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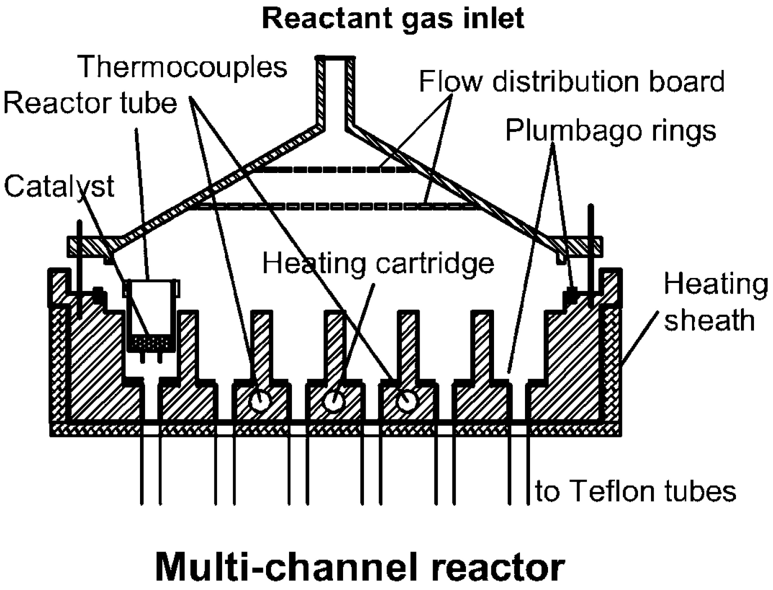

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High-Throughput Selection for Heterogeneous Catalysts

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A catalyst library of 80 samples with different mass ratios of rare earth elements, cobalt (Co), cerium (Ce), and indium (In), was prepared by impregnation of a fresh HZSM-5 zeolite support. A high-throughput detection setup, based on UV absorption spectroscopy, was developed for heterogeneous catalyst selection. The catalytic properties of the library were tested in the selective catalytic reduction of NO by methane at 673 K. Among the Co/Ce series, the catalyst with Co/Ce = 2:1 and Co/H−ZSM5 = 2.5% has shown remarkable efficiency (up to 78%). In the Ce/In series, the reactivity of the catalyst with the support composition of Ce/In = 1:1 and Ce/H−ZSM5 = 2.0% was ≤88%. Our initial experiments definitely indicated that this simple and inexpensive multichannel setup can be applied for the selection of other heterogeneous catalysts. According to the variation of the UV light intensity, resulting from the absorption of the reactant or product, it was possible to monitor the relative quantity of reactants or products during a catalytic reaction.

Introduction

The emission control of NOx in exhaust gases is one of the greatest engineering challenges in the extension of the practical and commercial application of diesel and lean-burn engines.[1] One solution is selective NOx reduction using hydrocarbons (HC) in an oxidizing atmosphere. NOx reduction (deNOx) in such an exhaust gas environment is very difficult because of the oxidizing atmosphere. Selective catalytic reduction (SCR) with HC is one of the techniques for NOx abatement in oxidizing atmosphere.[1] Although Cu−ZSM-5 is well-known to be a very active catalyst for this reaction,[2] it does not have enough durability to be of any practical use.[3] Platinum-supported catalyst is known to be active at relatively low temperatures (473−673 K) and is suitable for diesel engine exhaust applications.[4] However, the catalyst's NOx reduction activity is not enough to be of practical use. The main component of the catalyst aimed at low-temperature operation with hydrocarbon reductant in passenger cars is platinum supported on alumina. High-temperature heavy duty applications preferentially need noble-metal-free catalysts. The concept of the SCR of NOx requires reasonable amounts of hydrocarbons in the exhaust gas. Normally, the hydrocarbon concentration at the engine outlet is low and not sufficient for effective NOx conversion. As a consequence, hydrocarbons have to be supplied by adding secondary fuel into the exhaust pipe. Lab-scale investigations with model exhaust gases most frequently use propane, propene, and methane.

