Porous iron and ferric oxide pellets for hydrogen storage: texture and transport characteristics

Karel Soukup, Jan Rogut, Jacek Grabowski, Marian Wiatowski, Magdalena Ludwik-Pardala, Petr Schneider, and Olga Šolcová

Abstract—Materials for hydrogen storage based on the recovery reduction of Fe₃O₄ to iron and back iron oxidation to Fe₂O₃ by water vapor were studied. The preparation conditions for cylindrical pellets from ferric oxide/aluminium oxide powders were optimized on the basis of experimental textural data as well as on mechanical stability of prepared pellets. The optimal calcination temperature of pellets suitable for steam iron process was found to be 850 °C. Transport parameters for Fe₂O₃/Al₂O₃ and Fe/Al₂O₃ samples, which can be utilized for optimization of porous structure for hydrogen storage, were determined by the chromatographic technique in the single pellet-string arrangement.

Keywords—Hydrogen storage, Steam iron process, Transport parameters, Inverse gas chromatography.

I. INTRODUCTION

Hydrogen storage is one of the hydrogen economy problems because of the lack of safe, efficient and low cost storage methods. So far, three main ways are used: liquefaction, compression and use of solid adsorbents (carbon nanotubes, activated carbon, fullerenes, absorbing alloys and metal hydrides based on Mg, Na, Li, B, etc. [1]). These methods have weak points: liquefaction is economically very demanding owing to the necessary cryogenic system; a serious safety problem is connected with hydrogen compression; and solid adsorbents can adsorb only a small amount of hydrogen.

There exists another, long known approach for hydrogen storage which is based on the steam iron process [2] in which the recovery reduction of Fe₃O₄ to iron and back iron oxidation to Fe₂O₃ by water vapor [3]–[7] is applied:

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2 \leftrightarrow 3\text{Fe} + 4\text{H}_2\text{O} \]  

(1)

In this method, theoretical amount of hydrogen stored as Fe metal is 4.8 wt. %. At high temperature and pressure the reaction equilibrium is shifted to the right (i.e. hydrogen storage), at lower temperature and pressure the equilibrium is shifted to the left (i.e. hydrogen recovery). High repeatability of these cycles can be achieved by addition of various additives to iron. The very clean produced hydrogen (no CO traces) is suitable for fuel cells and the system is cheap and safe.

Fe₂O₃ is a precursor from which iron and Fe₃O₄ is obtained. Therefore, we have tried to prepare porous pellets of Fe₂O₃ and Fe with the use of Al₂O₃ (α-alumina) as a suitable additive and studied their textural and transport characteristics. The information on pellets texture was obtained from nitrogen physical adsorption isotherms and mercury porosimetry. True pellets densities followed from helium pycnometry. Pellets transport characteristics were studied by the chromatographic method in the single-pellet-string column arrangement (SPSC) [8].

II. EXPERIMENTAL

A. Preparation of Fe₂O₃/Al₂O₃ composite powders

Composite Fe₂O₃/Al₂O₃ samples with 1:1 Fe/Al molar ratio were prepared as follows: first, the Al₂O₃ sample (POCh Gliwice, Poland) was grinded in the agate mill for 3 hours to obtain fine alumina powder. In a typical case 404 g of Fe(NO₃)₃·9H₂O was dissolved in hot demineralised water and 51 g of Al₂O₃ fine powder was mixed for approximately 10 minutes in 200 ml hot demineralised water. Then, the solution of Fe(NO₃)₃ was added into the mixed Al₂O₃ suspension and 225 g of 25 % ammonia was continuously poured with the rate 1 cm³/s. The Fe(OH)₃ precipitation process on the Al₂O₃ support was carried out according to the equation:

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2 \leftrightarrow 3\text{Fe} + 4\text{H}_2\text{O} \]
Fe(NO$_3$)$_3$ + 3 NH$_4$OH → Fe(OH)$_3$ + 3 NH$_4$NO$_3$  \hspace{1cm} (2)

The prepared solution was gelated slowly and thereafter the product was mixed for 10 minutes. The prepared solution was drained off in a Buchner funnel for 5 hours; the resulted sediment was washed with water and afterwards dried at 150 °C. The brown hydrated particles of contaminated Fe(OH)$_3$ were grounded in the quern mill and calcined in a muffle furnace at 1000 °C until the brown smoke of NO$_x$ disappeared. The powder was cooled at ambient temperature and washed with 5 l of water, dried and calcined at 1000 °C again. The composite was grounded in the agate mill after cooling and then sieved to fraction with grains diameter below 0.063 mm. The larger grains were grounded again. 82 g of Fe$_2$O$_3$/Al$_2$O$_3$ powder was prepared by this technique. The SEM photo of prepared Fe$_2$O$_3$/Al$_2$O$_3$ particles is shown in Fig. 1. Black clusters represent ferric oxide. The white clusters correspond to alumina. From Fig. 1 a good homogeneity of the prepared mixture of Fe$_2$O$_3$/Al$_2$O$_3$ can be recognized.

