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Synchrotron X-ray microprobe and computed microtomography for characterization of nanocatalysts

K.W. Jones [a,*], H. Feng [b], A. Lanzirotti [c], D. Mahajan [d,e]

[a] *Laboratory for Earth and Environmental Sciences, Building 901A, Brookhaven National Laboratory, Upton, NY 11973, USA*
[b] *Montclair State University, Montclair, NJ 07043, USA*
[c] *Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, USA*
[d] *Energy Sciences and Technology Department, Brookhaven National Laboratory, Upton, NY 11973, USA*
[e] *Materials Sciences and Engineering Department, Stony Brook University, Stony Brook, NY 11794, USA*

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Abstract

Gas-to-liquids (GTL) is a viable pathway for synthesis of clean fuels from natural gas. One of the attractive synthesis options is the Fischer–Tropsch (F–T) method using an iron catalyst to yield a broad range of hydrocarbons. We collected catalyst samples during three separate F–T runs that utilized nanophase (mean particle diameter (MPD): 3 nm and 20–80 nm) and micrometer-sized (32.5 μm) Fe_2O_3 that served as catalyst precursors. The collected samples were characterized with micro-X-ray fluorescence and computed microtomography at the National Synchrotron Light Source (NSLS). Results found with two different measurement techniques indicated that there was heterogeneity on a spatial scale corresponding to volumes of roughly 10^3 μm^3.

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Keywords: Synchrotron X-ray microprobe; Computed Microtomography; Fischer–Tropsch; Catalysts; Hydrocarbons

1. Introduction

Gas-to-liquid fuel conversion (GTL) refers to processes in which natural gas is catalytically converted, in sequential steps, to clean fuels. Employment of natural gas or biogas starting materials can reduce reliance on petroleum fuels that are in short supply. When burned, clean fuels produce lower concentrations of aromatic compounds, particulate matter, SO_x and NO_x than conventional gasoline or diesel fuels and are thus more environmentally acceptable. They also have higher cetane

* Corresponding author. Tel.: +1 631 344 4588; fax: +1 631 344 5271.
E-mail address: jones@bnl.gov (K.W. Jones).

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numbers than petroleum derived diesel fuels and can therefore improve the performance of diesel engines.

Since the GTL pathway yields environmentally friendly fuels, it is likely that large-scale clean fuels production plants will be built in the near future. One such production method is based on the well-known Fischer–Tropsch (F–T), a catalyzed conversion of natural gas derived synthesis gas (primarily a mixture of carbon monoxide and hydrogen) to yield a mixture of hydrocarbon fuels (gasoline, diesel, waxes, etc.). The F–T catalyst can be selected from metals such as iron, cobalt and ruthenium depending very much on the nature of the desired product and the process economics. The present commercial F–T technology falls short of the ultimate atom economy that is needed and therefore, enhancing catalyst performance is of great importance. One possible avenue to explore is the effect of nanosizing the F–T catalyst (commercial catalyst is micrometer-sized). Nanosized catalysts are appealing since they can provide higher surface area, amorphous surfaces and more active reaction sites per unit area than larger particles of the same material.

The objectives of the present experiment were to establish the activity/catalyst-size relationship and to use the synchrotron X-ray technique to complement other spectroscopic techniques that have been previously employed to determine time resolved changes in catalyst composition, morphology, and state that accompany the F–T reaction. The synchrotron X-ray beams were used to determine if the catalysts are uniformly distributed in the product material or whether they form agglomerates, possibly as a result of their colloidal nature, that could effectively diminish the relative differences in surface area expected from the sizes of the catalyst particles. Other investigations on this topic have been reported by Jones et al. [1] and Mahajan et al. [2,3].

2. Experimental approach

We were interested in measuring the distribution of the catalysts in a waxy medium (by taking samples directly out of the F–T reactor) using X-ray fluorescence techniques. The applicability of the method for examination of nanosized catalysts is dependent on the mass to be measured compared to the spatial resolution of the X-ray microprobe and the escape depth of the X-rays measured. The mass of individual catalyst particles was calculated assuming a spherical shape and a density of 5.25 g/cm for Fe_2O_3. The values for the particle volume and the corresponding mass of Fe as a function of the particle diameter are shown in Fig. 1. Detection limits for Fe on the X26A beam line at the NSLS are about 1 fg with a beam diameter of about 10 μm under normal conditions at the NSLS. Thus, single particles with a diameter of around 70 nm will be detectable.

The amount of material analyzed depends on the analytical method employed. The simplest approach is to employ X-rays with energy just above the Fe K X-ray absorption edge to scan across a thick sample of the product material. The volume of material analyzed then is fixed by the size of the beam and the absorption of the incident X-rays and the emerging Fe K X-rays. The relative number of detected fluorescent X-rays for a wax with a CH_2 composition, density of 0.95 g/cm^3, and negligible amounts of $FeCH_2$ is given in Fig. 2 as a function of the depth in the sample at which the X-rays are produced. Summing these values shows that 90% of the observed X-rays are produced in a

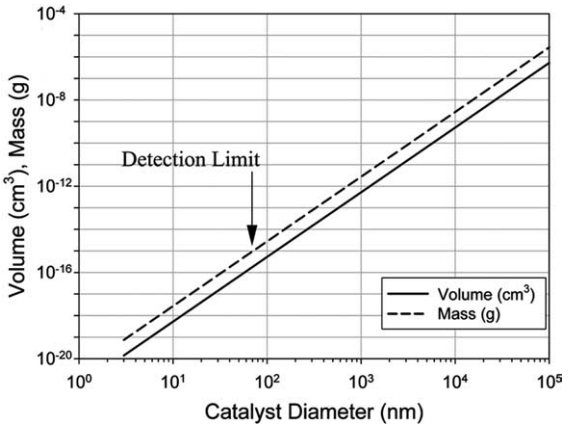

Fig. 1. The mass of the Fe content of a catalyst particle of Fe_2O_3 and its volume are shown as a function of the particle diameter. The arrow gives the single particle detection limit. Particles with a smaller diameter are not detected.