



Structural and textural properties of $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts and their importance in the catalytic reforming of CH_4 with H_2S for hydrogen production



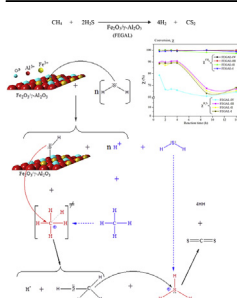
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HIGHLIGHTS

- $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts may be suitable for hydrogen production.
- Hydrogen production depends on Fe^{3+} ions with tetrahedral sites into $\gamma\text{-Alumina}$.
- Structural properties of impregnated $\gamma\text{-Alumina}$ can be seen by RDFs.

GRAPHICAL ABSTRACT



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ABSTRACT

Newer catalysts for the methane reforming with H_2S are designed, which are based on $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, nanocrystalline $\gamma\text{-Al}_2\text{O}_3$ supports, and 1.0 to 6.0 wt% Fe. The main phases are identified as hematite and $\gamma\text{-Al}_2\text{O}_3$, with sizes of about 2–4 nm. The structural features are characterized by X-ray diffraction, Rietveld's Refinement and Radial Distribution Function analysis. The textural properties of these catalysts are determined by N_2 sorption and surface fractal dimension calculations. Also, the electronic states are inferred by Mössbauer and UV–Vis (diffuse reflectance) spectroscopies. The activity of $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts in the methane reforming is tested in a fixed bed type reactor. Further calculations indicate that $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts go through a charge transfer decrease, which depends on the iron content, i.e., from 1.08 to 0.88 eV; Mössbauer spectroscopy reveals that Fe^{3+} ions adopt a tetrahedral coordination, which coincides with their higher activity for hydrogen production, with respect to catalysts having octahedral coordination. The specific surface area of these catalysts is about $84 \text{ m}^2 \text{ g}^{-1}$, with a mean pore diameter of 2.5 nm. A mechanism for the methane reforming with H_2S is proposed herein.

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1. Introduction

Recently, shale oil and gas recovery increased substantially as a

consequence of newer fracking technologies application [1,2], which has modified the trends in natural gas (NG) and oil production in the U.S.A [3]. Now, forecasts indicate that P2 type reserves of natural gas will increase further in the near future [4,5]. The NG is commonly composed of methane and minor amounts of light hydrocarbons, CO_2 , mercaptans and hydrogen sulfide (H_2S), mainly. Thus, continued production of larger volumes of gas will bring massive amounts of impurities associated with, in particular

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H₂S, which is toxic and deleterious for downstream processes in the oil and gas industries [6]. For example, it causes catalyst deactivation, pipes corrosion, valves and storage tanks, with economic losses in general. Additionally, the increase of gas production will require additional infrastructure for sulfur recovery from H₂S in refineries and gas production centers. In contrast with these drawbacks, from a chemical viewpoint H₂S affords a potential for hydrogen recovery, as it holds one molecule of hydrogen per molecule of H₂S. Furthermore, significant amounts of H₂S are produced by HDS and from separation gas sweetening processes [7,8]. These acid streams are treated commonly by the Claus process [9] for sulfur recovery, according to the overall reaction $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$, where $1/3\text{H}_2\text{S}$ is partially oxidized to SO₂, then it reacts with $2/3\text{H}_2\text{S}$, to produce sulfur and water. However, in this process the hydrogen associated to H₂S molecule is transferred to wastewater. Alternatively, hydrogen recovery is possible from H₂S by means of hydrocarbons reforming, a reaction that yields molecular hydrogen and carbon disulfide, i.e., $2\text{H}_2\text{S} + \text{C}_n\text{H}_{2n+2}$ Structural and textural properties of Fe₂O₃/γ-Al₂O₃ catalysts and their importance in the catalytic reforming of CH₄ with H₂S for hydrogen production → nCS₂ + (n+2)H₂; in particular, methane reforming is given by $2\text{H}_2\text{S} + \text{CH}_4 \rightarrow \text{CS}_2 + 4\text{H}_2$, which yields one molecule of carbon disulfide (CS₂) and four molecules of hydrogen with minor amounts of side products having carbon-bonded sulfhydryl groups (–C–SH or R–SH). These reactions are highly endothermic, i.e., $(\Delta H^0)_{298\text{K}} = 232.4 \text{ kJ mol}^{-1}$, though do not produce greenhouse gases (CO and CO₂) [10] as the conventional steam methane reforming (SMR) does [11]. This alternate route minimizes a waste and it produces a valuable chemical agent, i.e. CS₂, which is currently used as a substrate for enhancing enzyme activities and it is a raw material for cellophane and rubber fabrication, and it is a potential source for sulfuric acid production. Also, CS₂ can be a source of liquid hydrocarbons within the gasoline range, i.e., $\text{CS}_2 + \text{H}_2 \rightarrow -[\text{CH}_2-]_n + 2\text{H}_2\text{S}$ [12,13], where the H₂S produced can be recycled. In a previous study, a pinch-point analysis was done by Aspen HYSYSTEM simulation methods for determining the conditions of minimal carbon production at equilibrium conditions [14]. Therefore, temperature is the major factor affecting methane conversion, i.e., at $T > 1073.15 \text{ K}$ the conversion is 100% for all the H₂S/CH₄ ratios, while the temperature for maximum carbon formation is at about 973 K. The carbon pinch-point decreases with increasing feed ratio, i.e., for $\text{H}_2\text{S}/\text{CH}_4 \leq 4$ the formation of carbonaceous soot occurs easily, which influences the hydrogen production negatively, the opposite effect occurs with higher H₂S/CH₄ ratios. These reactions are promoted by vanadium oxides and sulfides, which were reported by some authors [15], who performed H₂S removal from the product for shifting the equilibrium conversion. Also, manganese nodules were used for H₂S decomposition, with a reaction order of 0.5 [16]. Earlier research work used silica beads (532 CP), cobalt molybdate (HR-801) and even 1% pre-sulfided platinum (182 CP) type catalysts, which enhanced the reaction rate, where cobalt-molybdate catalyst were the most active ones [17–20]. The bond dissociation energies of Fe–O and Fe–S materials are 409 and 339 kJ mol^{–1}, which are intermediates with respect to other non Fe-based materials as ZnO and ZnS₂, which have dissociation energies of 284.1 and 205 kJ mol^{–1}, while ZrO and ZrS have energies of about 760 and 575 kJ mol^{–1} respectively. Thus, the Fe-based materials are potential catalysts for producing high purity hydrogen via Redox type cyclic mechanism, i.e., by the Steam-Iron process, which uses water as the oxidant and some reducers like CO, CO₂ [21,22] or glycerin [23] for the zero-valence Fe species regeneration. Moreover, hydrogen production from water and Fe in the presence of HS[–] anions as catalysts seems to occur under mild hydrothermal

