High-Throughput Screening of Heterogeneous Catalysts by Laser-Induced Fluorescence Imaging

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Catalytic gas processing is a multimillion dollar concern in the chemical industry. A minor increase in the yield, a minor decrease in undesirable byproducts, the creation of novel products, or an extension of the lifetime of the catalyst are all urgent issues. An efficient approach toward understanding these complex systems is through combinatorial assays. In situ screening of these arrays under continuous flow in a microreactor system will quickly reveal the best combination of catalyst and reaction conditions.

The power of combinatorial chemistry is apparent in medicinal chemistry research.[1] It is also developing rapidly into an attractive alternative to the traditional discovery process of heterogeneous catalysts. Combinatorial synthetic techniques based on gas-phase deposition and liquid dosing[2] allow us to prepare a large number of potential catalytic materials in a high-throughput fashion. Recently high-throughput screening methods by IR thermography,[3−5] laser-induced resonance-enhanced multiphoton ionization,[6] microprobe sampling mass spectrometry,[7] and fluorescence indicators[8,9] have been reported. In the present paper, we introduce laser-induced fluorescence imaging (LIFI) as an alternative for high-throughput in situ screening of heterogeneous catalysts with micrometer-scale spatial resolution and millisecond temporal resolution. This scheme is based on the fact that the creation or destruction of chemical bonds alters the fluorescence properties of suitably designed molecules. By irradiating the region immediately above the catalytic surface (within 100 mm) with a laser, the fluorescence intensity of a selected product or reactant can be imaged by a charge-coupled device (CCD) camera to follow the catalytic activity as a function of time and space. Unlike thermography,[3−5] the fluorescence signal is specific and the response is linear. Interferences from variations in surface composition and the associated material emissivity are also absent. Secondary reactions do not contribute to the signal. Even thermoneutral reactions can be followed. Using this technique, dense arrays of catalyst formulations can be screened simultaneously to provide rapid access to the optimal combination of conditions.

We monitored the catalytic activity of vanadium pentoxide in the oxidation of naphthalene to naphthoquinone by oxygen, which is an important industrial process. With 488-nm excitation, naphthoquinone fluoresces while naphthalene and the other major product, phthalic anhydride, do not fluoresce. The reaction is carried out at 330−370 °C in a flow cell shown in Figure 1.

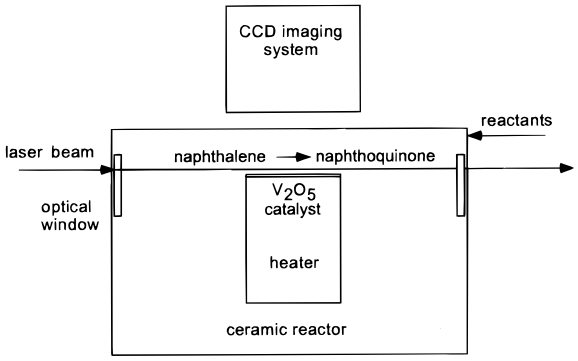

Figure 1. Experimental arrangement for in situ spatial and temporal measurements of catalytic activity. The laser beam (300 mW) is focused into a sheet parallel to the surface to excite the product molecules such that the recorded fluorescence intensity reflects the local reaction rate.

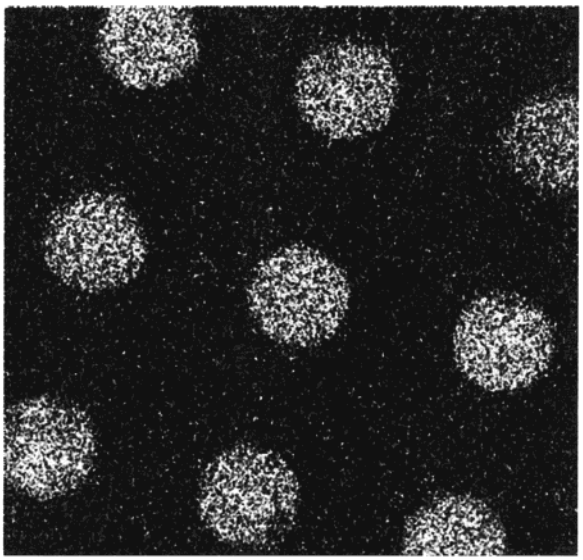

Figure 2. Fluorescence imaging of reaction products on top of an array of V_2O_5 wells that are each 400 μm in diameter, 400 μm deep, and with 400-μm spacing in between.

Fluorescence emission at 515−545 nm is collected by a cooled scientific CCD camera.

To evaluate the spatial resolution of LIFI, we used a 4× microscope objective to image a 2 mm × 2 mm area (Figure 2) with 3 s exposure time. In this array, 400-μm diameter wells that are 400 μm deep are created on a stainless steel plate with 400-μm spacing between them. No naphthoquinone fluorescence was detected above the V_2O_5 surface until oxygen gas carrying 7% naphthalene is introduced into the reactor. Therefore, background signal can be recorded in the absence of the reactants and subtracted from each subsequent image. On comparing the optical image of the catalyst and the fluorescence image, a 20-μm shift in the flow direction can be observed. These experiments demonstrate that LIFI has good detection performance and the spatial and temporal resolution needed for high-throughput screening of heterogeneous catalysts. The sample packing density can therefore reach 250 × 250 subunits/cm^2 for 40-μm wells.

