating loop surrounding the block tightly. Catalyst is placed into a smaller sample tube that has an open end with screw thread and a flow permeable end. The sample tube is fixed in a well and sealed against the steel body with plumbago ring to ensure the feed gas totally passing through catalyst bed. At the bottom end of each well, a stainless steel capillary is connected to reduce the effluent of the gas. All the 10 capillaries are carefully selected and tested to ensure no clear differences due to fabricate error on flow rate. The whole reactor was heat-insulated using asbestos on the external surface. The

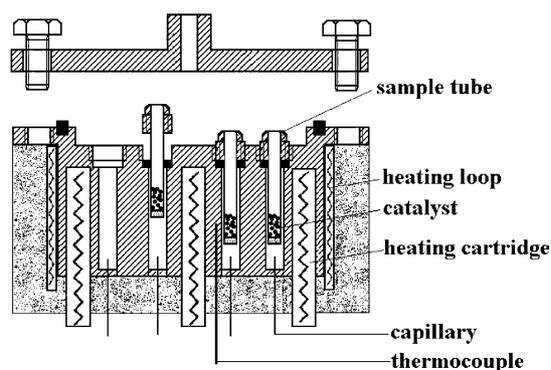


Fig. 1. A schematic drawing of the multistream reactor.

differences of the heating ramp between the sample tubes, which were calculated by measuring the temperature changes with thermocouples in the tubes filled with catalysts under flowing air, are less than 2% under the testing temperature-program (with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$), and the heating rate in each tube is calculated in an initial experiment. The gas could be introduced from the top of the reactor into all the wells simultaneously, and then passed through flow permeable ends of the sample tubes, entered into the MSMSS via the capillaries.

The MSMSS consists of a multistream valve and a mass spectrometer (Hiden Analytical). Each way of the valve was connected to a reaction stream by a capillary from the reactor. Any stream could be automatically selected and partly entered into quadrupole mass spectrometry via a warmed quartz inert capillary. All other streams including part of the selected stream could be released by a common exhaust pipe.

The HZSM-5 zeolite ($\text{Si}/\text{Al} = 60$) was obtained from Fushun Petrochemical Corp. PetroChina. SAPO-34 and SAPO-11 molecular sieves were synthesized in our laboratory according to the reported methods [16,17]. The supported catalysts were prepared by impregnating HZSM-5 grains (40–60 mesh) with precursor solutions prepared by computer-controlled Varian sample preparation system (model SPS-5). A solution of $\text{Ni}(\text{NO}_3)_2$ or RuCl_3 was added to a tube (100 mL) containing 20 g fresh HZSM-5 zeolite. After impregnation under room temperature for 24 h, the solutions were removed from the tubes and the zeolite grains were dried for 12 h at $120\text{ }^\circ\text{C}$. Catalysts subsequently were calcined for 4 h at $550\text{ }^\circ\text{C}$ under air atmosphere.

In the TPD experiment, 10 fresh catalyst samples (about 0.05 g in each tube, 40–60 meshes), including duplicates (HZSM-5) and blank (quartz grains), were selected and placed into the sample tubes. The catalyst samples were then pretreated at $650\text{ }^\circ\text{C}$ for 1 h in a stream of helium. Subsequently, ammonia was adsorbed at $100\text{ }^\circ\text{C}$ from a He gas flow containing 3 vol% of NH_3 . After sufficient flushing with pure He under this temperature (about 2 h in our experiment) to remove physically absorbed ammonia, the reactor was cooled to $50\text{ }^\circ\text{C}$ and the TPD measurement up to $650\text{ }^\circ\text{C}$ was started with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in a He flow (15 ml/min). At the initial period of the temperature-program, the heating rates in most of the sample tubes are not linear, and only the data between 100 and $600\text{ }^\circ\text{C}$ for each sample were selected to describe the TPD curves, for in this temperature raising period, linear heating rates were obtained in all the sample tubes.

To avoid the influence of H_2O , m/e 16 instead of 17 was used to monitor NH_3 , and at the same time, m/e 2, 18, and 28 were detected to monitor H_2 , H_2O , and N_2 , respectively. To ensure that there are no effects from last

sample, 6 s of flushing time was set before acquiring data of each stream, and the sampling time was 2 s. In our experiment, 6 s flushing time is not enough to get a steady-state, and we observed the remained mass ions from last sample. However, the amount of the remained gas sample is very small, and it affects insignificantly the composition of the detected stream, which has been confirmed by comparing the curves of the blank port with the sample-loaded ones. So 6 s flushing time is enough to get good quality TPD spectra, although it is not long enough to remove all the remained gas sample from last port. We were able to get about 38 data points of each detected mass ion for each sample during the linear temperature period (from 100 to 600 °C), which is deemed sufficient for the description of the TPD curves accurately.

3. Results and discussion

The NH₃-TPD curves of 10 catalyst samples are shown in Fig. 2. The results of NH₃-TPD indicate that the developed measurement technique allows easy discrimination of the individual ports. No “crosstalk” between the neighbor ports is observed, which could be clearly confirmed by comparing the TPD curves of catalytic and blank ports. The NH₃-TPD curves of different catalyst ports are readily discernible, illustrating the potential utility of the system as a high-throughput characterization tool. The curve repetition of the duplicated samples (HZSM-5) indicates that this technique is a reliable method for the high-throughput characterization of the acidity of solid catalysts by NH₃-TPD.

