Water-gas shift reaction catalyst under synchrotron light

For most chemical reactions on an industrial scale, catalysts are used to reduce the energy barrier of the reactions. This can increase the reaction rate, give manufacturers selectivity regarding the reaction products or lower the reaction temperature.

The study of the structures and properties of catalysts as a means of improving them has largely been empirical. However, synchrotron radiation has made it possible to study their structure as a whole, which has helped companies to develop improved industrial products.

CHALLENGE

Haldor Topsøe is a Danish multinational chemical company specializing in the development and production of catalysts for the chemical, fertilizer and petroleum industries. For their research on new catalysts they frequently come to large-scale facilities like PETRA III at DESY, where they use the brilliant synchrotron radiation to gain a better understanding of the structure of catalysts and the interaction between their components.

In this exemplary case study, a catalyst for the water-gas shift reaction was examined. During the water-shift reaction, carbon monoxide (CO) and water (H_2O) react to form carbon dioxide (CO_2) and hydrogen (H_2): $CO + H_2O \rightleftharpoons CO_2 + H_2$. This reaction is widely used in the chemical industry to produce hydrogen, which is then involved in the production of other important substances like methanol or ammonia.

According to the International Energy Agency, the global demand for H_2 was over 70 megatons in 2018. The water-shift reaction is quite sensitive to the reaction temperature. Hydrogen formation is reduced at higher temperatures, which pairs well with the effect of a catalyst to lower the reaction temperature.The main component of the catalyst examined is magnetite (Fe_3O_4), an iron oxide mineral accompanied by smaller amounts of chromium for stabilization and copper to further enhance the reaction. The interaction of the components with the reactants and their local structure are key properties, which scientist would like to examine in order to improve the performance of the catalyst.

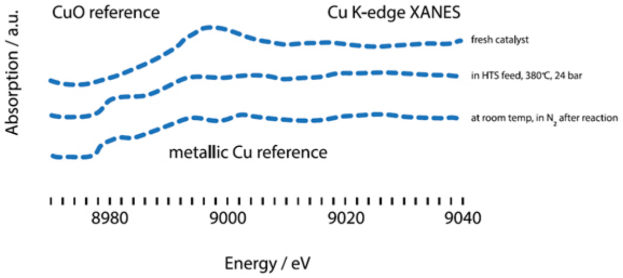

Figure 1: X-ray absorption spectra of the catalyst under three different conditions: Before the reaction, during the reaction, after post-reaction washing.

METHOD

The synchrotron radiation from PETRA III was used for X-ray absorption fine structure (XAFS) experiments to examine the catalyst under different conditions. The in-situ XAFS measurements were carried out at the Cu K-edge and Cr K-edge, exciting 1s electrons, the electrons closest to the nucleus, to valence bound states and resulting in characteristic peaks. First, the fresh catalyst was examined at 24 bar; second, the catalyst at 12 bar and 380 °C in feeding gas, a mixture of carbon monoxide, carbon dioxide, argon, hydrogen and water vapor; and lastly the catalyst after washing with nitrogen at 12 bar and room temperature.

INSIGHTS AND ANALYSIS

The brilliant synchrotron radiation from PETRA III helped to resolve the different energy states of copper during the catalysis, revealing important interactions between the catalyst's components. The good resolution of XAFS made it possible to distinguish between different oxidation levels of certain elements. The experiments showed how the nature of the Cu in the catalyst changed under varying conditions (compare Figure 1, the disappearing peak near 9000 eV in the uppermost line). Scientist were able to conclude that only metallic Cu and no copper oxide compounds are present during the catalytic process. Furthermore, the amount of Cu needed to promote the catalysis is quite small, ~ 1 wt %, and hence catalysis happens at Fe_3O_4 sites and is enhanced by metallic Cu. Aside from XAFS's ability to resolve elements in near energetic states, XAFS also provides information about the local structure and geometry of the samples of interest. As an example, chromium is present as Cr^{3+} in each condition, but upon exposure to the feeding gas and increasing temperature the local environment changed, leading to the assumption that Cr^{3+} migrates into the catalyst during the reaction.

BENEFITS

The synchrotron experiments at DESY helped Haldor Topsøe to identify the catalytic mechanism of their water-gas-shift reaction catalyst. The knowledge gained during the experiments ranged from oxidation states, to geometry and local environment, allowing conclusions to be drawn about the active species, the role of Cu and the movement of Cr ions during the reaction. The studies also helped to reduce the amount of precious Cu needed to achieve an effect, which could help to reduce production costs. With their new understanding, Haldor Topsøe is now ready to develop a better catalyst for one of most important reactions in industrial chemistry.

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