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High-Throughput Screening Using Fourier-Transform Infrared Imaging

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ABSTRACT Efficient parallel screening of combinatorial libraries is one of the most challenging aspects of the high-throughput (HT) heterogeneous catalysis workflow. Today, a number of methods have been used in HT catalyst studies, including various optical, mass-spectrometry, and gas-chromatography techniques. Of these, rapid-scanning Fourier-transform infrared (FTIR) imaging is one of the fastest and most versatile screening techniques. Here, the new design of the 16-channel HT reactor is presented and test results for its accuracy and reproducibility are shown. The performance of the system was evaluated through the oxidation of CO over commercial Pd/Al_2O_3 and cobalt oxide nanoparticles synthesized with different reducer-reductant molar ratios, surfactant types, metal and surfactant concentrations, synthesis temperatures, and ramp rates.

KEYWORDS high-throughput, FTIR imaging, screening, cobalt oxide, CO oxidation

1 Introduction

Catalysis has had a tremendous impact on the chemical industry over the last century. It has been estimated that 90% of chemicals are derived from catalytic processes [1] and about 90% of these processes include heterogeneous catalysis [2]. Despite the large number of catalytic processes, the discovery and deployment of advanced materials from laboratory to application often take a considerable amount of time, typically requiring 10–20 years, and often relying on trial and error [3].

High-throughput experimentation (HTE) has been shown to accelerate the discovery and development of new catalyst formulations and routes for desired products, while optimizing reaction conditions. Since the early 1980s, HTE methodologies have been shown to improve the success of research and development (R&D) through the rapid synthesis and screening of large material libraries [4–9]. HTE methodologies are capable of generating large datasets and populating material properties and catalytic activities. However, existing HTE methodologies suffer from the lack of a widespread adaptation of standards for materials synthesis, characterization, and data management. In 2011, the Materials Genome Initiative (MGI) was launched by the US government to accelerate the discovery, development, and deployment of advanced materials, while reducing the cost of R&D [10]. In order to enhance the adaptation of standards and to positively impact material discovery and commercialization, one of the objectives of the MGI is to facilitate the sharing of HTE tools. This is done by creating a searchable online database for large library sizes and establishing HTE centers with on-site synthesis, screening, and characterization capabilities [10].

Generating a common high-throughput (HT) database requires the effective implementation of combinatorial workflows consisting of experimental design, material synthesis, material characterization, and data collection processes [11]. The Dow Chemical Company, for example, has successfully implemented HT workflow through several automated syntheses, testing units, and HT characterization tools. In a recent study, they have shown that over 1000 catalysts were synthesized and tested for their activity in propane oxidative dehydrogenation [4]. The data obtained from each workflow step is stored in a single database in order to effectively screen materials and speed up the development process, which fits well with the objective of the MGI [4]. In addition to the establishment of an effective combinatorial workflow, successful catalyst evaluation can be divided into a series of steps that include a primary screening to discover promising materials for the application of interest; a secondary, more detailed investigation of the selected materials from the primary screening; and subsequent scaling-up and commercial testing [5]. Previously in our group, HT screening methodologies were successfully applied to identify novel catalyst formulations for the catalytic cracking of military jet fuel (JP-8) to liquefied petroleum gas. The approach combined a rapid, qualitative primary optical screen via thin-film techniques,

a series of quantitative screens using milligrams of powder catalysts, and a final verification of the best samples using a single-sample reactor [12].

Although HTE methodologies have been effectively used to screen catalyst formulations, the implementation of combinatorial approaches to the development of heterogeneous catalysis remains a challenge due to the dynamic nature of the catalyst material. The performance of a catalyst typically depends on many parameters associated with its structure, composition, synthesis conditions, and deactivation, as well as the binding strength of reactants and products of interest [12–15]. The optimization of this parameter space could involve up to 3 000 000 parallel runs [9], which is not possible to complete even using state-of-the-art HTE methodologies. Both stochastic and deterministic methods have been proposed in order to reduce the size of the catalyst library and decipher the quantitative relationship between parameter space and catalyst activity. Of these methods, the most commonly used in HT analysis include design of experiments (DOE), artificial neural networks, and genetic algorithms. The details of these methods and their successful implementation to the HTE are described elsewhere [7, 16–22].

