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Supported manganese sorbents for H_2S capture

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Highlights

- Manganese sorbents well suited for high-temperature gas cleaning.
- Support effects influence sorbent behavior.
- Zircinia-supported Mn shows high stability.
- Strong metal oxide-support interaction influences the sorbent performance.

1. Introduction

Biomass gasification and subsequent fuel synthesis is a realistic route to 2nd generation biofuels, allowing the production of drop-in fuels that can replace fossil fuels in existing engines and infrastructure. There are, however, many technical and economical hurdles for this kind of process, and increasing the overall thermal efficiency is an important goal [1,2]. The produced syngas contains undesired species and contaminants (tar, alkali, sulfur species etc.) that has severe detrimental effects on downstream equipment and catalysts, and gas cleaning and gas conditioning are important steps. From a process design point of view high-temperature gas cleaning is beneficial, since cooling down and reheating the gas carries a penalty in terms of energy efficiency and investment cost. A key contaminant in biomass-based syngas is hydrogen sulfide, and this contaminant needs to 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 (the stable state is MnO above 400 °C) 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, volatilisation and carbide formation) [3]. Here we present results investigating the sorption capacity of supported MnO, including support effects, stability and we will also report on issues related to the mechanism as well as upscaling and use in reactor systems.

2. Methods

Manganese sorbents supported on alumina, titania, zirconia and ceria were prepared by aqueous wet impregnation using Mn-nitrate precursor. Following the impregnation, the samples were dried (100 °C, 24 h) and calcined (600 °C, 5 h) to decompose the salt. The nominal manganese loading was 15 wt%. Their properties as sorbents were investigated in a laboratory setup consisting of a gas feeding and metering system, a quartz fixed bed reactor and an analytical section using a quadrupole mass spectrometer to monitor the H_2S concentration, see [4-5] for further details. The testing was done using a dry gas mixture containing 0,4 vol% H_2S and 40% H_2, the balance being inert gases (Ar, N_2). The sample weight was 0,1 g, and the gas flow-rate was 50 Nml/min. The regeneration was done at the same temperature and pressure, using a gas containing 5,2 vol% O_2. Before the first sulfidation cycle the samples were pre-reduced in 50% H_2 during heating to the sorption temperature (650 °C) and keeping at 1 hour at this temperature before the first exposure to the H_2S-containing gas.

3. Results and discussion

The testing was performed as cycles. Each cycle consisted of an adsorption period, where the samples were exposed to 0,4 % H_2S until breakthrough. All the samples initially adsorbed H_2S down to a very low level, challenging the detection limit of the MS. After some time the concentration of H_2S in the exit gas started to increase, and when the concentration equaled that of the inlet concentration the total capacity can be calculated from the amount of H_2S adsorbed. Subsequently the sorbent was regenerated by switching to the oxygen-containing gas. The only sulfur species detected during regeneration was SO_2. Fig. 1 shows the sorbent capacity and the development of the capacity with increasing number of cycles. The dotted line in the figure represents the theoretical capacity, assuming that H_2S reacts with MnO, forming MnS and water. The initial sorption capacity declines in the following order: Mn15-CeO_2 > Mn15-Al_2O_3 > Mn15-ZrO_2 > Mn15-TiO_2. The high initial capacity of the CeO_2-supported sample is to some extent linked with the support itself having some capacity to capture H_2S, and the total capacity exceeds that calculated based on the Mn content alone (represented by the dotted line in Fig. 1). After a number of cycles, the capacity of all the systems is strongly reduced and the order has changed, now the capacity ranking is Mn15-Al_2O_3 > Mn15-CeO_2 > Mn15-ZrO_2 > Mn15-TiO_2. In terms of deactivation (final capacity compared to the initial capacity), it appears that the ZrO_2-supported sample maintains the capacity the best. However, further work needs to include the effect of steam, a key constituent of the raw syngas.

