

Kinetics of a catalytic hydrogenation reaction

Introduction

Catalytic hydrogenation forms the basis of many important industrial processes. Common processes are the hydrogenation of olefins, aromatics and various unsaturated compounds, and the catalytic reduction of nitro groups to the corresponding amino compounds. Examples include the production of margarine from vegetable oils, and the production of aromatic amines from the corresponding nitro-benzenes. The latter reaction is important in the synthesis and production of a wide range of chemicals, intermediates and products, ranging from dyes and pigments to pharmaceutical products.

Many nitro-reduction reactions are performed in the presence of a heterogeneous catalyst. In the selection of a suitable catalyst, it is important to be able to maximize the yield in the reaction while minimizing the possibility for side reactions. An understanding of the kinetics of the reaction is important in order to detect the presence of any intermediates. Certain intermediates are undesirable because they may result in hazardous reaction conditions and/or they may yield undesirable side reactions. The order of the kinetics can help indicate the presence of intermediates. Also, the overall kinetics can indicate the rate determining steps, an important factor where side reactions are involved. Such studies assist in the selection of the optimum catalyst for the reaction.

An appropriate monitoring system is required for this type of a kinetics study in order to obtain the maximum amount of information on the species involved in the reaction. Ideally, this is obtained in real time, and at a rate complementary to the speed of the reaction. Fourier transform infrared (FTIR) has been considered for such reactions, and in certain cases it has been successful. However, infrared measurements often exhibit difficulties

associated with sampling and spectral interferences from solvents, especially with polar media. Raman spectroscopy offers distinct advantages in both areas. The technique may be interfaced to the reaction via fiber optics, with either an immersion probe or a non-invasive external probe, and the Raman spectra of many frequently used solvents are relatively weak compared to their IR spectra. The benefits of Raman spectroscopy for the study of reaction kinetics are discussed below.

Experimental

The current reaction involves the reduction of ortho-chloronitrobenzene with hydrogen, at atmospheric pressure, in methanol with a platinum/carbon catalyst to form ortho-chloroaniline. The reaction is known to follow one of two pathways shown in Figure 1.

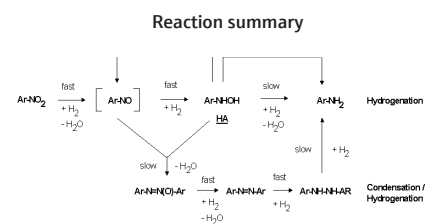


Figure 1: Two reaction pathways for the reduction of ortho-chloronitrobenzene with hydrogen in methanol with a platinum/carbon catalyst to form ortho-chloroaniline

At elevated pH, the reaction can be shown using chemometrics to follow the upper route, with the two intermediates predicted for the condensation/hydrogenation not being present. In this study, the impact of a vanadate-based catalyst can be demonstrated, where the reaction order changes, and where the formation of the predicted hydroxylamine intermediate no longer occurs.

Results

The Raman measurements described in this application were obtained with a Raman Rxn2 analyzer from Endress+Hauser, powered by Kaiser Raman technology. This system provides a non-invasive method for studying the

Benefits at a glance

- *In situ* measurements can be taken in the presence of heterogeneous catalysts
- Measurements are not affected by solvent interferences
- Chemical reactions can be monitored by non-invasive means through the walls of a glass reactor or a sight glass
- Raman probes can be coupled to the spectrometer over large distances using fiber optic cables
- Spectral information may be acquired throughout the entire vibrational spectrum, even down to low wavenumbers

reaction. Example spectral data are presented in Figure 2, with a three-dimensional representation providing the spectral changes that occur over the timespan of the reaction for ortho-chloronitrobenzene. The consumption of reactants is observed by reduction in Raman band intensities in the progression of spectra from front to back.

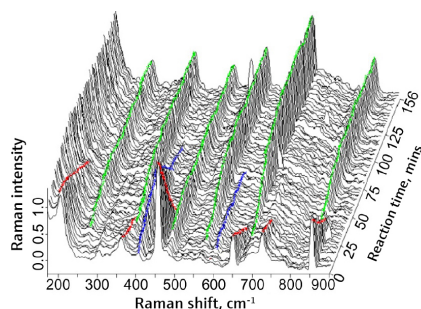


Figure 2: Three-dimensional representation of changes occurring during reduction of the nitro entity

A study of the standard reaction system, involving the platinum/carbon catalyst, indicates the formation of the hydroxylamine intermediate, as predicted in the reaction summary. The introduction of the vanadate catalyst into the system provides an increase in the reaction rate, and the results of the Raman monitoring indicate a change from second order to zero order. This change is denoted by the absence of the hydroxylamine intermediate, and is supported by a fit of the measured reaction rates to those predicted for a zero order reaction. A comparison of the observed kinetics for the current study is presented in Figure 3.

Discussion

Reaction monitoring experiments can be performed by FTIR, but a significant degree of interference is experienced from the solvent, methanol. Subtraction of the solvent spectrum is necessary before the spectral information from the reaction products can be extracted. This is undesirable because as the reaction proceeds, the interactions between the solvent and the reaction products change, making it difficult to achieve a complete subtraction of the solvent bands. Residuals and artifacts remain in the reactor spectra after subtraction, and these can interfere with the interpretation of the data.

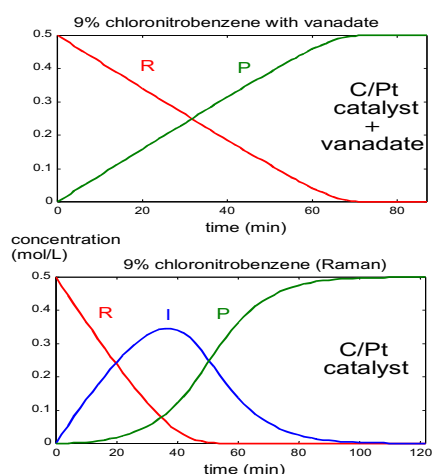


Figure 3: Reaction kinetics for the hydrogenation of ortho-chloronitrobenzene by carbon/platinum catalyst in methanol, with and without the presence of vanadate

Sampling is a problem with FTIR, because the choice of optical window materials is limited. For example, it is impossible to view a reaction through a glass reactor because the material is opaque for most of the mid-infrared region. Although immersion probes exist, interfacing to the main spectrometer is constrained, either by optical limitations of mid-infrared optical fibers or by the use of physically cumbersome optical conduits. Raman spectroscopy does not suffer from these inconveniences since the lasers used for sample illumination readily transmit through glass. When used in conjunction with a Raman Rxn2 or Raman Rxn4 analyzer, Endress+Hauser's Rxn-10 probe with a non-contact optic permits the monitoring of a chemical reaction through the walls of a glass reactor or a sight glass. These may be coupled to the spectrometer over large distances via standard silica-based optical fibers, allowing Raman measurement over a wide spectral range, even down to low wavenumbers.

Acknowledgement: application information provided by Solvias.