The challenges associated with the dynamic nature of the catalyst and the large parameter space of catalyst libraries can be overcome by developing sophisticated HT screening tools that can predict catalytic activity rapidly and accurately. Successful development of these tools often depends on the design of parallel reactors, reaction conditions, and the capability of analysis equipment. To date, most HT screening tools rely on optical, mass-spectrometric, and chromatographic techniques [9, 13, 23–25]. In the following section, the details of several of these techniques are discussed briefly. In addition, the Fourier-transform infrared (FTIR) imaging developed in our group is described and compared with state-of-the-art HT screening tools.

2 Brief overview of methodologies for the screening of heterogeneous catalysis

Optical screening techniques in HTE include infrared (IR) thermography, cataluminescence (CTL), laser-induced fluorescence imaging (LIFI), resonance-enhanced multiphoton ionization (REMPI), and FTIR. Early studies have applied IR thermography to determine catalyst activity based on the radiation energy emitted by the catalyst surface. Radiation energy is highly sensitive to the temperature on the catalyst surface, such that small temperature variations can be picked up by the detector. IR thermography therefore allows the catalytic activity of an exothermic reaction to be quickly screened. For example, Olong et al. have used emissivity-corrected IR thermography to screen catalysts for low-temperature soot oxidation [26]. The relative heats of the oxidation reactions of up to 207 catalysts were analyzed in parallel. Due to the unpredictability of intimate contact between soot and a catalyst, the accuracy of the data obtained in the HT analysis was validated by conventional techniques such as thermal gravimetric analysis (TGA). The results indicate that the combination of Cu, Ce, Ag, and Co catalysts has the

best performance for low-temperature soot oxidation in both the HT and conventional experiments [26]. Despite the fast response time of IR thermography in the preliminary screening of catalytic activities, the chemical composition of the products formed during the reaction cannot be determined, which inhibits a wide applicability of the technique [24–31].

Like IR thermography, CTL has been applied to screen exothermic reactions, such as the catalytic oxidation of combustible gases [32]. The mechanism of CTL relies on detecting the chemiluminescence emissions of a combustion reaction occurring on a catalyst surface. The CTL intensity can be correlated with the catalyst activity [33]. Na et al. adapted CTL-based array imaging to monitor the CO oxidation activity of Au- and Pt-supported TiO_2 catalysts. One of the major advantages of CTL is that it can simultaneously provide a fast response time and evaluate the activity of catalysts at the temperature of interest. However, because the CTL responses of each catalyst are not known, the catalytic activity of metallic or bimetallic catalysts must be calibrated based on a second analysis technique such as gas chromatography (GC) or mass spectrometry (MS) [32].

LIFI is another optical technique that has been applied to HT catalyst screening. The principle of LIFI relies on the destruction or creation of chemical bonds that modify the florescence properties of the molecule. As the Ar^+ laser sheet irradiates the area above the catalyst, the change in the fluorescence intensity of products and unreacted species over the catalyst is detected by a charge-coupled device (CCD) camera, which can provide both IR thermography and florescence detection. Unlike IR thermography, the florescence intensity of species is linearly correlated and could provide information about the relative activity change of a particular reaction. Su et al. have employed LIFI and IR thermography in the HT screening of binary vanadia-based catalysts for naphthalene oxidation. They have shown that a library consisting of 15 catalysts can be screened *in situ* in 15 s. Due to their nature, only fluorescent species can be detected using LIFI. In addition, the signal-to-noise ratio (SNR) is inversely proportional to temperature due to increased blackbody emissions at high temperatures [34, 35].

While the aforementioned optical techniques utilize truly parallel HT approaches, REMPI spectroscopy has been used in HTE in a sequential manner using automation approaches [13, 36, 37]. In REMPI, a tunable ultraviolet (UV) laser beam is used to ionize reaction products, which are detected through an array of microelectrodes. This technique allows the researcher to analyze polyatomic molecules and radicals, and to distinguish isomers *in situ* in the parts-per-billion range. One of the drawbacks of this technique is that the suitable laser frequency for many molecules is unknown, limiting the applicability of this technique to catalyst screening [36, 37]. Senkan and Ozturk combined REMPI with microchannel array reactors to screen the dehydrogenation of cyclohexane to benzene [37]. In total, 66 ternary combinations of Pt, Pd, and In supported on alumina were tested in less than 5 h.

MS is a well-developed methodology that can be applied to HT screening in order to analyze complex gas mixtures in a sequential manner. Cong et al. utilized MS to investigate