The TPD spectra of NH₃ from the HZSM-5 samples show a low-temperature peak at ca. 210 °C and a high-temperature peak at ca. 430 °C, and all the SAPO samples show two peaks in the NH₃-TPD curves, corresponding, respectively, to the desorption of NH₃ from weak acid sites and from strong acid sites. In the case of SAPO-34, the position of the high-temperature peak is approximately 100 °C higher than that observed for SAPO-11. The shift of the high-temperature peak cannot necessarily be related to differences in the acid strength of sites. This may be caused by influences of the individual pore width and structure of the void volume of the different types of molecular sieves on the diffusion of the desorbing ammonia molecules [18]. Indeed, the shifting of the high-temperature peak for small pore SAPOs (SAPO-11 and SAPO-34) had been observed by other authors [19,20].

The decreasing of the high-temperature peak area and the shifting of the maximum peak of the supported samples to low temperature (including the HZSM-5 and SAPO molecular sieves) indicate that the supported metal oxides not only affect the numbers but also the

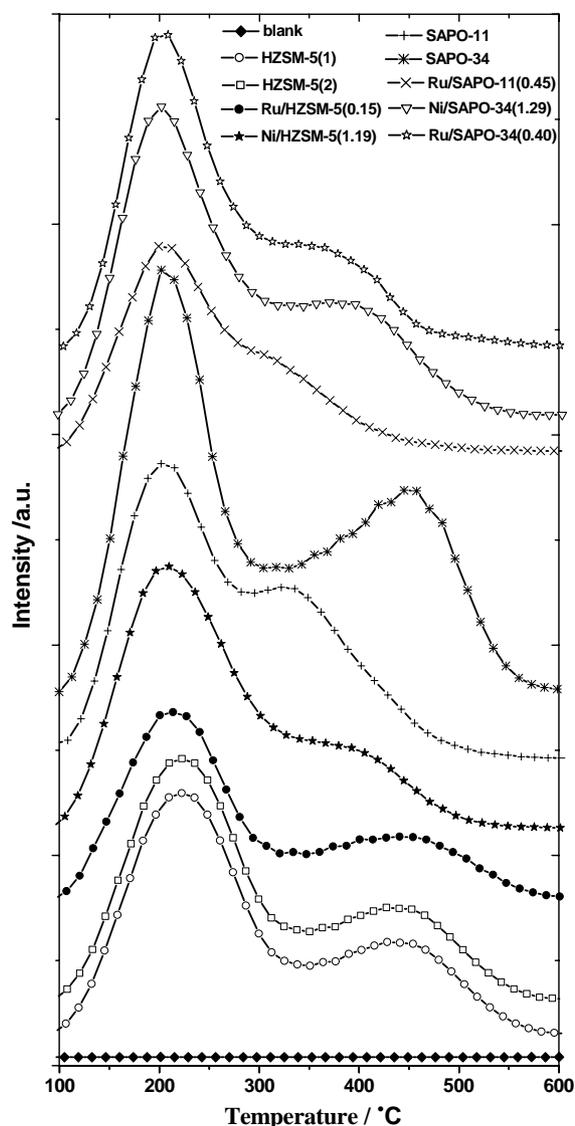


Fig. 2. NH₃-TPD curves of samples by high-throughput characterization.

strength of strong acid sites, which is in line with the previous work [21].

The reduction of some supported metal oxides and the decomposition of ammonia over supported catalysts have been observed by monitoring the signal intensity change of some mass ions from the effluent. The signal changes of the selected mass ions in the effluent over Ru/SAPO-34 are shown in Fig. 3.

The curves in Fig. 3 indicate that the supported Ru₂O₃ is reduced at ca. 250 °C firstly, which could be confirmed by the signal change of H₂O and N₂, then the reduced metal catalyzes the decomposition of the desorbed NH₃ with temperature increasing, and H₂ and N₂ were obtained at ca. 450 °C. The reduction of metal oxides and the decomposition of ammonia are observed at all the supported catalysts investigated. This indicates

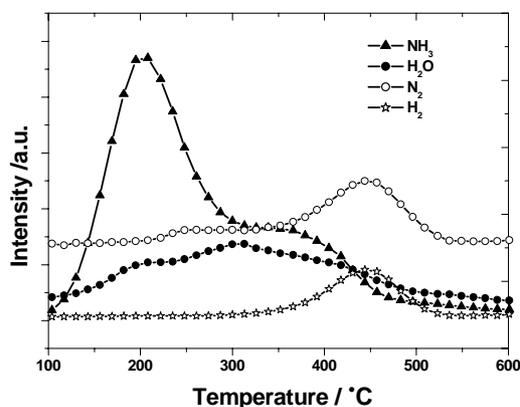


Fig. 3. The curves of the effluent compositions over Ru/SAPO-34.

that the NH_3 -TPD method is not appropriate for examining the acidity of some supported catalysts.

4. Conclusions

In summary, the multistream mass spectrometer screening (MSMSS) technique together with a multistream reactor is very useful for high-throughput characterizing the acidity of solid catalysts. Using the developed technique, it is possible to achieve a characterization capacity of 10 samples per day. The demonstrating of the feasibility of high-throughput TPD can be significant in convincing the hardened traditionalists in the heterogeneous catalysis community that, combinatorial methods indeed should have an important place in scientific catalyst research and development. The developed technique could also be used for almost all the temperature-programmed analysis theoretically with careful designed multistream reactors.

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