Development of Fe-based Catalysts for Purification of Coke Oven Gases

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Abstract

Fe-based catalysts of different geometry are developed for the purification of coke oven gases: bulk, supported on alumina and supported on alumina silicate monoliths. Adsorption and decomposition of H₂S on the catalysts developed are studied. Influence of active component content, type of support material and modification by Mn and Mo on the catalyst activity in de-H₂S process is elucidated. Supported monolith catalysts show superior activity over bulk and supported spherical catalysts in H₂S decomposition reaction and demonstrate stable operation in ammonia decomposition process during 2 hours at 900 °C giving 100% ammonia conversion.

Introduction

Main impurities of coke oven gases (COG) are H₂S and NH₃. More than 99% of these impurities, which form harmful products upon oxidation or processing of COG, have to be removed taking into account environmental and technological aspects. On the other hand, COG containing up to 60% of hydrogen is considered as essential source for production of pure H₂. Therefore, an efficient and low cost process for cleaning of COG is highly desirable.

According to literature data, many metal sulfides MₓSᵧ, where M = Na, K, Li, Fe, Co, Ni, Cr, Mo, V and metal oxides MₓOᵧ, where M = Fe, Cr, Cu, Mn, V, Ti, Mo, Al, Zn are active in H₂S decomposition reaction [1-17]. When metal oxides are used, the first step in the process of H₂S decomposition is the transformation of metal oxide into metal sulfide. Metal sulfide formed acts as a catalyst for the process of H₂S decomposition. It was found that metal sulfide made in result of treatment of metal oxide by H₂S shows superior activity compared with the ready-made metal sulfide in reaction conditions [5].

Different sulfides form the following order according to their activity in H₂S decomposition reaction: CoS₂[18]<MoS₂[19]<Co-Mo-S[20]<Ru-Mo-S[21]. It is necessary to note that besides Mo- and V-based catalysts, which are commonly studied in de-H₂S reaction, Fe₂O₃ catalyst also deserves attention as it exhibits high level of activity not only in H₂S decomposition process, but in ammonia decomposition reaction as well [11,13,14], making this catalyst very promising for the use in the complex cleaning of COG. In [17] a mixture of more than 10 oxides (Fe₂O₃, MnO₂, SiO₂, ZnO, CaO et al.) was studied in the H₂S decomposition reaction. It was shown that initially hydrogen sulfide is absorbed by the catalyst and as a consequence both hydrogen sulfide and hydrogen are not detected in the reaction mixture. During adsorption the catalyst transforms into metal sulfides and then decomposition of H₂S begins. It was concluded that the activity of this complex catalyst is determined primarily by Fe₂O₃ taking into account its relative high quantity in the catalyst (42.6 wt.%) and its capability of easy formation of sulfides compared with other oxides.

The subject of this paper is the development of Fe-based catalysts of different geometry for purification of coke oven gases.
Experimental

Bulk Fe₂O₃ catalysts were synthesized via thermal decomposition of different Fe-containing salts at 600°C, tableted and sieved to 1-2 mm (samples from F-1 to F-7, Table 1). Supported spherical catalysts were prepared by wetness impregnation of different supports by Fe(NH₄)₃(C₂O₄)₃·3H₂O solution and calcination at 600°C (samples from F-8 to F-11, Table 2). Spherical γ-Al₂O₃ (1-2 mm) and α-Al₂O₃ (2-3 mm), ZrO₂ and SiO₂ sieved to 1-2 mm were used as a support material for the deposition of active component. Modification of supported Fe-containing catalysts by Mn and Mo was performed by wetness impregnation of ready-made 2.9%Fe/γ-Al₂O₃ (F-8) and 4.1%Fe/α-Al₂O₃ (F-9) catalysts by the use of Mn(NO₃)₂ and (NH₄)₆Mo₇O₂₄ solutions (samples Mn/F-8, Mn/F-9 and Mo/F-8, Mo/F-9, Table 2). Prepared spherical catalysts F-8 (2.9wt.%Fe/γ-Al₂O₃) and F-9 (4.1wt.% Fe/α-Al₂O₃) were crushed into powder, deposited from suspension containing catalyst powder and γ-Al₂O₃ as a binder onto alumina silicate monoliths B and calcined at 600°C (samples F-8/B and F-9/B). Content of Fe introduced into Fe-8/B catalyst amounts to 0.23 wt.%, whereas in F-9/B catalyst – 0.33 wt.%. Phase composition of the catalysts was registered by XRD using HZG-4 (Cu Kα radiation) diffractometer with copper radiation in the 2θ range of 10-70 degrees. Specific surface area of the samples was measured by BET method. Quantitative analysis of elements in supported spherical and monolith catalysts was performed by the use of method of atom-absorption spectroscopy.

