**Investigations of molybdenum-promoted manganese-based solid sorbents for H2S capture**

Jianyu Ma1, Kumar R. Rout2, Maximilian Sauer3, Mehdi Mahmoodinia1, Edd A. Blekkan1\*

*1 Dept. of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway*

*2 SINTEF Industry, NO-7465 Trondheim, Norway*

*3 Technical University of Munich, Germany*

*\*Corresponding author:* *edd.a.blekkan@ntnu.no*

**Highlights**

* Mo-promoted Mn-based solid sorbents for desulphurization were studied
* Real-time residence H2S concentration was monitored on-line
* Mo addition promoted sorbent capacity and stability significantly

**1. Introduction**

Biomass gasification and subsequent fuel synthesis is a realistic route to 2nd generation biofuels. However, the produced syngas contains undesired species and contaminants (tar, alkali, sulfur species etc.) that has severe detrimental effects on downstream equipment and catalysts [1]. Therefore, gas cleaning and gas conditioning are important steps. From a process design point of view high-temperature gas cleaning is beneficial in terms of energy efficiency and investment cost. A key contaminant in biomass-based syngas is hydrogen sulfide, and this contaminant must be removed in order to avoid rapid deactivation of catalysts for fuel synthesis, e.g. cobalt-based Fischer-Tropsch catalysts [2]. Several materials have been proposed for high-temperature sulfur removal and manganese is reported to be a promising candidate based on thermodynamics (calculated sorption properties at high temperatures) as well as other chemical features (resistance to reduction, volatilization and carbide formation) [3]. The properties of sorbents can be improved by addition of promoters. Molybdenum oxide is selected in this study as a promoter on account of its ability to provide higher desulphurization capacity and improve stability of catalysts [4].

**2. Methods**

A series of Mo-promoted manganese sorbents supported on alumina were prepared by incipient wetness impregnation method using Mn-nitrate and ammonium molybdate as precursors. The samples were dried at 90°C and calcined at 700°C to decompose the salt. The nominal Mn loading was 15 wt% and Mo loadings were 2wt%, 5wt% or 8wt%, and 8wt% made using 2-step impregnation. Their H2S sorption properties were investigated in a laboratory setup, see [5] for further details. The sorption was done on pre-reduced samples at 600°C using a dry gas mixture containing 0,4 vol% H2S and 40% H2, the balance being inert gases (Ar, N2). The regeneration was done at 650°C and ambient pressure, using a gas containing 25 vol% air. The testing was performed as 10 cycles of sorption - regeneration. The residual H2S level was monitored at different sorption temperatures with a specific sulphur analyzer, Thermo-Fisher 450i.

**3. Results and discussion**

All the samples initially adsorbed H2S down to a very low level. After some time the concentration of H2S in the exit gas started to increase (breakthrough), the sorption was then terminated by flushing the reactor with inert gas. The sorbent capacity before breakthrough were calculated from the amount H2S adsorbed. Subsequently the sorbent was regenerated by diluted air. The only sulfur species detected in the gas phase during regeneration was SO2. The initial sorption capacities declined in the following order: 15Mn5Mo-Al2O3> 15Mn8Mo-Al2O3> 15Mn8Mo-2step-Al2O3>15Mn2Mo-Al2O3>15Mn-Al2O3, indicating that addition of Mo increases sorbent initial capacity. After one cycle, the capacities for sorbent 15Mn8Mo-Al2O3 and 15Mn8Mo2step-Al2O3 increased obviously and remained stable for subsequent cycles. However, the capacity of 15Mn2Mo-Al2O3 suffered large deactivation and turned to be even lower than sorbent without Mo. The sorption capacity after 10 cycles declined in the following order: 15Mn8Mo-2step-Al2O3> 15Mn8Mo-Al2O3> 15Mn5Mo-Al2O3>15Mn-Al2O3>15Mn2Mo -Al2O3.

The residence H2S concentration after sulfidation by 15Mn8Mo-Al2O3 was as low as around 1.95ppm at a sorption temperature of 400°C. At 600°C, the residual concentration increased to around 2.65ppm. In contrast, the 15Mn-Al2O3 showed a similar result at 400°C, 2.4ppm, however, a significantly higher value of 11ppm was recorded at 600°C sorption temperature.



**Figure 1.** Capacities of Mn-based sorbents promoted with Mo.

**4. Conclusions**

The addition of Mo is found to be beneficial for Mn-based sorbents, in terms of capacity, stability and residual H2S concentration in the gas phase after sorption.

**References**

1. G.W. Huber, S. Iborra, A. Corma, Catal, Eng, Chem. Rev. 106 (2006) 4044–4098.

[2] A.H. Lillebø, A. Holmen, B.C. Enger, E.A. Blekkan, WIREs Energy. Environ. 2 (2013), 507–524.

[3] W.F. Elseviers, H. Verelst, Fuel 78 (1999) 601–612

[4] Laosiripojana, N., and S. Assabumrungrat. Applied Catalysis A: General, 290.1-2 (2005): 200-211.

[5] S. Chytil, M. Kure, R. Lødeng, E.A. Blekkan, Fuel, 196 (2017) 124–133.