4. Conclusions

Supported, Mn-based sorbents show promising properties as sorbents for H_2S capture. The support influences the capacity, both in terms of initial capacity as well as the stability over repeated cycles.

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Keywords
H_2S; solid sorbents; Manganese oxide; Support effect

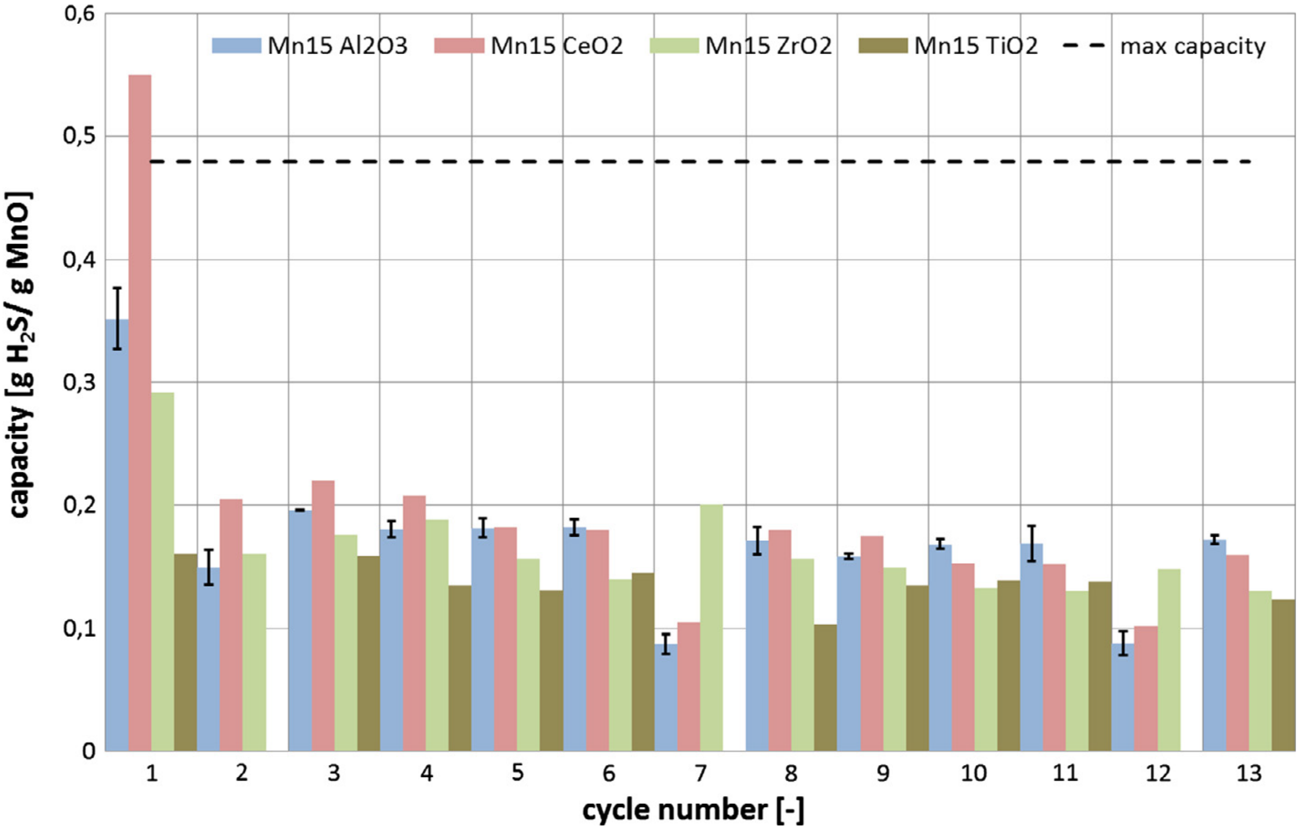

Figure 1. Sorbent capacity. The samples were prereduced, and also exposed to H_2 overnight at the reaction temperature (650 °C) before cycle 2, 7 and 12. (Reproduced from [5] with permission from the publishers.)