On-line Spectroscopic Studies and Kinetic Measurements of Liquid-Phase Heterogeneous Catalytic Systems

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Abstract

A versatile and compact experimental apparatus for the on-line spectroscopic study of liquid- phase catalytic systems was designed and characterized with respect to gas-liquid mass transfer, liquid-solid mass transfer and intra-particle diffusion. The utility of the system was demonstrated by two semi-batch differential heterogeneous catalytic reactions in d_8-toluene/h_8-toluene, the racemic hydrogenation of acetophenone (Aceph) and 2-butanone over Pt/Al_2O_3. The use of very sensitive on-line FTIR measurements and multivariate analysis techniques to obtain spectral data lead to the following observations: (i) solvent activation during reaction leads to observable hydrogenation and H-D exchange in both catalytic systems; (ii) very interesting short time-scale behavior occurred after some perturbations; and (iii) water had a strong inhibiting effect on the hydrogenation rates. The second observation included rapid initial hydrogenation of Aceph on the fresh catalyst and observable unusual spectral changes caused by hydrogen bonding between water and 2-butanone. A Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was used to fit the kinetic data of acetophenone hydrogenation to 1-phenylethanol (Phel) in h_8-toluene, at 0 ^oC and near 1 bar hydrogen pressure, with the effects of water and solvent included. A model involving a pair-wise addition of adsorbed dissociated hydrogen to the adsorbed substrate provided the best fit of the data. The regression of the kinetic data suggested that there was a statistically significant contribution of water to the competitive adsorption on the catalyst surface. In general, the present contribution suggests the utility of on-line liquid-phase spectroscopy together with multivariate techniques for exploratory studies of heterogeneous catalytic systems.

Introduction

In the chemical sciences, it is becoming more common to use on-line/in-situ spectroscopic measurements, instead of off-line/ex-situ measurements. Indeed, the advantages are quite evident in the field of homogeneous catalysis. In-situ spectroscopic measurements of the liquid phase were used to measure the instantaneous concentrations of both intermediates and reagents, to obtain exact turnover frequencies and to understand the detailed reaction mechanism [1-2]. In contrast, on-line spectroscopic measurements of the associated fluid-phase in heterogeneous catalysis, in order to determine the products and accurate kinetics, have received considerably less attention. The present contribution addresses the design, characterization and utility of an experimental apparatus suitable for the on-line spectroscopic study of the liquid phase of heterogeneous catalytic systems.

The designed experimental setup allows not only on-line FTIR measurements but also a few non-obvious opportunities for system identification. First, the catalytic reactions can be performed in semibatch mode due to the multiple sampling/injection block. This allows very extensive experimental designs to be carried out, resulting in a very wide range of reaction conditions to be covered in one run [3]. Secondly, experimental designs consisting of multiple perturbations permit the application of band-target entropy minimization (BTEM) and two-band-target entropy minimization (tBTEM) to analyze the spectroscopic data [4-6]. Finally, with on-line FTIR measurements, concentrations of solutes could be measured quickly and with high precision, and the instantaneous reaction rates could be evaluated very accurately. These aspects greatly improve the quality and reliability of the kinetic data which facilitate the least squares fitting of LHHW models as well as comparisons among models [7-8].

Results and Discussion

Experimental apparatus

The experimental apparatus consists of a stirred tank (25-100 ml), a pump, a tubular reactor, spectrometer(s), and an injection block for liquid-phase perturbations, all in a closed recycle configuration. A photo of such an experimental system is shown in Fig. 1.The system was characterized with respect to gas-liquid mass transfer, mixing, liquid-solid mass transfer and intra-particle diffusion [7].

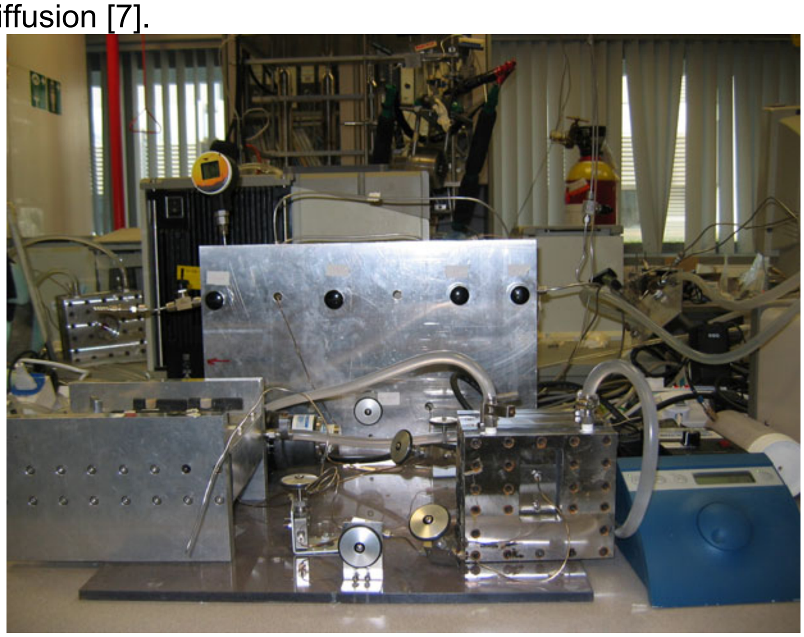

Fig. 1. A photo of a recycle system applicable to the liquid-phase heterogeneous catalytic reactions.

