

A versatile and compact experimental apparatus for the on-line spectroscopic study of liquid-phase heterogeneous catalytic systems

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Abstract

A versatile and compact experimental system is described for the study of fine-chemistry liquid-phase heterogeneous catalysis. The general experimental system consists of a stirred tank (25–100 mL), pump, tubular reactor, spectrometer(s), and injection block for liquid-phase perturbations, all in a closed-recycling configuration. The basic designs of the in-house-constructed components are provided. The system was characterized with respect to gas–liquid mass transfer, mixing, liquid–solid mass transfer, and intraparticle diffusion. The utility of the system is demonstrated with a heterogeneous catalytic reaction—the racemic hydrogenation of acetophenone over $\text{Pt}/\text{Al}_2\text{O}_3$ —using on-line Fourier transform infrared (FTIR) analytics. Liquid–solid mass transfer and intraparticle diffusion were studied by varying the liquid hourly space velocity (LHSV) as well as the catalyst particle sizes used. The reaction rates based on the instantaneous reagent concentrations were precisely evaluated using on-line FTIR measurements. The rather novel inclusion of an injection/sampling block was particularly useful for performing multiple perturbations of reagents, a situation neither normally available nor convenient for the experimentalist, thus facilitating outstanding spectral deconvolution using band-target entropy minimization. The small total liquid-phase volume involved (≈ 15 ml) would facilitate the frugal use of chiral reagents/auxiliaries as well as isotopically labeled components.

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1. Introduction

In the chemical sciences, the use of on-line or even in situ spectroscopic measurements, in contrast to off-line and ex situ measurements, is becoming more common. Indeed, the advantages of this approach can be great. This is already quite evident in the field of homogeneous catalysis, where in situ spectroscopic measurements under industrially relevant reaction conditions are becoming rather common [1]. Instantaneous concentrations of both intermediates and reagents can be measured, exact turnover frequencies can be obtained, and a detailed mechanistic understanding can be achieved [2]. In heterogeneous catalysis, in situ spectroscopic characterization of the solid catalysts under industrially relevant reaction conditions is usually restricted to extended X-ray absorption fine structure/X-ray absorption near edge structure [3,4], Mössbauer

spectroscopy [5], Fourier transform infrared (FTIR)/diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy [6–8], Raman spectroscopy [9], ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy [10], and magic angle spinning–nuclear magnetic resonance [11]. On-line spectroscopic measurement of the associated fluid phase to determine the products and accurate kinetics has received considerably less attention. Because most heterogeneous catalytic fine-chemical syntheses are conducted in a liquid phase as a solid–liquid suspension (slurry) or occasionally in a packed bed, there exists considerable opportunities to combine various types of technical know how to achieve useful on-line spectroscopic measurements of the fluid-phase alone.

There are some important hardware considerations for on-line spectroscopic studies of liquid-phase fine-chemical heterogeneous catalytic systems. First, the experimental system benefits from a recycle configuration, to minimize the quantities of chemicals used. Second, both packed-bed and gas–liquid stirred tank are needed for maximum experimental flexibility.

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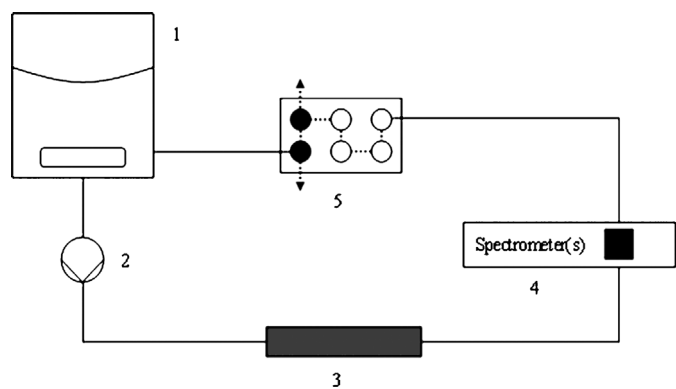


Fig. 1. General schematic diagram of a recycle system applicable to small-volume fine-chemical heterogeneous catalytic liquid-phase reactions. Components: (1) stirred tank, (2) pump, (3) packed bed, (4) spectrometer(s), (5) injection/sampling block (open symbols are six-way HPLC injection valves, closed symbols are six-way HPLC sampling valves).