An efficient approach toward understanding heterogeneous catalytic reactions is through combinatorial assays. The power of combinatorial chemistry is apparent in medicinal chemistry research.[5] The realization of combinatorial methodology can make the discovery process hundreds, even thousands, of times more efficient.[6] It is also developing rapidly into an attractive alternative to the traditional discovery process for heterogeneous catalysts. Combinatorial synthetic techniques based on gas-phase deposition[6] and liquid dosing[7] allow us to prepare a large number of potential catalytic materials in a high-throughput fashion. In the past decade, significant progress has been made in high-throughput screening of heterogeneous catalysts, such as fluorescence indicator,[7] IR thermography,[8] laser-induced resonance-enhanced multiphoton ionization,[9] scanning microprobe mass spectrometry[10] laser-induced fluorescence imaging,[11] etc.. Even so, because of the complexity and diversity of heterogeneous catalytic reactions, there is still a long way to go in the development of sundry high-throughput screening techniques to meet different requirements.

Progress in high-throughput testing with parallel reactors and short analysis times rendered the screening of a large number of catalysts within a short time possible.[12] One application of a combinatorial catalyst, the Pt−Pd−In−Na system, to the SCR of NO has been reported by withdrawing small samples from the microreactor exits using a capillary sampling probe followed by on-line mass spectrometer gas analysis.[13] Multicomponent catalysts, the Ag−Co−Cu−In system, have been prepared via the combination of non-platinum group metals and have been evaluated by on-line time-of-flight mass spectrometry.[14]

Recently, an alternative high-throughput screening setup for heterogeneous catalysts, based on the UV absorption spectrum technique, has been developed. This setup was applied in the combinatorial discovery of active catalysts for selective catalytic reduction of NO by methane over rare-earth-supported catalyst promoted by HZSM. According to the variation of UV light intensity, from the UV absorption of NO, it is possible to determine the relative quantities of the reactants or the products before, during, and after a

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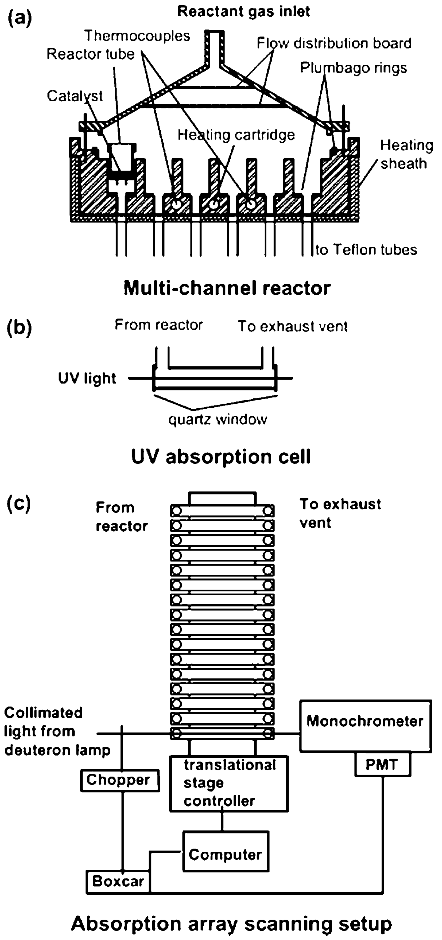

Multi-channel reactor

UV absorption cell

Absorption array scanning setup

Figure 1. Schematic diagram of the(a) multichannel reactor, (b) UV absorption cell, and (c) absorption array scanning setup.

catalytic reaction. The approach reported here differs from those in the literature[7−11,13,14] in the following three aspects: (1) the working temperature of the catalysts was 673 K, which meant that precious metal components were not suitable as constituents of the catalyst; (2) the active elements chosen were cobalt (Co), cerium (Ce), and indium (In) as the most prominent examples with deNOx activities at medium reaction temperatures; and (3) the whole setup was quite cheap and easy to operate, without any complicated vacuum system, such as a mass spectrometer. Using this setup, we investigated 80 HZSM5-supported rare earth catalysts. The reactivity of the catalyst with the support composition of Ce/In = 1:1 and Ce/H−ZSM5 = 2.0% was ≤ 0.88. Our initial experiments definitely indicated that this simple and cheap setup could be used for high-throughput screening of the SCR of NO and of other heterogeneous catalytic reactions by modifying the UV light wavelength.