Prepared catalysts were tested in a 1% H₂S-99% Ar flow. Catalyst was placed into quartz reactor, free volume of reactor was filled by sieved quartz (1-2 mm). Catalyst was treated in N₂ first at 150°C during 30 min and then at 600°C during 30 min. Activity test included activation of the catalysts by reaction mixture at 600°C till establishment of a steady outlet concentration of H₂S and subsequent study of H₂S decomposition at the temperatures of 600→700→800→900→800→700→600°C at residence time equal to 1 s. Duration of catalyst activation was characterized by value ρ representing total amount of H₂S (mnmole) fed into the reactor divided by the weight of a catalyst sample at which a steady level of H₂S conversion is achieved.

Activity test in de-NH₃ reaction was performed as follows: catalyst was placed into quartz reactor, at first was treated in He at 150°C during 30 min, then at 600°C during 1 hour and catalyst activity was measured within temperature interval of 600-900°C. Both fresh catalyst and catalyst after activity test in H₂S decomposition reaction were tested in NH₃ decomposition reaction.

Table 1

| Sample | Initial salt of Fe | Fresh catalyst | Catalyst after activity test |
|--------|--------------------|----------------|-----------------------------|
|        |                    | XRD | S_{BET}, m²/g | Total duration of activity test, hrs | XRD | S_{BET}, m²/g |
| F-1    | Iron(III) nitrate nanohydrate Fe(NO₃)₃·9H₂O | α-Fe₂O₃ | 8.3 | 12 | Fe₁sS | 0.14 |
| F-2 (sublimated during calcination) | Iron(III) chloride FeCl₃ | | | | | |
| F-3 (calcined at 700°C) | Ammonium iron(II) sulfate hexahydrate Fe(NH₄)₂(SO₄)₂·6H₂O | α-Fe₂O₃ | 13.0 | 19 | | |
| F-4    | Iron(III) oxalate pentahydrate Fe₂(C₂O₄)₃·5H₂O | α-Fe₂O₃ | 8.3 | 10 | Fe₂S₈ | 0.12 |
| F-5    | Ammonium iron(III) oxalate trihydrate Fe(NH₄)₂(C₂O₄)₃·3H₂O | α-Fe₂O₃ | 2.9 | 33 | Fe₂S₈ | 2.1 |
| F-6    | Iron(III) citrate hydrate FeC₆H₅O₇·nH₂O | α-Fe₂O₃ + Fe₂O₄ | 9.3 | 28 | Fe₁sS | ~ 0 |
| F-7    | Ammonium iron(III) dihydrocitrate citrate hydrate 2FeC₆H₅O₇·NH₄C₆H₅O₇·nH₂O | α-Fe₂O₃ | 6.7 | 50 | Fe₁sS | ~ 0 |
Results and discussion

**Bulk catalysts**

XRD showed formation of $\alpha$-Fe$_2$O$_3$ after calcination at 600°C in all samples, except sample F-6, synthesized via thermal decomposition of iron (III) citrate hydrate, where formation of additional phase Fe$_3$O$_4$ was registered, Table 1. Specific surface area of the samples varies within interval of 2.9-13.0 m$^2$/g.

