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Possibilities of High-Temperature Desulphurization and Dechloration of a Producer Gas

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Producer gas contains several types of impurities, the limit of which is its further utilization. Depending on the used feedstock and type of gasifier the main impurities are dust, tar, sulphur compounds, HCl, and HF. In producer gas from biomass gasification the main impurities are tar, H_2S, COS, and HCl. In order to use the producer gas in SOFC (solid oxide fuel cells) or Fischer-Tropsch synthesis the concentration of impurities has to be lower than 1 ppmv.[1]

For high temperature desulphurization are commonly used CaO, Fe_xO_y ZnO, CuO, MnO based sorbents. In experimental studies for deep desulphurization, rare earth sorbent such as Ce_2O_3, CeO_2, La_2O_3 have also been investigated. For the evaluation of different sorbents equilibrium concentrations of H_2S and HCl were calculated from thermodynamic data given by Barrin.[2] Input gas composition was 40 vol. % of H_2, 10 vol. % of H_2O, and 30 vol. % of CO_2. At temperatures in the range of 600–800 K ZnO, Ce_2O_3 and La_2O_3 based sorbents are able to ensure output concentrations of H_2S and COS below 1 ppmv and below 0.01 ppmv, respectively. The best equilibrium concentration at 800 K can be achieved by Ce_2O_3. However, trivalent Ce isn't stable and in the presence of CO_2 or H_2O undergoes oxidation to CeO_2 with much higher equilibrium concentration of H_2S. ZnO sorbents are also problematic due to volatility of elemental zinc under reducing conditions.

Producer gas equilibrium concentrations of HCl containing 10 vol. % of H_2O and 100 ppmv of HCl or 10 ppmv respectively, were calculated to predict interferences with HCl during gas desulphurization and the possibility of simultaneous desulphurization and dechloration (de-HCl) by one of these sorbents. ZnO and Ce-based sorbents show a higher equilibrium concentration of HCl. Therefore interferences caused by HCl during desulphurization can be excluded. La_2O_3 exerts the lowest equilibrium concentration of HCl in the producer gas and reacts in temperatures up to 900 K. It should be noted that for deep de-HCl soda-based sorbents are needed. According to thermodynamic calculation the reaction of Na_2CO_3 with H_2S should be negligible.

In the experimental part of the desulfurization and de-HCl studies, H_2S interference during dechloration was measured. Gas hourly space velocity was around 3000 h^{-1} (standard temperature and pressure). Output gas HCl concentration was about 3 ppmv which shows that it was not affected by H_2S. However a sharp decrease of sorbent capacity was observed, due to the formation of elemental sulfur from H_2S which was investigated under the condition of a model gas with dry nitrogen (without water vapor and hydrogen). The formation of elemental sulfur (S_x molecules) and its adsorption on sorbents plugs sorbent pores. Therefore the presence of hydrogen and water vapor in gas is desirable to suppress this phenomenon.

According to thermodynamic calculations Ce_2O_3 exerts the highest affinity to H_2S and is capable of deep desulfurization at temperatures up to 800 K. Ce_2O_3 can be stabilized by La_2O_3 or MnO addition under common reduction conditions. Therefore Ce_2O_3 sorbents doped by La_2O_3 seem to be promising producer gas sorbents.

References

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2. Barin, O. Knacke, *Thermochemical data of pure substances.* 3^{rd} ed. Weinheim: VCH **1995**.