Experimental Section

A schematic drawing of our multichannel reactor system is shown in Figure 1a. It has 24 wells (1 cm inner diameter and 10 cm in depth) tap drilled in a stainless steel cylinder holder. Three electrical heating cartridges were placed in the middle of the holder. The whole reactor was heat-insulated from the environment by placing a heating sheath and asbestos insulating slabs on the external surface of the reactor. Two flow-distribution plates were used to establish a uniform gas flow through each well. In each well, a smaller reactor tube, which had one open end with screw thread and one flow-permeable end, was sealed against the well with a graphite ring to ensure that the feed gas passed completely through the catalyst bed. Stainless steel grids were welded at the outlet ends of reactor tubes to support the catalyst samples and prevent leakage of the samples into the UV absorption cells. Teflon tubes (40 cm in length) were used to connect the outlets of the wells to the UV absorption cells. The use of Teflon tubes with 4 mm inner diameter, which kept almost the same flow resistance as the reactor tubes, minimized the effect of pressure drops over the catalyst beds.

The maximum temperature difference between the wells, especially the temperature deviations from the wells 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, was less than 5 K at 723 K. 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. After it reacted on the catalyst surface, the gas mixture passed through the flow-permeable ends of the reactor tubes and entered the scanning UV absorption cells via the Teflon tubes, illustrated in Figure 1b. The outlet pipelines were maintained at 400 K to prevent condensation and adsorption of reagents.

The scanning UV absorption array system, as shown in Figure 1c, consisted of a broadband deuterium lamp (model L7893, Hamamatsu), an analogue lock-in amplifier with chopper (model 5209, PerkinElmer Instruments), a half-meter monochromator with 1 nm spectrum resolution, a photomultiplier tube (PMT, Hamamatsu), and a one-dimensional computer-controlled translation stage. The deuterium lamp emitted UV light in the 190−400 nm range. To produce a parallel beam, a plano-convex lens (25 mm focal length, 15 mm diameter) was used to focus the beam on a 0.6 mm diameter pinhole. This spatial filter eliminated unwanted wavelengths. An incident achromatic beam localized at different distances from the lens from wavelength to wavelength because of the wavelength-dependent lens refractive index. The other wavelengths were focused before or after the pinhole position, and then a negligible quantity of these wavelength energies was transmitted throughout the pinhole. A second lens (fused silica, 75 mm focal length, 25 mm diameter) was placed on the opposite side of the pinhole to make a parallel beam. The transmitted UV light (about 3 mm diameter) across the UV absorption cell was then focused at the entrance slit of the monochromator. The absorption differences in cells were measured by PMT and the lock-in amplifier and were recorded by a computer. The UV absorption cells were fixed on the translation stage, controlled by the same computer. The whole measurement was controlled automatically by software developed in our group. The UV light was set at 214.5 nm, which was the maximum absorption wavelength of NO. During the testing and screening processes, all catalyst samples were operated for an identical contact time which was a basis for comparing the results from different streams and also for comparing them with the results of fixed-bed reactions.

ZSM-5 zeolite with an Si/Al ratio of 25 was obtained from Nankai University. The supported catalysts were prepared by impregnating HZSM-5 (Si/Al = 25) grains (40−60 mesh) with precursor solutions prepared by a computer-controlled sample preparation system (model SPS-5, Varian).[15] A solution of metal nitrates ($Co(NO_3)_2$, $Ce(NO_3)_3$ and $In(NO_3)_3$) was added to a tube (100 mL) containing 5 g of fresh HZSM-5 zeolite (Si/Al= 25). After impregnation for 24 h at room temperature, the solutions were removed from the tubes, and the zeolite granules were dried for 8 h at 393 K. The catalysts were subsequently calcined for 4 h at 823 K. Fresh catalyst samples (0.3 g in each tube, 40−60 mesh) were placed into the reactor tubes. For comparison, an industrial sample of Pt/Al_2O_3 was also used. The catalyst samples were pretreated at 723 K for 27 min in an argon flow. After activation, the temperature was lowered to the desired test temperature (673 K), and then the reagent gas mixture was moved into the reactors.