The stirred tank provides a gas buffer in the event that a gaseous reagent is used. Third, the system must have a device for reliably changing/perturbing the fluid compositions during the course of the experimental run. Such a device could be a series of high performance liquid chromatography (HPLC) rotary valves. A schematic diagram of such an experimental system, including a pump for recirculation and a spectroscopic cell, is shown in Fig. 1.

The use of a general experimental system such as that shown in Fig. 1 for reliable kinetic studies entails a number of considerations. These include characterization of the system in the absence of reaction, that is, (i) gas–liquid mass transfer for the stirred tank and (ii) mixing and recycle residence time distribution in the entire system, as well as characterization of the system in the presence of reaction to confirm (iii) negligible liquid–solid transport resistance, (iv) negligible intraparticle diffusion resistance, and (v) differential conversion over the packed bed. The latter is important to provide complete uniformity of concentration and temperature throughout the catalyst bed [12].

Perhaps most important, classical methods of off-line analysis are intrinsically ill suited for system identification. On-line measurements are far more appropriate than sampling [13]. The general experimental setup shown in Fig. 1 allows not only on-line FTIR measurements, but also a few nonobvious opportunities for system identification. First, because of the convenient multiple-valve injection/sampling block, the system can be readily used in semibatch mode (even under high internal pressures), allowing very extensive experimental designs and resulting in coverage of a very wide range of reaction conditions in a single run [14]. Second, extensive experimental designs consisting of multiple perturbations permit the application of very advanced signal deconvolution programs, like band-target entropy minimization (BTEM), to the very large sets of spectroscopic data [15–17]. The injection/sampling block shown in Fig. 1 was designed to facilitate such multiple perturbations and meet the prerequisites for successful deconvolution. Finally, the aforementioned two issues combined can facilitate the rapid and reliable determination of the algebraic structure of the cat-

alytic network [18], and then the detailed kinetics [19], at least in homogeneous catalytic systems.

Briefly, it should be noted that BTEM is essentially a soft-modeling approach to obtaining the pure component spectra of species without any a priori information. The experimentalist does not need to know or estimate the number of species present in advance. Moreover, no presuppositions are needed concerning the particular type of spectral characteristics present, that is, whether the spectral bands follow a Lorentzian, Gaussian, Pearson, or other distribution. It is recognized that copious spectroscopic data, obtained from a large number of perturbations, helps to untangle spectroscopic signals, because spectral co-linearities are more readily avoided and greater signal variation can be obtained. Thus BTEM has been repeatedly used to identify new and nonisolatable species and transient intermediates.

In the present contribution, an experimental system similar to Fig. 1 is presented, including details of the components designed and constructed in-house and its tests for on-line heterogeneous catalytic spectroscopic measurements of the fluid phase. The selected reaction is the racemic hydrogenation of acetophenone over Pt/Al₂O₃. This reaction was selected because hydrogenation—specifically, enantioselective hydrogenation—is a topic of constant academic interest and considerable economic importance to the agrochemical, fine-chemical, and pharmaceutical industries [20]. Although the present example of racemic hydrogenation of acetophenone over Pt/Al₂O₃ is not stereo-specific, it does allude to its modified form and hence to the intensely studied Orito reaction [21–27] and extensions to more sophisticated on-line/off-line spectroscopies, including circular dichroism measurements [28]. Finally, by keeping the experimental system simple and hence cost-effective, the experimentalist is able to reserve entire setups for different catalytic systems, thereby avoiding the problem of cross-contamination between catalytic experiments.

2. Experimental

2.1. General issues

The catalyst used in this study is a commercial product, Engelhard 4759 (5% Pt/Al₂O₃), with the following catalyst properties: mean particle size, 55 μm; BET, 140 m²/g; mean pore radius, 50 Å; real density, 5.0 g/mL; platinum loading, 4.65%; platinum dispersion, 0.28; apparent density, 1.9 g/mL. The catalyst was pretreated in a fixed-bed reactor by flushing with 3–4 L/h N₂ (99.9%) at room temperature for 10 h, followed by a reduction treatment in H₂ at 400 °C for 120 min. After cooling to room temperature in H₂, the catalyst was immediately transferred to a Schlenk tube and kept under argon.

Toluene (Mallinckrodt; 99.9%) was distilled from sodium–potassium alloy under purified argon for around 5 h to remove the trace water and oxygen. Acetophenone (Aceph; Aldrich, 99%) and 1-phenylethanol (Phel; Acros organics, 98%) were mixed and shaken with anhydrous 4 Å molecular sieves to remove trace water and oxygen.

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