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## **Possibilities of High Temperature Desulphurization of a Producer Gas.**

Brynda, Jiří  
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## Possibilities of High Temperature Desulphurization of a Producer Gas

*Student: Ing. Jiří Brynda*

*Supervisor: Ing. Sjarhei Skoblja, Ph. D.*

*Supervising Expert: Doc. Ing. Karel Svoboda, CSc.*

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, H<sub>2</sub>S, 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<sub>x</sub>O<sub>y</sub>, ZnO, CuO. Fe<sub>x</sub>O<sub>y</sub> and CaO based sorbents are not capable to achieve sufficiently low output H<sub>2</sub>S 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 Cu<sub>2</sub>O 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 Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> seem to be suitable for deep high-temperature desulfurization. These calculations suggest that Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> are able to ensure output concentrations of H<sub>2</sub>S and COS below 1 ppmv and 0.01 ppmv, respectively, in the temperature range of 600–800 K and gas containing 40 vol. % of H<sub>2</sub>, 10 vol. % of H<sub>2</sub>O and 30 vol. % of CO<sub>2</sub>. 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 Ce<sub>2</sub>O<sub>3</sub> in the presence of CO<sub>2</sub> or H<sub>2</sub>O to CeO<sub>2</sub>, which has a much higher equilibrium concentration of H<sub>2</sub>S. Complex thermodynamic calculations suggest a formation of inactive and thermally stable oxy-carbonate La<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> in presence of CO<sub>2</sub>.

In the experimental part of the desulfurization studies, H<sub>2</sub>S sorption on CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-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 H<sub>2</sub> and N<sub>2</sub>. Prepared CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub>, the sorbent was capable to attain output H<sub>2</sub>S 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 H<sub>2</sub> and 10 vol.% of CH<sub>4</sub>. To find the extent of reduction, both reduced and non-reduced CeO<sub>x</sub> 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<sup>IV</sup> and 49% of Ce<sup>III</sup> compared to 35% of Ce<sup>IV</sup> and 65% of Ce<sup>III</sup> in the reduced sorbent. In the following experiments, a sorbent prepared and prereduced in this way was tested in dry producer gas: CO<sub>2</sub> = 14.4 vol.%, CO = 39.4 vol.% and H<sub>2</sub> = 46.2 vol.% with 250 ppmv of H<sub>2</sub>S.

Experiments with the reduced CeO<sub>x</sub>-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 Ce<sub>2</sub>O<sub>3</sub>. This is caused by an immediate reoxidation of reduced cerium oxide by H<sub>2</sub>O and CO<sub>2</sub> in producer gas. For application of the CeO<sub>x</sub>-based sorbent in desulfurization of producer gas it is necessary to prepare a stabilized Ce<sub>2</sub>O<sub>3</sub>. The possibilities of stabilization of Ce<sub>2</sub>O<sub>3</sub> will be investigated in the following experiments.