The reagent gas mixture, consisting of NO (2000 ppm), CH_4 (2000 ppm), O_2 (5% in volume), and argon (for balance), passed the catalysts at a total flow rate, gaseous hourly space velocity (GHSV), of Flow = 5400 mL h^{-1}. The gas flow rates were regulated by digital mass-flow controllers. In all of the experiments reported here, only dry feed was used.

Results and Discussion

The active rare earth elements chosen were Co, Ce, and In, as the most prominent examples with deNOx activities at high reaction temperatures. A catalyst library of 80 samples, composed of combinations of the three elements in different mass ratios from 0.5 to 5%, was prepared by automated impregnation of a proprietary alumina support. The catalytic properties of the library were tested in SCR of NOx by methane at 673 K by a parallel 24-channel microreactor system with automated UV absorption multichannel scanning analysis.

The determination of analyte concentration via light absorption has widespread application in production and research settings. The Beer−Lambert law[16] provided a simple expression relating the transmitted electromagnetic power to the concentration of the analyte. Absorbance (A) = $\log(I/I_0) = \epsilon CL$, where I and I_0 are the intensities of the transmitted and incident radiation, ϵ is the extinction coefficient, C is the concentration of absorbent, and L is length of the light path through the absorbent. The absorbance (A) provided an easy method to estimate the analyte concentration. For given absorbent ϵ and light path L, A was proportional to the concentration C. Because of catalytic reduction, the concentration of NO would decrease after passing through the reactor tube. To conveniently compare the reactivity of the different catalysts in our experiments, the reactive factor R was defined as $R = A/A_0$, where A and A_0 represent the absorbance of UV light by NO after and before the catalytic reaction, respectively. By applying time-resolved detection of absorbance (A), we could monitor the relative quantity of the reactants or the products before, during, and after a chemical reaction. The UV wavelength was set at the maximum absorption wavelength of NO to achieve the maximum sensitivity. Detection of each absorption cell was completed in 100 ms.

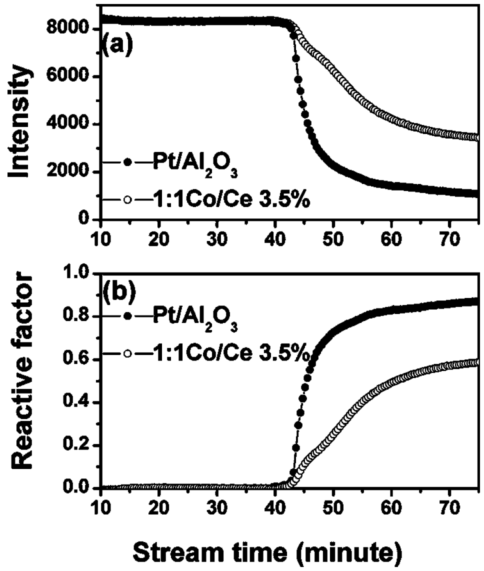

Figure 2. Experimental results of the SCR of NO by methane by 3.5% Co/Ce and a Pt industrial catalyst, $T = 673$ K, Flow = 5400 mL h^{-1}: (a) absorption data (b) corresponding reactive factors.

Before the assay of the activities of rare earth elements can be started, it must be calibrated. There were some variances (less than 10%) among the different absorption cells because of fabrication errors and misalignment of the light in each cell, which would cause some differences in estimation of the reactivity of catalysts. To minimize these systematic differences, before the evaluation of different catalysts, each channel needed to be calibrated. Transmission of the UV light of 2000 ppm NO in argon was measured to obtain the normalization factor for each channel (reactor tube and UV absorption cell) with the same amount of H−ZSM5 as later catalyst samples.

