Ambient Temperature Adsorptive Desulfurization of Natural Gas

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Introduction

Fuel Cells such as the proton exchange membrane and solid oxide fuel cells require hydrogen as fuel. The most common way to produce the hydrogen is by catalytic reforming of natural gas. Currently natural gas is the fuel of choice because of its relative abundance, safety in handling and supply infrastructure. Sulfur odorants are added to the natural gas for safe handling during transportation and use. Typical sulfur species in the natural gas in the US are dimethyl sulfide (DMS), tertiary butyl mercaptan (TBM), carbonyl sulfide (COS) and hydrogen sulfide (H_2S). In addition, trace amounts of water are also present. In Europe the natural gas typically contains tetra hydrothiophene (THT) and ethyl mercaptan (EM) and DMS is commonly used in Japan. This sulfur has to be removed to avoid poisoning of the catalysts in the fuel processor. This paper describes the effect of different sulfur components in the natural gas on the adsorptive desulfurization and sulfur uptake capacity of zeolite and base metal sorbents. The influence of moisture in the natural gas on desulfurization and sulfur uptake over zeolitic and non-zeolitic materials, at ambient conditions, has been investigated. The effect of using moisture traps is also described.

Materials and Methods

The zeolite-based adsorbents were prepared from zeolite - X by conventional ion exchange. Non-zeolitic, base metal, sorbents were prepared by impregnation of amorphous oxides with appropriate base metals.

Results and Discussion

Adsorbent materials were tested for ambient temperature adsorptive desulfurization of natural gas. Both utility and simulated natural gas (wherein typical sulfur components such as DMS, THT, TBM/EM, COS and H_2S were included) were used for testing. While zeolite X-based material were efficient in the removal of DMS, THT and mercaptans, they were less effective for COS removal. Base metal oxides using transition metals, like Cu, Mn, or Fe were more active in the latter function. A combination of different adsorbents would be necessary for an optimal removal of the various impurity components present in the natural gas. A significant finding of the present study is that the presence and concentration of H_2O in the natural gas significantly influenced the performance of the various sorbents in adsorptive desulfurization. The amount of sulfur adsorbed in the case of the zeolite X - based catalyst for a 50 ppb breakthrough level was 5.86%, wt. When water was present in the mixture, this is reduced to 3.6% ,wt (Fig.1). There is competitive adsorption of dimethyl sulfide (DMS) and water for adsorption sites in the cavities of the zeolite. Under certain transient conditions, the amount of DMS exiting the reactor was even higher than that at the inlet. This is, probably, due to the fact that, at higher partial pressures of H_2O, the DMS molecules are being displaced from their adsorption sites by the incoming H_2O. Alternate zeolites (Y, mordenites etc) and base transition metal oxides have also been explored.

Significance

The need for an adsorbent solution for the desulfurization, *at ambient conditions*, of natural gas is gaining importance as fuel cells become commercial. The advantages and disadvantages of different types of material (both zeolitic and non-zeolitic) are compared. The adverse influence of traces of water in the natural gas and possible solutions are addressed in detail.

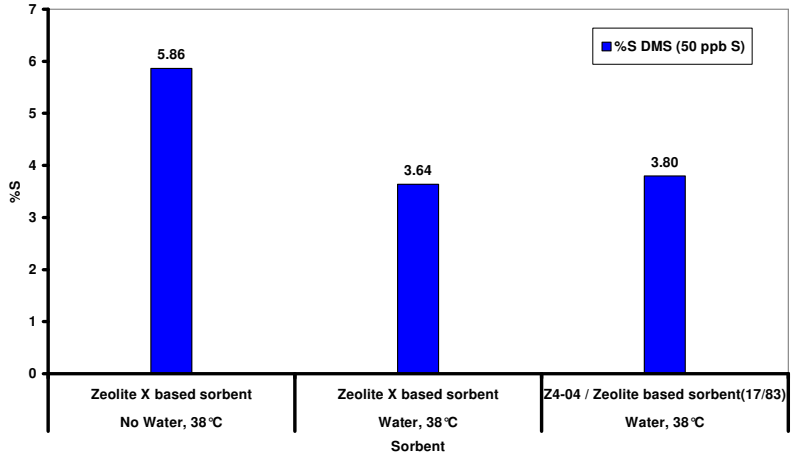

Figure 1. Effect of water on the various sorbents. Test conditions: Space velocity 10,000 hr^{-1}, 2 bar, Feed (10ppm DMS + 85ppm H2O in synthetic natural gas)

References

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