Rapid Kinetic Measurements in Ammonia and Methanol Syntheses

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Kinetic measurements in heterogeneous catalysis are essential for the derivation of rate expressions that are necessary for the design of reactors and that can serve for data extrapolation beyond the measured data range. To accelerate the acquisition of kinetic data, the method of quasi-isothermal temperature-programming has been applied to a study of the kinetics of the ammonia and methanol syntheses. Both reactions were performed in a microcatalytic reactor setup near industrial reaction conditions. For the ammonia synthesis, the technique turned out to be a useful screening method for Ru-based catalysts, which allowed power-law rate expressions to be derived rapidly. Moreover, the in situ temperature-programmed surface reaction of N\(_2\) with gas-phase H\(_2\) (N\(_2\)-TPSR) was studied in detail, allowing for its application as a fast method for catalyst screening within the class of unpromoted Ru-based catalysts. However, in the methanol synthesis, the applicability of the quasi-isothermal temperature-programmed method is limited to qualitative catalyst screening because of the methanol adsorbing capacity and the slow change of the state of the working Cu/ZnO/Al\(_2\)O\(_3\) catalyst.

Introduction

The improvement of ammonia and methanol synthesis catalysts has an important economic impact because of their large-scale industrial use. Two ways to achieve improved state-of-the-art catalysts can be considered: either fundamental research aiming at a deeper understanding of the working catalyst, which involves in situ and kinetic studies, or trial-and-error-based testing of catalysts. In pioneering research at BASF, Mittasch\(^1\) studied more than 8000 compositions in a combinatorial-like way of testing catalysts for ammonia synthesis. To date, more than 100 000 other formulations have been investigated, but the multipromoted iron catalyst, still used today, turned out to be the best commercial catalyst for the Haber process. However, 60 years later at BP, about 500 Ru-based catalysts were tested in a set of laboratory-scale screening reactors and high-pressure pilot plants. Finally, Tennison et al.\(^2\) developed ruthenium-on-graphite copromoted with barium and cesium into a commercial alternative catalyst, which is now used in the reduced-energy Kellogg Advanced Ammonia Process (KAAP).\(^3,4\) Based on the fundamental academic work of the groups led by Aika, Ertl, Muhler, and Kowalczyk in the last three decades, a fundamental and comprehensive study has recently been performed, providing new insights into the ammonia synthesis catalyzed by ruthenium (see ref 5 and references therein).

In 1966, ICI introduced a low-pressure, low-temperature version of the methanol synthesis process with a new class of catalysts: a copper/zinc oxide/alumina (Cu/ZnO/Al\(_2\)O\(_3\)) catalyst that is now widely used in a variety of compositions.\(^6\) Although the process has been successfully commercialized, an inspection of the literature reveals that open questions still remain regarding the nature of the active sites, the state of the copper in the working catalyst, and the effect of ZnO in methanol synthesis.

In recent years, the combinatorial approach has also been applied in heterogeneous catalysis as a means of finding new classes of catalyst compositions for improved activity and selectivity.\(^7\) The application of high-throughput synthesis and screening techniques leads to a large number of catalysts. Because measurement time is limited and often just one set of standard operating conditions is applied, the need for rapid kinetic data acquisition close to industrial conditions and over a broad parametric range arises. Furthermore, from an industrial point of view, a detailed kinetic study is considered to be more reliable for extrapolation beyond the measured kinetics when the data are obtained in laboratory-scale reactors near industrial reaction conditions in a classical way.

The temperature-scanning reaction method and technology developed and patented by Wojciechowski and co-workers has been applied in recent studies as a promising possibility for performing kinetic experiments more conveniently and rapidly.\(^8\)–\(^11\) This method involves ramping the input temperature to a reactor and recording the composition of the effluent gas and the bed temperature without waiting for isothermal steady state to be established. As a result, reaction rates can be derived directly from the measured concentrations in the effluent with the assumption of an appropriate reactor model.

The present work was undertaken to study the applicability of the quasi-isothermal temperature-programmed mode for collecting kinetic data more rapidly under industrially relevant reaction conditions in order to obtain a reliable kinetic database and provide experimental guidelines for the usage of this method in catalyst screening.

Experimental Section

Catalyst Preparation. Magnesia-supported ruthenium catalysts (Ru/MgO) were prepared from ultrapure