To clearly demonstrate the application of this setup in the selection of SCR catalysts, Figure 2 illustrates the results of Pt/Al_2O_3 industrial catalyst and 3.5% Co/Ce (mass ratio 1:1) supported by H−ZSM5. The abscissa title “stream time (minute)” is the time from switching on of reagent gas mixture to detection of UV absorption. This time included the flow time from switch to detection and the reaction time. After calibration, the absorbance of NO in these two channels (including reactor tube and absorption cell) was illustrated in Figure 2a. According to the definition, the reactive factors for different channels were directly obtained, as indicated in Figure 2b. The reactivity of the industrial catalyst sample Pt/Al_2O_3, 0.91, was estimated to be quite close to the value measured by gas chromatography,[17] which meant that whole setup was reliable. The results in Figure 2b clearly indicated that this simple and inexpensive setup could be applied in the combinatorial discovery of active catalysts for SCR of NO by methane. The reactivity of the catalyst sample with 3.5% Co/Ce (mass ratio 1:1) was 0.58. The interval between data points in Figure 2a was 30 s, which was short enough for monitoring the SCR of NO, compared with longer intervals in other methods, for example, 10 minutes in multistream mass spectrometer screening.[15]

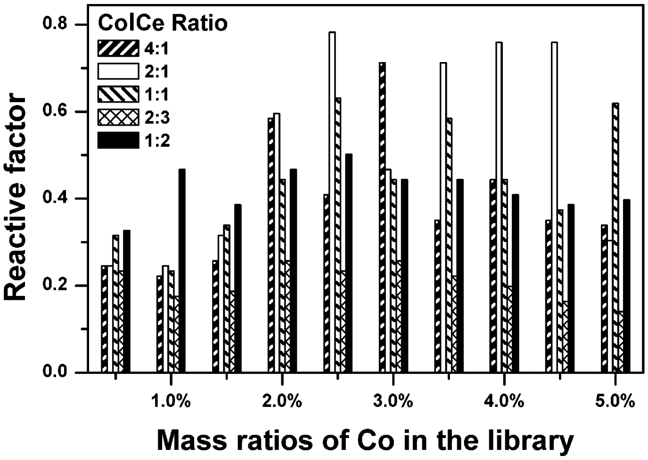

Figure 3. Reactive factors of different mass ratios of Co/Ce on H−ZSM5.

A Co−Ce/H−ZSM5 series with different mass ratios of Co/ Ce were investigated using this method. The reaction conditions were kept the same as in Figure 2 (i.e., $T = 673$ K, Flow = 5400 mL h^{-1}). Catalysts with a relatively rich Ce component showed relatively low reactivity, for example, for the Co/Ce ratio of 2:3 and 1:2, the reactive factors were always less than 0.5, as illustrated in Figure 3. A comparison of the 1:1, 2:1, and 4:1 Co/Ce ratios showed that an excess of Co over Ce would be helpful in the SCR of NO. The catalyst with the support composition of Co/Ce = 2:1 and Co/H−ZSM5 = 2.5% (mass ratio) has shown remarkable activity; its reactive factor, R, was $\leq$0.78.

In the same manner, a series of catalysts with different mass ratios of Ce to In supported by H−ZSM5 were investigated. Indium (In) ws one of the few elements able to activate the relatively inert methane reductant. It has been extensively studied as an active component in zeolite systems.[18−20] The most notable property of indium zeolite catalysts was, however, their favorable response to promotion by a third component (e.g., noble metals,[21] Fe_2O_3,[22] cobalt,[23] or CeO_2).[24] Promoted In zeolites have been reported to achieve excellent NO conversions in dry feed with both methane and short alkane reductants, and the poisoning effect of water, which was rather strong with unpromoted catalysts, was significantly diminished and almost absent at a temperature of 800 K.[18] It was necessary to find some promoted In zeolite catalysts with considerably high reactivity in the SCR of NO by methane. Our initial results were illustrated in Figure 4. In Figure 4, the results of catalysts with Ce/In mass ratio of 1:1 supported by pure HZSM5 and 1:1 HZSM5/ Al_2O_3 were also given for comparison of activity variation. For the series with the HZSM5/Al_2O_3 mass ratio of 1:1, the reactive factors were about 0.6, which showed no clear dependence on the Ce concentrations. For the series with 2:3 Ce/In mass ratio, the reactive factors were always lower than 0.2. The series of catalysts with 1:1 Ce/In mass ratio on HSZM5 showed a clear dependence of the reactive factors on the Ce concentrations. The catalyst with s 2.0% In component, supported by HZSM5, with a Ce/In mass ration of 1:1, had the highest activity, about 0.88.

