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Advanced Nonsteady-State Method for Reaction Rate/Concentration Analysis: Ammonia Decomposition Example

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Highlights

- Nonsteady-state experimental method for calculating rate/concentration dependencies.
- CoFe decomposition catalysts are discriminated in transient rate/concentration space.
- Reaction rate governed by industrial catalysts described as a function of gas and surface composition.

1. Introduction

Nonsteady-state experimental methods are particularly useful for providing detailed understanding of how catalytic surfaces control complex multistep reaction mechanisms. A reaction network of optimal complexity must adequately represent the observed kinetic behavior with as few *a priori* assumptions as possible. Herein we focus on the Temporal Analysis of Products (TAP) experimental methodology [1] which provides high quality nonsteady-state kinetic data for reactions governed by complex, multicomponent industrial catalysts. An efficient method for decoupling diffusion/reaction phenomena and extracting values of the nonsteady-state chemical transformation rate is described. Using the so-called *Y-Procedure* analysis methodology [2], the concentration and reaction rate can be determined without any presumption regarding the type of kinetic dependence; a 'model free' approach.

The analysis of rate/concentration dependencies for ammonia decomposition to N_2 and H_2 is described over a series of bimetallic CoFe catalysts. The stoichiometric relationships between NH_3, N_2 and H_2 are examined in the course of reaction. Concentrations of surface intermediates have been estimated based on "uptake-release" combinations together with the total amount of the catalytic active sites. Consequently, the skeleton mechanism of ammonia decomposition reaction is presented, and intrinsic kinetic coefficients (distinguished by gas and surface concentration) are estimated as well.

2. Methods

Catalyst were prepared by adding different amounts of cobalt (II) nitrate hexahydrate dissolved in water to a polycrystalline α-Fe powder to yield nominal compositions of 0, 0.25, 0.5, 0.75, 1 monolayers. The materials were reduced in H_2 for 17 hours at 450 °C and transferred to the TAP reactor system in a thin zone configuration without exposure to ambient conditions. Ammonia decomposition experiments were performed at 550 °C by pulsing a NH_3/Argon and monitoring the exit flux time dependencies of ammonia, argon, nitrogen and hydrogen. Experimental data was analyzed using the Y-procedure inverse-diffusion method to calculate reaction rate and both gas and surface concentration in the catalyst bed as a function of time. Mathematically, the Y-procedure consists of the following steps:

1) An exact solution of the reaction/diffusion equations in the Laplace domain,
2) Switching to the Fourier domain to allow efficient computation,
3) Introduction to discretization and filtering in the Fourier domain to operate with real data in the time domain subject to noise.

3. Results and discussion

Time-dependent reaction rate data shown in Figure 1 demonstrate NH_3 decomposition and N_2 generation proceed in the same reaction step while the production of H_2 is a distinct reaction step. In all cases materials were observed to convert ammonia to N_2 and H_2 with progressive accumulation of N species on the surface. With increasing cobalt content the rate of ammonia decomposition is observed to accelerate at lower ammonia gas concentrations. The production of N_2 likewise shifts towards lower gas concentrations but the rate is suppressed. The rate of H_2 production presents a first order dependence with respect to NH_3 concentration while a second order dependence is observed with respect to the N^* surface concentration. The concentration of surface intermediates are estimated based on 'uptake/release' combinations. The data presented in Figure 1 demonstrates the utility of the Y-Procedure analysis to observe the evolution of the hydrogen production rate with both gas and surface concentrations. Nonlinear kinetic dependencies are observed as the surface coverage changes during the gas pulse: at the same gas concentration two distinct rates are observed, one at high surface coverage early in the pulse response and a lower rate at corresponding low surface coverage later in the pulse.

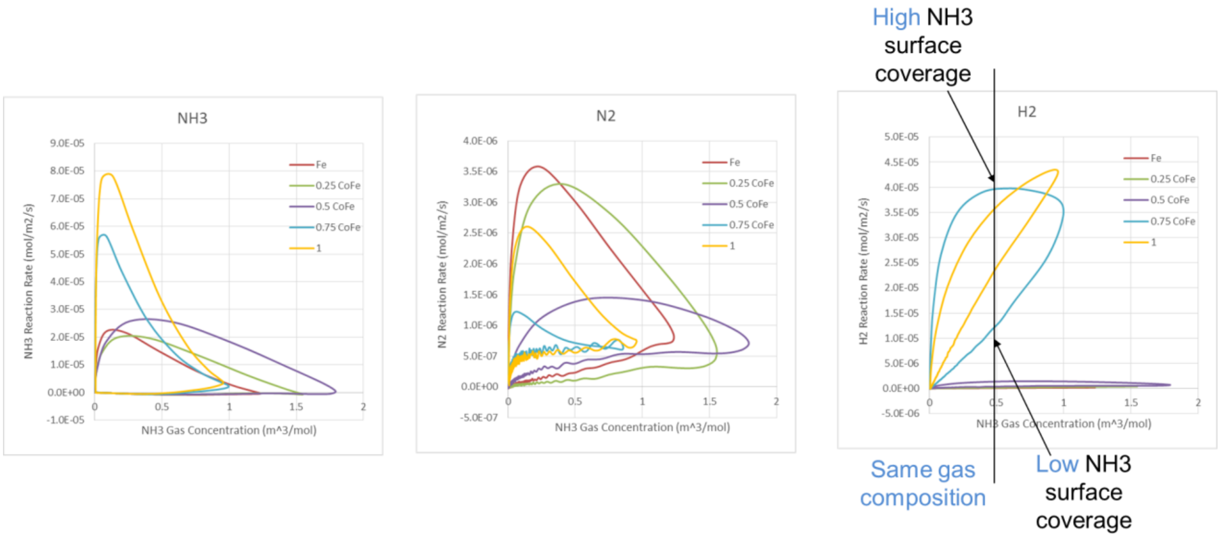

Figure 1. Rate data for NH_3 conversion, N_2 and H_2 production as a function of the NH_3 gas concentration as the surface coverage changes during the transient pulse response experiment for different bimetallic CoFe compositions.

4. Conclusions

The Y-Procedure approach to nonsteady-state reaction data provides researchers with a unique set of kinetic dependencies without presupposition of model. For any gas, the exit flow dependences obtained via thin-zone TAP pulse response experiments are transformed into three non-steady state characteristics: gas concentration, rate of change and uptake/release which can be used for estimating the surface storage of different gases. In the analysis of NH_3 decomposition stoichiometric relationships were observed between NH_3 and N_2 but not for H_2. Consequently, these H_2 participates in a distinct reaction step. From this data a skeleton mechanism of the ammonia decomposition reaction is presented and intrinsic kinetic coefficients are estimated as well.

References

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Keywords

Transient kinetic; ammonia decomposition; TAP reactor; heterogeneous catalysis.