Towards direct production of CO-free hydrogen from methanol

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Methanol is at present one of the most promising chemical storage molecules for hydrogen to be used in fuel cell applications. One of the most pressing problems is, however, the reduction of the CO content of the steam reformate below the critical level of 50 ppm. We investigate the potential to achieve this goal in one step without having to use subsequent gas purification that significantly complicates the hydrogen generator for widespread application.

Thermodynamics predicts an equilibrium content of CO in the reformate in the order of 4%. This calls for drastic kinetic measures to significantly suppress this level of CO. In preliminary tests using a variety of the Cu/ZnO system it was found that under suitable kinetic conditions the CO level may indeed be suitably suppressed as the generation of CO occurs not in parallel but in a consecutive step to the reforming process. Under conditions avoiding this consecutive reaction, the activity of present catalysts is, however, too small to allow the preparation of a mobile reformer unit.

Consequences are the development of alternative reactor concepts to plug flow. Here microreactors and membrane reactors could be suitable choices. The alternative is the development of more active catalysts that further avoid the deactivation problems met with the Cu/ZnO system.

We report about studies to identify the nature of the active copper state as knowledge input for the development of new catalysts necessary for both strategies. It occurs that a special state of metallic copper is the active phase. It is electronically different from bulk copper as seen by NMR and transport properties. Its structure is a strained variety of bulk copper. To induce and preserve the strain the presence of oxygen and/or heteroatoms is essential.

This knowledge was put to test by activating the traditionally totally inactive Cu/ZrO_2 system for steam reforming. It was possible to devise a redox-based activation procedure for activating nanostructured Cu/ZrO_2 systems prepared by several methods of template-induced structuring.