Solvent activation

Observable hydrogenation and H-D exchange of solvent occurred in both catalytic systems. This observation was confirmed by a separate catalytic experiment with only d_8-toluene, H_2 and Pt/Al_2O_3 in a Schlenk tube. A strong broad vibration at 2903 cm^{-1} was deconvoluted via the application of BTEM in both catalytic systems and Schlenk experiment. A significant fragment at 106 m/z and the appearance of the fragments at close to 100 m/z (caused by d_8-toluene) and 106 m/z (caused by d_8-h_6 methylcyclohexane) provided GC-MS evidence.

Rapid initial hydrogenation of acetophenone on the fresh and hydrogen rich catalyst

1-phenylethanol (Phel), cyclohexyl methyl ketone (CMK) and cyclohexylethanol (Che) were observable products for acetophenone hydrogenation over Pt/Al_2O_3 under current reaction conditions. But the initial hydrogenation rate of Aceph on the fresh and hydrogen rich catalyst was unusually high. Within 10 minutes, ca. 2.2×10^{-5} moles of Phel and ca. 4.5×10^{-6} moles of cyclohexyl methyl ketone (CMK) were formed after the injection of ca. 1.7×10^{-4} moles of Aceph. During the next 10 minutes, only ca. 1×10^{-5} moles of Phel and ca. 2×10^{-6} moles of CMK were formed.

Ca. 0.02g catalyst was used, the surface platinum sites were ca. 1.3×10^{-6} moles and the surface sites on the support surface were ca. 4.3×10^{-5} moles. If these numbers are compared to the sum of Phel and CMK (ca. 2.7×10^{-5} moles) formed quickly after the first Aceph perturbation, it seems that spillover hydrogen was involved in the initial product formation.

Spectral changes caused by hydrogen bonding between 2-butanone and water

After each substrate perturbation the spectral absorbance of substrate (2-butanone) underwent an expected step increase, but then increased slowly for some time. As an illustration, the 25th, 35th and 45th experimental spectrum in the representative hydrogenation experiment at 2.07 bar hydrogen partial pressure was subtracted by the 14th experimental spectrum which was right after the first substrate perturbation. The resulting spectra are shown in Fig. 2. From this figure it can be seen that after each substrate perturbation the spectral absorbance of substrate (2-butanone) did indeed increase slowly after an expected step increase.

After water perturbation the spectral absorbance of substrate (2-butanone) underwent unexpected and definite step increases. As an illustration, the 454th, 455th and 456th experimental spectrum in three regions, namely 1300-1350, 1590-1750 and 2800-4000 cm^{-1}, was subtracted by the 453th experimental spectrum which was right before the water perturbation. The resulting spectra are shown in Fig. 3.

The same phenomena were observed after each perturbation of water in perturbation experiment with the presence of the catalyst and in the absence of hydrogen. The real absorbance of 2-butanone underwent unexpected and definite step increases after water perturbation. The observation of this phenomenon was made possible, to a significant degree, by the very sensitive on-line FTIR measurements and slow dissolution of water into anhydrous d_8-toluene. The changes in the experiment spectra were caused by hydrogen bond between 2-butanone and water.

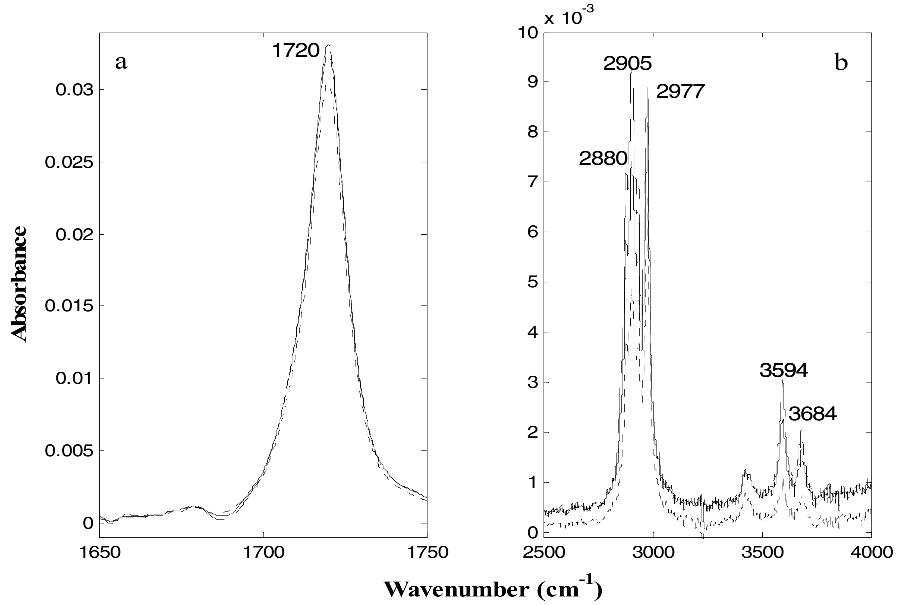

Fig. 2. Resulting spectra of the 25th, 35th and 45th experimental spectra subtracted by 14th experimental spectrum in hydrogenation experiment at ca. 2.07 bar hydrogen pressure.