Use of oxide catalyst for H$_2$S decomposition reaction requires preliminary activation of catalyst by means of H$_2$S adsorption in order to transform metal oxide into metal sulfide. Detailed study of H$_2$S adsorption on the catalysts developed was performed in order to clarify the process of sulfidation of metal oxide. These experiments were fulfilled at the temperature of 600°C in order to decrease the contribution of the H$_2$S decomposition reaction in the experiments. Main results on the H$_2$S adsorption on bulk Fe$_2$O$_3$ catalysts are given in Fig. 1 showing dependence of H$_2$S conversion (X$_{H2S}$, %, left axis) and quantity of hydrogen produced due to H$_2$S decomposition reaction (C$_{H2}$, vol.%, right axis) on the magnitude $\rho$. Value $\rho$ at which a steady level of H$_2$S conversion is achieved, can characterize the duration of catalyst activation. At the beginning of the experiments H$_2$S conversion attained value near 100%. Meanwhile, hydrogen was not registered in the reaction mixture. Thus, it can be concluded that almost all hydrogen sulfide is quantitatively adsorbed and interacted with the catalyst. After certain period of time, different for each catalyst, the increase of H$_2$S concentration in reaction mixture with simultaneous
increase of hydrogen concentration is observed. It is obvious that chemical transformation of a catalyst proceeds during H₂S adsorption by formation of a new phase which is active in H₂S decomposition reaction. Indeed, XRD registered sulfidation of the catalysts with formation of iron sulfide after reaction (Table 1, Fig. 2). It is interesting to note that duration of catalyst activation for the samples studied is different. The longest activation period was registered for the sample F-7 prepared via thermal decomposition of ammonium iron(III) dihydrocitrate citrate, while the shortest – for the sample F-4 prepared via thermal decomposition of iron(III) oxalate pentahydrate.

Fig. 1. Dependencies of H₂S conversion and quantity of H₂ produced (vol.%) on different bulk Fe₂O₃ catalysts (see Table 1). ρ represents amount of H₂S supplied (mmole) related to the 1 g of the sample.

Fig. 2. XRD patterns of bulk F-1 catalyst: a – fresh catalyst, b – catalyst after activity test.
Calculated reaction rates of H\textsubscript{2} formation according to the decomposition reaction H\textsubscript{2}S → H\textsubscript{2} + S on bulk Fe\textsubscript{2}O\textsubscript{3} catalysts are given in Fig. 3. Histogram of reaction rate of H\textsubscript{2} formation related to the 1 g of the sample (mole H\textsubscript{2}/s·g) demonstrates that Fe\textsubscript{2}O\textsubscript{3} catalyst synthesized via thermal decomposition of iron(III) nitrate nanohydrate (F-1) is the most effective. Essential decrease of specific surface area of the samples after activity test (down to ∼ 0 for F-6 and F-7) is observed (Table 1). The sample F-5 synthesized via thermal decomposition of ammonium iron (III) oxalate trihydrate demonstrates the highest thermal stability in respect to specific surface area. Although the catalysts F-1, synthesized via thermal decomposition of iron (III) nitrate nanohydrate, exhibited the highest activity in H\textsubscript{2}S decomposition reaction, the ammonium iron (III) oxalate trihydrate was chosen for the preparation of supported catalysts in order to exclude emission of toxic nitrogen oxides which are formed during iron (III) nitrate nanohydrate decomposition. Moreover, the sample F-5 synthesized by the use of Fe(NH\textsubscript{4})\textsubscript{3}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}·3H\textsubscript{2}O shows sufficiently high activity in H\textsubscript{2}S decomposition reaction and demonstrates the highest thermal stability in respect to specific surface area.

**Supported spherical catalysts**

Phase composition of spherical catalysts depends on the content of iron introduced and type of support material used (Table 2). Phase of α-Fe\textsubscript{2}O\textsubscript{3} was registered in the catalysts supported on α-alumina and zirconia, while active component in the catalyst F-8b (9.7%Fe/γ-Al\textsubscript{2}O\textsubscript{3}) was recognized as the solid solution of Fe\textsuperscript{3+} in γ-Al\textsubscript{2}O\textsubscript{3}.

Activity of the catalysts supported on γ-Al\textsubscript{2}O\textsubscript{3} and α-Al\textsubscript{2}O\textsubscript{3} depends significantly on the content of active component, Fig. 4. Reaction rate of H\textsubscript{2} formation decreases with increase of Fe content in the sample for catalysts supported on γ-Al\textsubscript{2}O\textsubscript{3}. Highest activity demonstrates catalyst F-8 with Fe content equal to 2.9%. On the contrary, increase of Fe content from 3.1 to 4.1% in the catalyst F-9 leads to increase of the catalyst activity.

Formation of iron sulfide (Fe\textsubscript{7}S\textsubscript{8} or Fe\textsubscript{1-x}S) was registered in the samples after H\textsubscript{2}S decomposition for all catalysts supported both on γ- and α-Al\textsubscript{2}O\textsubscript{3}. The catalyst F-8a (4.6%Fe/γ-Al\textsubscript{2}O\textsubscript{3}) is the only exception. Transformation of oxide active component to iron sulfide leads to change of catalyst colour from beige (F-8) or orange (F-9) to black colour. Significant decrease of specific surface area of the samples supported on γ-Al\textsubscript{2}O\textsubscript{3} is observed.

