

## The Role of Acid/Base Properties of NiO-MgO-ZrO<sub>2</sub> Catalysts for the Dry Reforming of Methane

J. Titus\*, M. Goepel\*, S. Schunk\*\*, N. Wilde\*, R. Gläser\*

\*Institute of Chemical Technology, Universität Leipzig, Germany

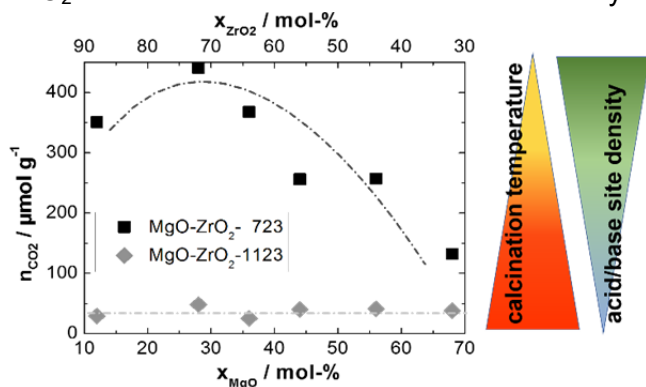
\*\*hte GmbH, Heidelberg, Germany

### Abstract

Synthesis gas is an industrially highly relevant feedstock. It can be produced via dry reforming of methane (DRM), although this route is not yet applicable on an industrial scale. Since DRM allows the conversion of CO<sub>2</sub> and CH<sub>4</sub>, it is an ecologically interesting process, especially if CO<sub>2</sub> is available, e.g., from off-gases. However, a major drawback of DRM over supported metal catalysts is the thermodynamically favored carbon formation resulting in catalyst deactivation. Several strategies are applied to overcome this problem, e.g., integration of the active metal within the catalysts structure or the application of dopants. Basic supports or modifiers promise reduced carbon depositions by enhancing the CO<sub>2</sub>-dissociation.

Here, we combined two strategies. Within NiO-MgO-ZrO<sub>2</sub>-catalysts, Ni was incorporated as a NiO-MgO solid solution to provide a high Ni-dispersion, while MgO should supply additional basic sites. NiO-MgO-ZrO<sub>2</sub> catalysts were investigated in DRM under ambient pressure at 1123 K. For comparison, the NiO-free MgO-ZrO<sub>2</sub> supports were studied regarding their acid/base site density and strength by TPD-NH<sub>3</sub> and -CO<sub>2</sub>.

Catalysts with a Ni- and Mg-content of 8-20 mol-% were most active with CH<sub>4</sub>- and CO<sub>2</sub>-conversions near the thermodynamic equilibrium, while the carbon deposition was negligibly low. Therefore, it was assumed that within this range of Ni- and Mg-contents, a balance between active phase and available basic sites was most suitable for DRM. Nevertheless, a further investigation of NiO-MgO-ZrO<sub>2</sub>, calcined at 1123 K revealed no direct correlation between the basic site density ( $n_{\text{CO}_2}$ ) and the MgO-content. Further, the ZrO<sub>2</sub>-content did not affect the acid site density. Besides NiO-MgO-ZrO<sub>2</sub>, pure MgO-ZrO<sub>2</sub> was



**Figure 1:** Basic site density from TPD-CO<sub>2</sub> ( $n_{\text{CO}_2}$ ) as a function of the MgO- and ZrO<sub>2</sub>-content for MgO-ZrO<sub>2</sub> calcined at 723 K or 1123 K, respectively.

investigated by TPD. As can be seen in Figure 1,  $n_{\text{CO}_2}$  is only affected by the MgO-content, if the material is calcined at 723 K. After calcination at 1123 K, which is closer to the DRM application, the basic site density is largely reduced and independent of the MgO-content. Thus, the basic properties of MgO cannot be made responsible for improved methane conversion in DRM. Rather a high Ni dispersion, a favorable Ni-MgO interaction or a stabilization of the desired tetragonal ZrO<sub>2</sub> phase have to be considered.