In a larger format, a 3 × 2 library that contained 6 identical V_2O_5 sample dots was prepared by pipetting 20-μg V_2O_5-cyclohexane slurry solution into small wells (2 mm wide and 0.5 mm deep with 2-mm spacing) on a stainless steel disk and dried in air. A camera lens instead of the microscope objective was used to image the 17 mm × 17 mm area. The variation in

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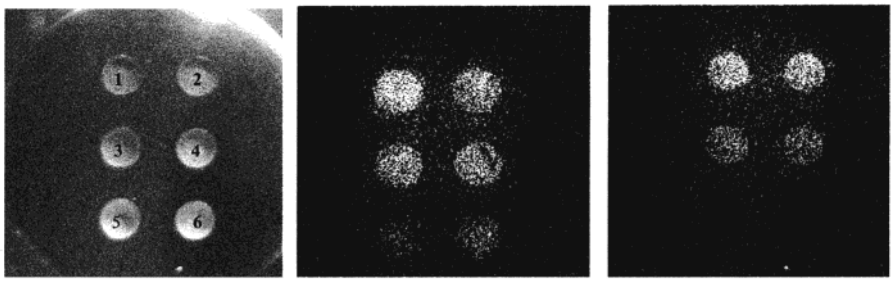

Figure 3. Catalytic screening by fluorescence imaging. (a) Optical image of six 2-mm diameter wells with 2-mm spacing between each containing different catalysts. (b) Fluorescence image of naphthoquinone produced above each well of vanadium pentoxide for (1) 60 mg, (2) 50 mg, (3) 40 mg, (4) 30 mg, (5) 10 mg, and (6) 20 mg. (c) Fluorescence image of naphthoquinone produced above each well for 50 mg of 1 and 2 - pure vanadium pentoxide, 3 and 4 - 1:1 vanadium and titanium oxides, and 5 and 6 - pure titanium oxide.

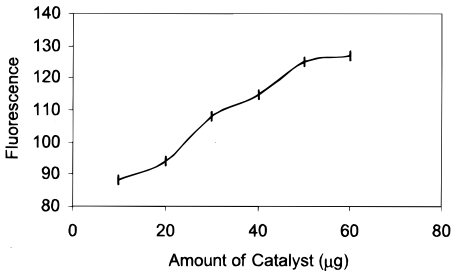

Figure 4. Fluorescence intensity (activity) as a function of the amount of catalyst in each well in Figure 3b.

fluorescence among the wells is 1.1%. Detection of minor differences in catalytic activity is thus feasible.

The 3 × 2 library was then constructed with six sample dots with different amounts of V_2O_5 (10 mg, 20 mg, 30 mg, 40 mg, 50 mg, and 60 mg), as shown in Figure 3a. In situ fluorescence images of this library are shown in Figure 3b. The relationship between catalytic activity (proportional to fluorescence intensity) and the amount of catalyst (Figure 4) is not linear because catalytic activity is proportional to the available surface area, not the mass of the catalyst. At low amounts, there is residual contribution from the background of laser scatter and thermal emission. Then, the intensity increases because the surface area increases linearly with the amount present. As a thick layer is formed in the well, material buried at the bottom of the wells is shielded and no further increase in surface area is effected. This occurs at 50 μg per well according to Figure 4. When adapted to 40-μm wells, the amount of material need for screening will be 20 ng each.

We used LIFI to test a simple 3 × 2 binary library, as shown in Figure 3c. Samples 1 and 2 are pure V_2O_5, samples 3 and 4 are 1:1 TiO_2 and V_2O_5 mixtures, and samples 5 and 6 are pure TiO_2. Figure 3c indicates that TiO_2 does not catalyze the oxidation reaction, and also neither promotes nor suppresses the catalytic activity of V_2O_5.

We studied the difference between LIFI and IR thermography in the array shown in Figure 2. The CCD camera is sensitive to radiation down to around 1000 nm. This is sufficient to record the short-wavelength tail of the blackbody radiation from the source because of the low dark count and low read noise of the camera. At 330 °C, only fluorescence can be observed by this camera. At and above 350 °C, however, signal can be detected in the wells that is above the background levels outside the wells, even in the absence of laser irradiation. This is near-IR emission from the catalytic material resulting from the exothermicity of the reaction, that is, IR thermography. A spectral profile characteristic of blackbody radiaton is confirmed by placing short-pass filters in front of the camera at successively longer and longer wavelengths between 800 and 1000 nm.

For studies conducted between 330 and 370 °C, the lower temperature favors S/N for LIFI while the higher temperature favors S/N for thermography. The spatial resolution of thermography is limited only by the pixel resolution of the imaging system while that of LIFI is further limited by the 20-μm flow distortion. In this setup, both sets of information can be obtained, for example, by chopping the laser radiation or by alternating transmission filters between the visible and the near-IR wavelengths. We note that CCD thermography is only useful at the high temperatures when blackbody emission begins to reach the responsive region of the device. When it does, the combination of nonspecific temperature increase (thermography) and species-specific concentration maps (LIFI) can offer unique insights into the catalytic process. Naturally, LIFI is only applicable to fluorescent species. The catalytic system here happens to involve highly fluorescent species. However, it should be possible to design model reactants for just about any catalytic reaction so that either the reactant or the product fluoresces on the breaking or making of the bond of interest.

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