As in all the other optical techniques, the direct UV absorption spectroscopy using a broadband light source was an interesting tool to assess minority species. It was thought to be the simplest tool to achieve qualitative (and possibly quantitative) time-resolved NO diagnostics.[25] The Beer−Lambert law was usually satisfactory, provided that a thorough understanding of its limitations was taken into consideration. These limitations were the result of the effects of temperature, wavelength, or analyte-surroundings interactions. Because of these limitations, the Beer−Lambert law usually applied only to low concentrations, where these interactions were insignificant. Therefore, quantitative evaluation of NO concentration in selective catalytic reduction might be not accurate enough. However, under fixed conditions (particles, shape, size, refractive index, wavelength of radiation), the loss in radiation intensity still could be related to variation of NO concentration. The primary purpose of present investigation was to demonstrate the viability of combinatorial approach for the discovery and optimization of selective NO reduction catalysts.

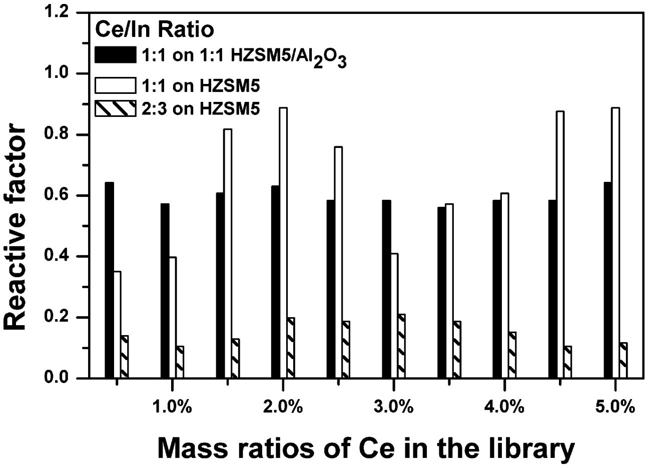

Figure 4. Reactive factors of different mass ratios of Ce/In on H−ZSM5.

Conclusions

In summary, a high-throughput quantitative screening system for rare earth catalyst libraries in the SCR of NO by methane has been developed on the basis of scanning multichannel UV absorption. The 24-channel microreactor system was experimentally proven to be reliable for the selection of heterogeneous catalysts of SCR of NO by methane under conventional fixed-bed reaction conditions. Rare earth component catalysts suitable for the SCR of NO by methane were prepared by a combination of non-platinum group metals known for their activity as single-component supported catalysts. For these three elements, a systematic combination resulted in an 80-member catalyst library, which was investigated for the catalytic performance by high-throughput testing facilities in a short time. In the library, the reactivity of the catalyst with the support composition of Ce/In = 1:1 and Ce/H−ZSM5 = 2.0% was $\leq$88%. To achieve further improvement of the deNOx activity, other promising rare components, for example, gallium (Ga), can be mixed into this library. Although the conversion efficiencies of NO by methane in our experiments were still lower than those of a Pt-based catalyst, the method in this report exhibited its potential for application in this field. Compared with other current primary screening techniques, such as IR spectroscopy, REMPI, LIFI, and multistream mass spectrometry, this setup showed convenience and applicability for the selection of other heterogeneous catalysts, merely by changing the detection wavelength.

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