

Ferrimagnetic ceramic adsorbents for cleanup of H₂S from exhaust gases

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Abstract

Adsorbents that exhibit magnetic properties in addition to other required process-relevant characteristics open up new perspectives for the dry reduction and/or elimination of H₂S and other sulfur compounds from exhaust gases. These adsorbents eliminate the sulfur compounds from exhaust gases by virtue of their coatings and their magnetic property which makes it possible the use of magnetically assisted and stabilized fluidization in an externally applied magnetic field.

In the present paper, the feasibility of the sorptive function of porous ceramic ferrimagnetic beads is ensured by sol–gel coating of zinc oxide without the formation of Zn–Fe-oxides and without considerable decrease of available pore volume. The results of material characterization by SEM, Auger electron spectroscopy, X-ray and mercury-porosity measurements and the loading capacity of a H₂S/N₂ model gas are presented and discussed. The resulting H₂S loading of the functionalized adsorbent beads is more than 10 times larger than that of the starting material.

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1. Introduction

The reduction and/or elimination of H₂S and other sulfur compounds from exhaust gases is of paramount importance, particularly for the post-processing of biomass and fermentation gases as regenerative fuels, as well as the synthesis of gases for decentralized applications of fuel cells (Donnerbauer, 2003; Schmalschläger, Blasé, & Gerstmayr, 2001). Dry-gas cleanup is generally accomplished by fixed-bed adsorbents consisting of highly porous and appropriately functionalized adsorbents, so that the H₂S concentration in the gas flow could be sufficiently decreased by catalytic oxidation, chemisorption, and/or physisorption. A novel idea is the use of ferrimagnetic adsorbents. The magnetic properties of such adsorbents can be used as an additional parameter for improving process management by means of an externally applied magnetic field (Halbedel, Hülsenberg, Häuser, Kätzel, & Jakob, 2002). In this case, the adsorbents in the reaction vessel are fluidized in the magnetic field, independent of the gas flow. In comparison to conventional dry-gas cleanup, processes involving these new magnetic adsorbents result in decreased fluidization energies, short-

ened processing times and/or increased throughput of harmful gases.

In this paper, we introduce such ferrimagnetic ceramic beads. The object was to evaluate the feasibility of such additional sorptive functionality by sol–gel coatings of zinc oxide without the formation of Zn–Fe-oxides and without considerable decrease of available pore volume.

2. Methods and materials

2.1. Production of the starting materials

The ferrimagnetic granules were prepared by using a fluid bed system (Type WG 500, TRIDELTA GmbH, Hermsdorf) from a sufficiently fine ground hard ferrite powder (chemical composition: SrFe₁₂O₁₉; specific surface after Blaine: >2300 cm²/g) aqueous slurry (Halbedel, Hülsenberg, Belau, Schadewald, & Jakob, 2005). The received granules were sieved to yield a size range of 315–630 μm. These granules were sintered in air at 1250 °C in a laboratory furnace.

2.2. Sol–gel coating for functionalization

For functionalization of these ferrimagnetic beads, a zinc oxide sol–gel solution of zinc acetate (ZnO·2H₂O; No. 96458,

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Nomenclature

c_0	pollutant entrance concentration (ppm)
$m_{A,0}$	filler mass of the ferrimagnetic beads (g)
m_P	pollutant mass on the ferrimagnetic beads (g)
$m_P/m_{A,0}$	relative loading capacity of the beads ($\mu\text{g/g}$)
p	pressure in the reactor (bar)
$r_{90}-r_{10}$	pore size range (nm)
r_m	mean pore size (nm)
t_D	break-through time of the reactor (min)
v_t	total specific pore volume of the beads (mm^3/g)
\dot{V}_G	flow rate in the reactor at process conditions (cm^3/min)
$\dot{V}_{G,SC}$	flow rate in the reactor at standard conditions (cm^3/min)

Greek letters

$\varepsilon_{\text{open}}$	open porosity of the beads (%)
ϑ_A	temperature of the beads ($^{\circ}\text{C}$)
$\rho_{P,SC}$	density of the pollutant under standard conditions (g/cm^3)

Fluka Chemical Corp., Ronkonkoma, NY) and water were first prepared from a solution made under heating by dissolving 60 g (0.73 mmol) of zinc acetate into 60 mL of water. The solution was acidified with 5 mL of 65% nitric acid and diluted with 120 mL of ethanol, then aged at 75 $^{\circ}\text{C}$. The total final volume was 80 mL.

