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Poster Abstract:

Cu/ZrO$_2$ catalysts for methanol steam reforming

F. Girgsdies, H. Purnama, A. Szizybalski, T. Ressler,
Department of Inorganic Chemistry, Fritz-Haber-Institut of the MPG,
Faradayweg 4-6, 14195 Berlin, Germany;
J.H. Schattka, Y. Wang, R.A. Caruso,
Colloid Department, Max-Planck-Institut für Kolloid- und Grenzflächenforschung,
Am Mühlenberg, Haus 2, 14476 Golm, Germany

The production of hydrogen by steam reforming of methanol is currently of great interest for the development of fuel-cell powered engines, especially for mobile applications. The majority of known catalysts for methanol steam reforming are based on copper combined with a variety of supports and additives. In addition to the more traditional Cu/ZnO catalyst,[1-3] Cu/ZrO$_2$ seems a promising candidate to learn more about the general mechanisms of this reaction. On the one hand, the morphology of the zirconia support may be controlled within certain limits by the use of various template techniques.[4, 5] On the other hand, the tendency of ZrO$_2$ to incorporate a wide range of metals (including copper) adds new challenges to the structural characterization of the catalyst.

The synthesis of the CuO/ZrO$_2$ samples involved the use of a polymer gel template, in this case an acrylamide/glycidyl methacrylate polymer formed in an aqueous Tween-60 solution. The gel was soaked in a propanol solution containing zirconium (IV) propoxide and copper(II) acetylacetonate. The impregnated gel was then placed into a 1:1 mixture of propanol/water and left overnight for hydrolysis of the metal complexes. The hybrid material was dried at room temperature, and then calcined at 450 °C under a nitrogen then oxygen atmosphere to remove the organic material. Samples with nominal copper loadings between 7.5 and 22.7 wt.-% were prepared.

A range of analytical techniques is employed to investigate the relationship between the structure of the catalyst and its reactivity, with special emphasis on the two complementary methods *in situ* X-ray diffraction (XRD) and *in situ* X-ray absorption spectroscopy (XAS) combined with on-line MS analysis. For kinetic studies a three channel plug flow reactor was constructed. The composition of the water/methanol feed delivered by means of a HPLC pump can be varied. The parallel design of three tubular reaction chambers (10 mm diameter, 100 mm length) inside an aluminum block allows to study three different catalysts simultaneously, saving time while ensuring exactly the same catalyst treatment.

Both XRD and XAS show that most or all of the zirconia support has crystallized in the tetragonal form, indicating the possibility of copper doping. However, when the catalyst is reduced the formation of copper metal is observed with XRD and XAS. The size of the copper crystallites is estimated to be in the order of 100 Å based on XRD peak profile broadening.

Surprisingly, *in situ* investigations on a 7.5 wt.-% Cu/ZrO_2 catalyst with XRD and XAS show only minor activity (< 0.2 vol.-% H_2) for methanol steam reforming after *in situ* reduction with hydrogen. However, the combination of a prolonged exposure to the steam reforming feed followed by an oxygen pulse into the reaction mixture results in substantial activity (> 1 vol.-% H_2). The addition of oxygen temporarily oxidizes the copper metal which then is re-reduced in the feed after the pulse.

The unusual behavior of the Cu/ZrO_2 system studied provides a unique chance to reveal structural differences in the catalyst before and after activation. Ultimately, this may lead to new insights into the relationship between structure and reactivity of copper based steam reforming catalysts.

References:

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