

In Situ MRI Studies of Catalyst Deactivation in a Trickle-Bed Reactor

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Introduction

Catalyst deactivation due to coke deposition continues to be the subject of much research effort. In particular, there is a need to be able to characterize changes in catalyst activity and selectivity, simultaneously with monitoring the chemical nature of the coke formed. If these measurements can be made *in situ* and non-invasively within a working reactor, it will become possible to understand the conditions which determine the chemical composition of coke and how this, in turn, influences catalyst performance. To date, such measurements have not been possible. This paper reports the implementation of two magnetic resonance (MR) techniques which enable us to do this. Further, because the MR measurements are spatially resolved, it is possible to map how catalyst performance and coke characteristics vary spatially within the reactor.

In this work, we utilize two MR techniques to study the spatial variation in chemical conversion and the chemical nature of the coke formed during a *trans*-3-pentenitrile hydrogenation reaction occurring within a trickle-bed reactor, as a function of time-on-stream (TOS). ^{13}C -DEPT MRI [1] is used to map chemical composition within the reactor. The methodology of Bonardet *et al.* [2] is used to characterize coke aromaticity. In this approach the spin-spin relaxation constant (T_2) of adsorbed probe molecules is measured; the more aromatic the coke, the shorter the T_2 [2]. Here, we use the liquid phase species within the reaction mixture as the probe molecules.

Materials and Methods

Pre-reduced 1.05 wt% Pd/Al₂O₃ catalyst trilobes were loaded into a cylindrical glass reactor, which was placed inside a Bruker Biospin DMX 200 vertical magnet. Continuous flows of 20 vol% H₂/N₂ and *trans*-3-pentenitrile were passed into the reactor at flow rates of 88 (1 barg) and 0.5 ml min⁻¹, respectively. During the 8 h reaction period, a set of two MRI experiments were performed at regular time intervals: One-dimensional (1D) ^{13}C DEPT MRI was implemented to map the chemical composition of the liquid along the direction of the flow (z -direction), and 1D CPMG (Carr-Purcell-Meiboom-Gill) profiles were taken to map ^1H T_2 of the liquid phase within the intraparticle space of the catalyst, and hence the aromaticity of the coke with which it interacts, at the same spatial locations.

Results and Discussion

Valeronitrile is the major product of hydrogenation of *trans*-3-pentenitrile, and is spectrally resolved from pentenenitrile in the ^{13}C NMR spectra, hence the yield of valeronitrile is calculated directly from the acquired spectra; Figure 1a shows these data for 4 spatial locations along the length of the bed. At any TOS, a gradual conversion from pentenenitrile to

valeronitrile along the reactor is observed. At all 4 positions within the reactor, the conversion of valeronitrile first increases to a maximum value as a function of TOS, then decreases due to catalyst deactivation. The maximum occurs at later times as distance increases from the reactor entrance, suggesting that the catalyst at the entrance of the reactor deactivates faster than that towards the exit. Figure 1b shows the intraparticle T_2 measurements at the same spatial positions as shown in Figure 1a. A decrease of T_2 with increasing TOS is observed at all positions within the reactor, indicating that the aromaticity of the coke increases as a function of time. At any TOS, T_2 near the entrance to the catalyst packing is lower than that near the exit, suggesting coke formed near the entrance is more aromatic, an observation consistent with more rapid deactivation at the entrance of the reactor.

Significance

For the first time, MRI techniques have been used to study the change in conversion due to catalyst deactivation and to characterize the chemical nature of the coke as a function of space and time *in situ* within a working trickle-bed reactor. In related work, we have used MR to image flow within such reactors. Thus, this work demonstrates that we have now developed a new and effective toolkit for characterizing flow, chemical conversion and coke formation in a continuous flow reactor.

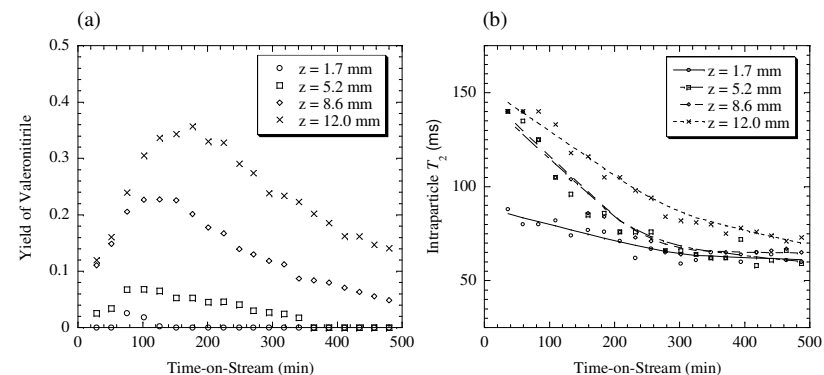


Figure 1. (a) Spatially resolved yield of valeronitrile as a function of time-on-stream, measured using quantitative 1D ^{13}C DEPT MRI. (b) ^1H T_2 of liquid at each spatial position as a function of time-on-stream, measured using 1D CPMG profiles. $z = 1.7$ and 12.0 mm define the locations along the length of the reactor at the entrance to the catalyst packing and just before the exit from the packing, respectively.

References

1. Sederman, A.J., Mantle, M.D., Dunckley, C.P., Huang, Z. and Gladden, L.F. *Catal Lett* 103, 1 (2005).
2. Bonardet, J.L., Domeniconi, T., N'Gokoli-Kekele, P., Springuel-Huet, M.A. and Fraissard, J. *Langmuir* 15, 5836 (1999).