To improve wettability, the ferrimagnetic beads before infiltration with the zinc oxide sol–gel solution has to be pre-treated as follows. The present beads were first dried at 120 $^{\circ}\text{C}$ and corroded in a 50% NaOH solution, rinsed with water and washed for a long time in ethanol. Finally, the beads were impregnated with a zinc oxide sol and dried in a rotating evaporator at 120 $^{\circ}\text{C}$.

Subsequent calcination was accomplished by treating the impregnated and dried beads in a laboratory chamber furnace at 360 $^{\circ}\text{C}$ for 2 h in air. The resultant agglomerates were easily separated in a rotating vessel after ~ 1 h. The functionalized ferrimagnetic beads were separated by using a permanent magnet.

2.3. Evaluation of the loading capacity of the ferrimagnetic adsorbents

The following steps were followed to characterize the loading capacity of the non-functionalized and functionalized ferrimagnetic beads in a fixed-bed reactor:

- (1) Pour the beads into the reactor.
- (2) Pass a $\text{H}_2\text{S}/\text{N}_2$ model gas of known composition through the filled reactor.
- (3) Evaluate the gas at the output of the reactor by gas analysis.

Fig. 1 shows schematically the loading behavior of the beads in the laboratory reactor. As long as the ferrimagnetic beads adsorb sufficiently the pollutant H_2S , no pollutant will exit the reactor. However, if the reactor suffers break-through, i.e., if the

adsorbents are unable to adsorb any more pollutants because the loading capacity of the beads has been reached, the pollutant concentration of the gas leaving the reactor gradually increases from zero to the concentration of the entering gas. Thus, if the flow rate in the reactor \dot{V}_G and the pollutant entrance concentration c_0 are known and maintained constant and the filler mass of the beads $m_{A,0}$ is also known, the break-through time t_D can be used to define the sorption characteristics of the ferrimagnetic beads, and the relative loading capacity $m_P/m_{A,0}$ under standard conditions (0 $^{\circ}\text{C}$, 1 bar) can be obtained,

$$\frac{m_P}{m_{A,0}} = \frac{c_0 \rho_{P,SC} t_D \dot{V}_{G,SC}}{m_{A,0}}, \quad (1)$$

where m_P is the pollutant mass on the ferrimagnetic beads after the break-through time t_D , $m_{A,0}$ the mass of the ferrimagnetic beads, and $\rho_{P,SC}$ the density of the pollutant under standard conditions. The flow rate in the reactor under standard conditions $\dot{V}_{G,SC}$ can be determined from the measured flow rate in the reactor \dot{V}_G , the temperature of the beads ϑ_A , and the pressure in the reactor p ,

$$\dot{V}_{G,SC} = \dot{V}_G \frac{273.15}{273.15 + \vartheta_A} p. \quad (2)$$

Fig. 2 shows the experimental setup used for evaluating the relative loading capacities of the ferrimagnetic beads with H_2S . The model gas used had a certified H_2S concentration of $c_0 = 100$ ppm (Messer Griesheim GmbH, Kassel). The reactor, which was made of borosilicate glass with low thermal expansion and high chemical stability (Duran[®], Schott Glas Mainz, Germany), had an inside diameter of 20 mm and a height of 180 mm. All parts that came into contact with the gas were coated with H_2S -resistant materials (pipework with high-grade steel 1.4571 and gaskets with PTFE).

The pollutant concentration, $c(t)$, at the reactor outlet was determined using a micro gas chromatograph (Model CP 2002, Chrompack, Inc., Raritan, NJ). Every ~ 2 min, exiting gas was extracted through gas probes (2 mL) and the contents were analyzed with the gas chromatograph. The detection limits of the gas chromatograph were based on thermal conductivity by comparison with helium.

Gas flow through the reactor was adjusted by means of a mass flow controller (Model MFC F 201 D-FAC-33-P, Wagner Mess- und Regelungstechnik GmbH, Offenbach) to remain constant at 100 mL/min, thus ensuring that, with equal bead porosities, the flow velocities between the ferrimagnetic beads would always be approximately the same, and independent of other processing parameters.

The reactor was heated to temperatures up to 300 $^{\circ}\text{C}$. The operating gas temperature, ϑ_G , and the temperature of the bulk adsorbent, ϑ_A , were determined using temperature sensors embedded in the reactor head or positioned in the adsorbent, respectively. Before each loading, the laboratory reactor was rinsed with nitrogen, at a rate of 250 mL/min, for 5 min and five times the entire empty volume of the experimental setup. Manually valves V_{1-4} (BEST Ventil + Fitting AG, Doelzig) made it possible to change the direction of flow.

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