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Possibilities of High-Temperature Desulphurization and Dechlorination 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, H₂S, 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 Ce₂O₃, CeO₂, La₂O₃ have also been investigated. For the evaluation of different sorbents equilibrium concentrations of H₂S and HCl were calculated from thermodynamic data given by Barrin.² Input gas composition was 40 vol. % of H₂, 10 vol. % of H₂O, and 30 vol. % of CO₂. At temperatures in the range of 600–800 K ZnO, Ce₂O₃ and La₂O₃ based sorbents are able to ensure output concentrations of H₂S and COS below 1 ppmv and below 0.01 ppmv, respectively. The best equilibrium concentration at 800 K can be achieved by Ce₂O₃. However, trivalent Ce isn't stable and in the presence of CO₂ or H₂O undergoes oxidation to CeO₂ with much higher equilibrium concentration of H₂S. ZnO sorbents are also problematic due to volatility of elemental zinc under reducing conditions.

Producer gas equilibrium concentrations of HCl containing 10 vol. % of H₂O 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 dechlorination (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. La₂O₃ 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

1. Svoboda K.; Hartman M.; Trnka O.; Čermák K. *Chemické listy*. 2003, 97, 9–23.
2. Barin, O. Knacke, *Thermochemical data of pure substances*. 3rd ed. Weinheim: VCH 1995.