Table 1Lattice parameters of Fe₂O₃ (Hematite) structure utilized in Rietveld refinement.

Fe ₂ O ₃ R–3C (167)			Lattice: Rhombohedral			Occupancy
			Atomic fractional coordinates			
Atom	Type	Site	x	y	z	
Fe (1)	Fe ³⁺	6b	0.0000	0.0000	0.0000	0.1667
Fe (2)	Fe ³⁺	6a	0.0000	0.0000	0.2500	0.1667
O (1)	O ^{2–}	18d	0.5000	0.0000	0.0000	0.5000
Lattice parameters			Angles			Density (g cm ^{–3})
a	b	c	α	β	γ	
5.0356 Å	5.0356 Å	13.7489 Å	90°	90°	120°	5.270

conditions, with formation of FeS and FeO as the intermediates [24]. Therefore, the present study is focused on designing a catalytic system based upon Fe₂O₃/γ-Al₂O₃ catalysts (FEGAL¹) for the acid gas (H₂S) reforming of methane, which could also involve the formation of HS[–] type species and other metal sulfide phases, that could promote conversion altogether. Also, among the methods used for determining the textural properties, Frenkel-Halsey-Hill and Box-counting were employed.

2. Experimental

2.1. Catalysts preparation

Nanocrystalline γ-Al₂O₃ support (GAL) was synthesized by the sol–gel method as follows [25]: A vessel containing an ethanol/water solution (1:2 M ratio) with stirring was heated up to 353 K, then 1/3 mol of Aluminum sec-butoxide (Strem Chemicals, Inc. 98%) was added by drop-wise during 1 h. After gelling, solids were dried in air at 373 K overnight and calcined at 773 K for 4 h (2° min^{–1}). FEGAL catalysts were prepared by the incipient wet impregnation method, using a solution of Fe(NO₃)₃·9H₂O (Sigma–Aldrich, 98%) to obtain 1.0, 2.5, 3.5 and 6.0 wt.% Fe on GAL support. Afterwards, the solids were dried at 353 K for 17 h and annealed at 723 K for 4 h at 2° min^{–1}.

2.2. Characterization

2.2.1. X-ray diffraction and Rietveld refinement

X-ray diffraction patterns were obtained with a Bruker Advance D-8 diffractometer with the Bragg–Brentano θ–θ geometry, using CuKα radiation and a Lynxeye type detector. The intensities were obtained in the 2-theta ranges between 10 and 100° with a step of 0.019447° and a measuring time of 264 s per point. The crystalline structures were refined by the Rietveld method using TOPAS-Academic software [26]. For Fe₂O₃ structures (Table 1), a rhombohedral lattice of 301.928 Å³ with thirty atoms, a Fe:O ratio of 2:3 and a space group R–3C (167) [27]; for γ-Al₂O₃ structures (Table 2), eighty atoms, Al:O ratio of 2:3 and cubic lattice of 494.914 Å³ and space group Fd3m (227) data were employed [27].

The theoretical crystal density (Tables 1 and 2) was calculated by the following equation [28]:

$$\rho_{\text{Crystal}} = \frac{(Z)(MM)(\text{Avogadro's number})^{-1}}{\text{Cell_volume}} \quad (1)$$

where Z is the number of molecules per cell and MM is the molecular weight.

¹ A list of symbols and acronyms utilized in this work is provided just above the References.

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