Activity data for Fe-containing catalysts supported on various materials (γ-Al\textsubscript{2}O\textsubscript{3}, α-Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, SiO\textsubscript{2}) and calcined at 600°C are presented in Fig. 5. Increase of H\textsubscript{2}S conversion with temperature rising from 600 to 900°C is observed. Meantime, the catalysts deposited both on γ-Al\textsubscript{2}O\textsubscript{3} and α-Al\textsubscript{2}O\textsubscript{3} demonstrate the highest level of activity. Formation of iron sulfide after activity test is registered for catalysts supported on γ-Al\textsubscript{2}O\textsubscript{3}, α-Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} materials.
whereas decrease of specific surface area is observed for all catalysts (Table 2).

Modification of the samples F-8 (2.9%Fe/γ-Al₂O₃) and F-9 (4.1%Fe/α-Al₂O₃) was performed to increase their activity. According to XRD analysis, modification of catalysts by manganese leads to formation of additional β-Mn₂O₃ phase compared with phase composition of initial catalysts (Table 2). Modification of F-8 by molybdenum does not change phase composition of the catalysts. XRD registers γ-Al₂O₃ similarly to initial F-8 catalyst. In turn, modification of F-9 sample by molybdenum changes significantly phase composition of the catalyst: interaction of Fe with Mo occurs leading to the formation of Fe₂MoO₄ or Fe₂(MoO₄)₃ phases. However, activity data, presented in Fig. 6, allows to conclude that modification of the samples F-8 and F-9 by Mn and Mo results in decrease of the catalyst activity, although formation of MnS and MoS₂ is observed after activity test according to XRD data (Table 2).

**Supported monolith catalysts**

To clarify the influence of catalyst geometry on its activity in H₂S decomposition process, comparative analysis of activity data for different catalysts was made: bulk Fe₂O₃ catalyst F-5, supported spherical F-8, F-9 and supported monolith catalysts F-8/B, F-9/B (Fig. 7). Activity of supported spherical catalysts (F-8 and F-9) exceeds activity both of bulk and supported monolith catalysts. But it is necessary to emphasize that content of introduced active component (Fe) in the catalysts compared varies within wide range: 70 wt.% for bulk Fe₂O₃ catalyst and less than 1 wt.% for supported monolith catalysts. In order to consider this fact, reaction rates of H₂ formation reaction related to the 1 g of introduced Fe were compared. It is seen that picture is changed significantly. Supported monolith catalysts show superior activity compared with bulk and supported spherical catalysts, Fig. 7.

Results described above were devoted to the study of catalysts in H₂S decomposition reaction. However, besides H₂S, COG contain substantial amount of ammonia. Therefore, independent experiments on decomposition of ammonia by the use of monolith F-9/B catalyst were performed. In order to elucidate the behavior of catalysts in the presence of H₂S and NH₃,
activity of fresh catalysts was compared with activity of catalyst tested preliminary in H2S decomposition reaction at the temperatures of 600→900→600°C. It was found that 100% ammonia conversion on the fresh supported monolith catalyst is observed starting from 750-800°C, whereas for catalyst after de-H2S test – starting from 900°C, Fig. 8. Monolith catalyst demonstrated stable operation in de-NH3 process at 900°C for 2 hours.

Conclusions

Fe-based catalysts of different geometry are developed for the purification of coke oven gases: bulk, supported on alumina and supported on alumina silicate monoliths.

Adsorption and decomposition of H2S reaction were studied on bulk Fe2O3 catalyst and Fe(NH4)3(C2O4)3·3H2O salt was chosen as the best starting material to be used for the synthesis of supported catalysts. Fe-containing catalysts supported on alumina show highest level of activity in H2S decomposition process compared with Fe-containing catalysts supported on ZrO2 and SiO2. It was found that modification of Fe-containing catalysts by Mn and Mo leads to the decrease of the catalyst activity.

Monolith catalysts synthesized show superior activity in de-H2S process over bulk and spherical catalysts when reaction rates of H2 formation related to 1 g of Fe introduced are compared. It was revealed that monolith catalysts demonstrate stable operation in ammonia decomposition process during 2 hours at 900°C giving 100% ammonia conversion.

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