

Figure 1. Comparison of data collected with the shaker mill at ID15 and our ball mill setup at MS beamline

Keywords: Mechanochemistry, in situ technique

MS36-O4 Hindered reduction of NiO on Al containing carriers studied by *in situ*

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Steam reforming of natural gas using Ni-based catalysts is an important process in production of synthesis gas and hydrogen. Activation of the catalyst is carried out by reducing NiO to Ni in a mixture of steam and hydrogen (or hydrocarbons) from as low as 450°C. Full reduction and stability are vital for optimal performance and lifetime of the catalyst system. A detailed understanding of the reduction process is therefore of great importance in relation to plant operation.

To better understand this process, reduction behavior of NiO supported on industrial-like steam reforming carriers was studied under wet reduction conditions (1% H₂ + 3% H₂O, in He) using *in situ* X-ray diffraction (XRD), temperature programmed reduction (TPR) and scanning transmission electron microscopy (STEM) mapping.

It is found that the interaction of NiO with the support greatly influences the reduction behavior. When free MgO is in the carrier, it will react with Ni²⁺ during impregnation and calcination to form a Ni_{1-x}Mg_xO solid solution, which results in increasingly high reduction temperatures with increased Mg content.

Increased reduction temperatures are also observed when the calcination temperature during preparation is increased. In this case, the higher reduction temperatures are caused by migration of Al-species from the support to the surface of the NiO particles during calcination.

Calcination at 850°C results in NiO particles completely covered by Al-species, forming a thin (<3nm) protective surface spinel, resulting in reduction temperatures above 700°C. Based on the observed data, it is proposed that Al-species are mobile during calcination already at 450°C. Formation of the protective surface spinel seems to be a general feature for Al-containing carriers as similar reduction behavior is observed on both MgAl₂O₄, calcium aluminate, and α -Al₂O₃ carriers.[1]

[1] Lundegaard, L. F., Tiruvalam, R. R., Tyrsted, C., Carlsson, A., Morales-Cano, F., and Ovesen, C. V. *Catalysis Today*, 2015, available online, article in press. (doi:10.1016/j.cattod.2015.08.055)

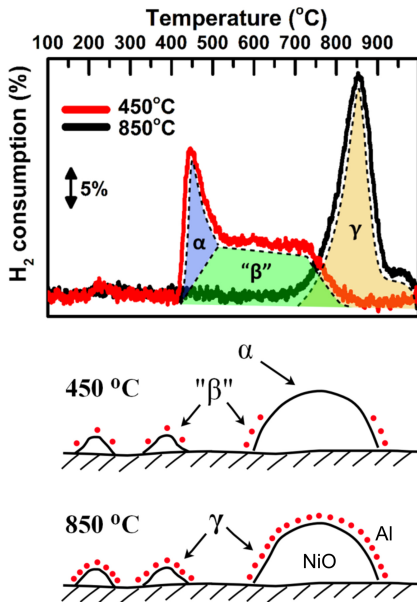


Figure 1. TPR results on Ni/MgAl₂O₄ catalysts calcined at 450°C (red curve) and 850°C (black curve). The mechanism resulting in the different contributions (α , " β " and γ) is proposed below.

Keywords: NiO reduction, Al migration, in situ XRD

MS36-O5 *In situ* diffraction studies during transition metal catalysis

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Transition metal compounds are nowadays tested as substituents for noble metal catalysts. Ammonia is an excellent hydrogen carrier and the decomposition of ammonia would be an elegant way to generate hydrogen for fuel cell applications without formation of CO_x. The most active catalyst so far is Ru on carbon nanotubes, but bimetallic compounds or metal nitrides are also under investigation as potential catalysts for ammonia decomposition. Noble metals are rather expensive and limited in availability. In contrast, metal nitrides are much cheaper and easy to prepare by the nitridation of metal oxides. In this work we study different transition metal catalysts during the decomposition of ammonia. Starting from transition metal oxides, the catalyst formation was studied by *in situ* X-ray diffraction under reaction conditions. Crystallographic studies with respect to phase changes, crystal structure variations, and microstructure properties have been performed [1,2]. The behavior under reaction conditions and the catalytic activity can significantly differ for each catalyst system: while some transition metal oxides reduce during the reaction with ammonia to the metals, others form nitrides after reduction. Changes of the chemical composition associated with structure changes as well as alterations of the microstructure properties of the catalyst in terms of domains size or defect variations may influence the catalytic activity. So far, iron oxides and cobalt alumina spinels were investigated as precursors for ammonia decomposition. In case of iron oxides nitrides are formed during the reaction with ammonia while for cobalt oxides metals form after activation [3,4]. Molybdenum-based catalysts are a very good example that various factors govern activity. Structure changes as well as changes of specific surface areas, and defect concentrations have to be considered [1,2]. In this work we also present studies on the use of bimetallic catalysts (Fe-Co, Fe-Ni) for ammonia decomposition. The formation of metal nitrides, metals and/or alloys during the reactions is monitored by *in situ* XRD using in-house laboratory instruments. The structural changes and detailed reaction pathways were studied by the evaluation of the diffraction data.

[1] Tagliazucca et al., J. Catal. 2013, 305, 277. [2] Tagliazucca et al., Phys. Chem. Chem. Phys. 2014, 16(13), 6182. [3] Feyen et al., Chem.-Eur. J. 2011, 17, 598. [4] Gu et al. J. Phys. Chem. C. 2015, 30, 17102.

Keywords: transition metal catalysts, ammonia decomposition, in situ diffraction