Catalyst support materials with enhanced hydrothermal stability

Marcos Schöneborn, Frank Alber*, Thomas Harmening
Sasol Germany GmbH, Anckelmannsplatz 1, 20537 Hamburg, Germany
**corresponding author: frank.alber@de.sasol.com*

Introduction

Most modern highly selective catalytic processes require catalysts with tailored shape, porosity and well-defined surface properties, such as the nature, number and strength of acidic or basic centers. Therefore, the choice of the most suitable support material is the first crucial step in the preparation of advanced heterogeneous catalysts.

Several processes, e.g. biomass conversion are carried out under aqueous-phase conditions with elevated temperatures, which require hydrothermally stable support materials [1,2]. Under these conditions, pure alumina undergoes a rehydration resulting in the transformation to crystalline boehmite [3]. This contribution deals with alumina-based support materials comprising well-defined physical properties and also hydrothermal stability.

Materials and Methods

All silica-alumina hydrates described herein are commercially available from SASOL under the tradename SIRAL®, the corresponding oxides under the tradename SIRALOX®. Pure and doped alumina (Al_2O_3) is available under the tradename PURALOX®. The preparation of these materials is a based on a SASOL proprietary alkoxide-based sol-gel process [4,5,6].

For characterization, the materials have been stirred in pure water under at 200°C for several hours. Afterwards, the phase composition was analyzed via powder X-ray diffraction. In addition the level of rehydration was analyzed via DSC and TG analysis.

Results and Discussion

Table 1 shows examples of support material that exhibit enhanced hydrothermal stability with comparison to pure alumina. Acidic dopants phosphate, tungstate or SiO_2 [7,8] improve the resistance of alumina towards rehydration. Also the alumina-based ternary oxide $MgAl_2O_4$ (spinel) shows excellent hydrothermal stability [9]. The addition of carbon has a similar stabilizing effect. Carbon is known to reduce surface acidity by blocking the relevant Brønsted and Lewis acidic sites [10].

Table 1. Weight loss and phase compositions of various materials after hydrothermal treatment

Material	H_2O [%] (DSC-TG)	Phase composition (XRD)
PURALOX® - Al_2O_3	16	AlOOH
SIRALOX® 5 (w/ 5 % SiO_2)	3	Al_2O_3
PURALOX® w/ 10% C	n.a.	Al_2O_3
PURALOX® w/ 8% "WO_3"	4	Al_2O_3
PURALOX® w/ 4% "P_4O_{10}"	4	Al_2O_3
PURALOX® Mg 28 – $MgAl_2O_4$	6	$MgAl_2O_4$, $Mg_2O(OH)_2$

Figure 1 illustrates the impact of SiO_2 doping on the hydrothermal stability of alumina after hydrothermal treatment, which is similar to conditions of various catalytic processes. Under the conditions applied, pure alumina is quantitatively converted to boehmite (AlOOH). In comparison, the phase composition of alumina with 5 wt% SiO2 does not change by this treatment.

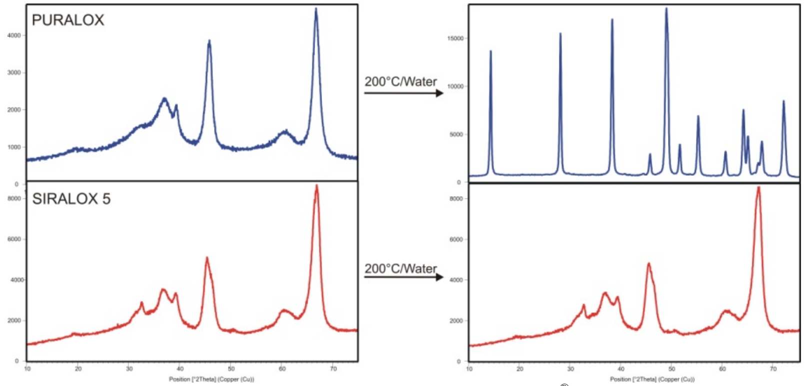

Figure 1. X-ray powder patterns of pure alumina (PURALOX®) and alumina with 5% SiO_2 (SIRALOX ®5) before and after hydrothermal treatment.

Significance

Various dopants like WO_3, "P_4O_{10}", SiO_2, MgO or carbon significantly improve the stability of alumina-based catalyst support materials. The combination of a proper dopant, which influences the surface chemistry of the support, is the key to various heterogeneous catalysts to be operated under harsh hydrothermal conditions.

References

1. Chheda, J.N.; Huber, G.H.; Dumasic, J.A. *Angewandte Chemie Int. Ed.* **2007**,*119*, 7298
2. Corma, A.; Iborra S.; Velty A. Chemical Reviews **2007**, *107*, 2411
3. Ravenelle, R.M.; Copeland J.R.; Kim W.G; Crittenden J.C.; Sievers C. *ACS Catalysis* **2011**, *1,* 552
4. *US Patent 4,590,289* (Condea)
5. *US Patent 5 045 519* (Condea)
6. *WO Patent* 98/23727 (Condea)
7. Chen, Y.W.; Lin C.S.; Hsu, W.C. *Catalysis Letters* **1989***, 3, 99*
8. Hahn, M.W.; Copeland, J.R.; van Pelt A.H.; Sievers S. *ChemSusChems* **2013***, 6,* 2304
9. Olsbye U.; Akporiaye D.; Rytter E.; Rønnekleiv M.; Tanstad E. *Applied Catalysis A* **2002***, 224,* 39
10. Pham H.N.; Anderson A.E.; Johnson R.L.; Schmidt-Rohr K.; Datye A.K. *Angewandte Chemie Int. Ed.* **2012**, *51*, 13163