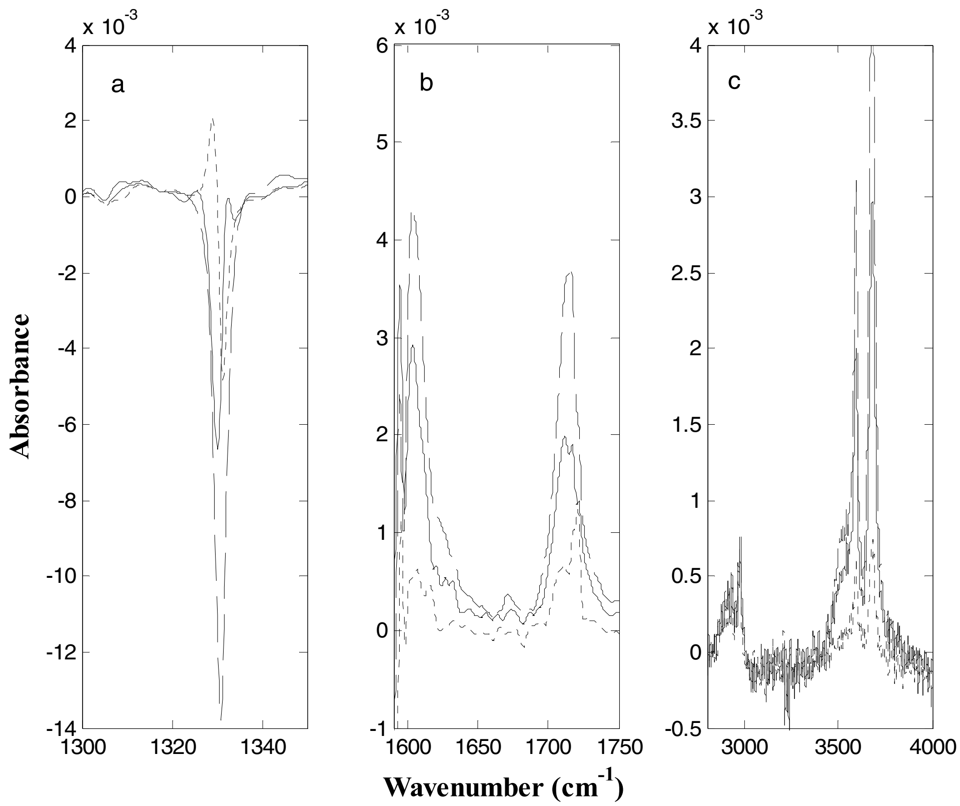

Fig. 3. Experimental subtracted spectra after the first water perturbation in hydrogenation experiment performed at 2.07 bar hydrogen pressure.

Kinetic study of acetophenone hydrogenation in h_8-toluene and proposed reaction mechanism

Concentrations of different species and reaction rates obtained from six well defined experiments in h_8-toluene were fit to a number of Langmuir-Hinshelwood-Hougen-Watson (LHHW) models where the effects of solvent and water were included. A model with a pair-wise addition of adsorbed dissociated hydrogen to the adsorbed substrate provided the best fit of the data.

The elementary steps for Aceph hydrogenation to Phel on Pt/Al_2O_3 at 0 ^oC and low hydrogen partial pressures were also proposed. The model included the competitive adsorption of substrate, water, Phel and solvent on the same active sites, dissociate adsorption of hydrogen, and pair-wise irreversible addition of dissociated hydrogen to adsorbed substrate. The surface reaction was the rate limiting step (RDS).

Effect of water on heterogeneous catalytic systems

For the acetophenone hydrogenation system, the injection of water into the reaction system resulted in a decrease in the rates of catalytic hydrogenation. The marked effect of water on the reaction rates is clearly due to the magnitude of the adsorption equilibrium constant on platinum for water ($K_{water}>K_{aceph}\approx K_{phel}>>K_{toluene}$). Therefore, there was a statistically significant contribution of water to the competitive adsorption on the catalyst surface.

For the 2-butanone hydrogenation system, water was not only involved in the competitive adsorption on the catalyst surface but also involved in the complicated interactions with the species presented in the catalytic system. Due to the existence of hydrogen bonding with water, after each substrate perturbation the spectral absorbance of substrate (2-butanone) underwent an expected step increase, but then increased slowly for some time.

The water effects have important implications for the study of liquid-phase heterogeneous catalysis. They suggest that non-traditional anhydrous experiments should be implemented when possible, especially for kinetic and reaction mechanism study.

References

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