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Possibilities of High Temperature Desulphurization of a Producer Gas

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Producer gas contains several types of impurities, which limit its further utilization. Depending on the used feedstock and gasifier type the main impurities are tar, dust, 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 Fisher-Tropsch synthesis the concentration of impurities must be lower than 1 ppmv.

Sorbents currently used for high temperature desulfurization are based on CaO, Fe_xO_y, ZnO, CuO. Fe_xO_y and CaO based sorbents are not capable to achieve sufficiently low output H₂S concentration at high temperatures. ZnO and CuO sorbents are problematic due to undergoing reduction at high temperatures. This reduction causes the formation of volatile elemental zinc in the case of zinc sorbents and reduction of active CuO to less active Cu₂O and Cu which exerts inferior desulfurization activity. For this reason new substances for high temperature desulfurization are being examined. The easiest way to assess the desulfurization potential of different substances at different conditions is according to their thermodynamic data. According to thermodynamic calculations several rare earth oxides such as Ce₂O₃ and La₂O₃ seem to be suitable for deep high-temperature desulfurization. These calculations suggest that Ce₂O₃ and La₂O₃ are able to ensure output concentrations of H₂S and COS below 1 ppmv and 0.01 ppmv, respectively, in the temperature range of 600–800 K and gas containing 40 vol. % of H₂, 10 vol. % of H₂O and 30 vol. % of CO₂. For a more complex thermodynamic calculation, methods based on the minimization of free Gibbs energy have to be applied. These more complex and accurate calculations suggest a possibility of oxidation of Ce₂O₃ in the presence of CO₂ or H₂O to CeO₂, which has a much higher equilibrium concentration of H₂S. Complex thermodynamic calculations suggest a formation of inactive and thermally stable oxy-carbonate La₂O(CO₃)₂ in presence of CO₂.

In the experimental part of the desulfurization studies, H₂S sorption on CeO_x/Al₂O₃ and La₂O₃/Al₂O₃-based sorbents was examined at the temperature 727 K at different gas compositions. First tests were carried out in gas without any oxidizing agent containing only H₂ and N₂. Prepared CeO_x/Al₂O₃ sorbent was reduced prior to each desulfurization experiment. This step indicated to be crucial for sorbent activity and capacity. These experiments proved possibility of high temperature desulfurization with Ce-based sorbent. But even with a sorbent prereduced by a gas with 50% vol. of H₂, the sorbent was capable to attain output H₂S concentration below 1 ppmv for only 2.5% of relative time of sorption. Slightly better results were attained when the reduction step was carried out at temperature 827 K for one hour in a gas consisting of 90 vol.% of H₂ and 10 vol.% of CH₄. To find the extent of reduction, both reduced and non-reduced CeO_x based sorbent were analyzed by XPS (x-ray photoelectron spectroscopy). According to the results of the analysis the non-reduced sorbent contains 51% of Ce^{IV} and 49% of Ce^{III} compared to 35% of Ce^{IV} and 65% of Ce^{III} in the reduced sorbent. In the following experiments, a sorbent prepared and prereduced in this way was tested in dry producer gas: CO₂ = 14.4 vol.%, CO = 39.4 vol.% and H₂ = 46.2 vol.% with 250 ppmv of H₂S.

Experiments with the reduced CeO_x-based sorbent did not proved any desulfurization activity in wet nor in dry producer gas, even though that XPS analysis proved that both reduced and nonreduced sorbent does contain active Ce₂O₃. This is caused by an immediate reoxidation of reduced cerium oxide by H₂O and CO₂ in producer gas. For application of the CeO_x-based sorbent in desulfurization of producer gas it is necessary to prepare a stabilized Ce₂O₃. The possibilities of stabilization of Ce₂O₃ will be investigated in the following experiments.