B. Preparation of cylindrical pellets Fe$_2$O$_3$/Al$_2$O$_3$

Mechanically stable cylindrical pellets of Fe$_2$O$_3$/Al$_2$O$_3$ (5 x 5 mm = diameter x height) were prepared from powdered mixture of aluminium oxide and ferric oxide. 77.55 g of the powdered sample was mixed with 11.08 g binder (based on a form of silica: Glazura Pw 137, Glazura s.r.o., Czech Republic). Water suspension was prepared by adding 71 ml of distilled water; the water suspension was thoroughly stirred for approximately 90 min and poured into 124 cylindrical holes (5 x 5 mm height/diameter) drilled into a stable plastic disc with a syringe. Pellets were then manually pressed out of the holes using a metallic piston. The pellets were dried by evaporation overnight at room temperature and finally, calcined with temperature gradient 2 °C/min in air at 550 °C (denoted as Sample 1), 700 °C (Sample 2), 850 °C (Sample 3) and 950 °C (Sample 4) for 10 minutes. The total number of prepared porous pellets was approximately 350.

C. Preparation of Fe/Al$_2$O$_3$ pellets

Fe$_2$O$_3$/Al$_2$O$_3$ pellets calcined at 850 °C (Sample 3) were reduced at 800 °C for one hour by hydrogen, which was sufficient for complete reduction of Fe$_2$O$_3$.

D. Pellets characterization

For high-pressure mercury porosimetry the porosimeter AutoPore III was used. Nitrogen adsorption isotherms were obtained with ASAP 2020. True (helium) density was determined with the AccuPyc 1330. All instruments are from Micromeritics, USA.

Textural properties are summarized in Table I, where $T_e$ denotes calcination temperature, $S_{BET}$ is the internal surface area determined from the classic BET isotherm, $V_{micro}$ is the micropore volume obtained from the modified (three parametric) BET isotherm and finally, $\varepsilon$ denotes the porosity calculated from the apparent density and the true density as $\varepsilon = 1 - \frac{\rho_{app}}{\rho_{true}}$.

Pore-size distributions for the samples calcined at various temperatures obtained by mercury porosimetry are depicted on Fig. 2.

![Fig. 1 SEM image of prepared Fe$_2$O$_3$/Al$_2$O$_3$ powders](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_e$ [°C]</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{micro}$ [mm$^3$/g]</th>
<th>$\varepsilon$</th>
<th>Mechanical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>550</td>
<td>6.7</td>
<td>1.7</td>
<td>0.46</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>18.2</td>
<td>4.3</td>
<td>0.66</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>850</td>
<td>17.5</td>
<td>4.2</td>
<td>0.66</td>
<td>++</td>
</tr>
<tr>
<td>4</td>
<td>950</td>
<td>0.4</td>
<td>0.7</td>
<td>0.08</td>
<td>+++</td>
</tr>
</tbody>
</table>
The inverse gas chromatography setup consists of a chromatographic column, a thermal conductivity detector (Micro-TCD 10-955, Gow-Mac Instruments Co., USA), calibrated mass flow-meters/controllers (Brooks 5850S, Brooks Instruments, the Netherlands), six port sampling valve (sample volume 250 μl) with an electric actuator (Valco Instruments Co. Inc., USA). Two columns with lengths 100 cm and 50 cm and identical inner diameter (0.67 cm) were packed either with ferric oxide (Fe₂O₃/Al₂O₃) or reduced (Fe/Al₂O₃) pellets. All chromatographic measurements were performed at laboratory temperature and pressure. Argon, nitrogen and helium were selected both as carrier and tracer gases. Five different carrier gas flow rates were used: 30, 60, 90, 150 and 250 cm³/min.

Approximately 3000 response points from the TCD detector were recorded on a digital data logger. After zero-line correction (less than 0.1 % of the maximum response height) about 90 uniformly distributed experimental points were normalized to the maximum of the tracer concentration. The final response signals were obtained by averaging three individual peaks for each carrier gas flow rate and carrier/tracer pair of gases. The transport characteristics were evaluated from averaged response signals.

### III. RESULTS AND DISCUSSION

From the textural and mechanical stability results summarized in Table I it can be clearly seen that Sample 4 prepared under the highest calcination temperature (950 °C) revealed the hardest solid structure. However, its basic texture properties represented by the surface area and porosity were the worst due to the sintering process which took place during the calcination. On the other hand, Sample 1, prepared under the lowest calcination temperature, was unsuitable for hydrogen storage owing to its very low mechanical stability. Samples 2 and 3 have similar texture properties (see Table I and Fig. 2); Sample 3 possesses, however, higher mechanical stability. On account of both textural and mechanical properties, Fe₂O₃/Al₂O₃ (Sample 3, calcined at 850 °C), as well as the reduced form of this pellet (Fe/Al₂O₃), were selected for the chromatographic evaluation of transport characteristics (see Table I). Textural properties of Fe/Al₂O₃ pellets are summarized in Table II.

![Pore-size distribution curves](image)

**Fig. 2** Pore-size distribution curves for all tested samples. (—): Sample 1 (calc. 550 °C); (— — —): Sample 2 (calc. 700 °C); (—— —): Sample 3 (calc. 850 °C); (—): Sample 4 (calc. 950 °C)

#### TABLE II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total intrusion volume</th>
<th>ρ₁₀₀</th>
<th>ρ₅₀</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 3</td>
<td>0.6339</td>
<td>4.037</td>
<td>1.039</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The effective diffusion coefficients of all tracer/carrier gas pairs in columns packed both with pellets Fe₂O₃/Al₂O₃ and Fe/Al₂O₃ were computed from corresponding diffusion times, \( t_{0/ν} \), obtained by time-domain fitting of column responses. An algorithm of this parameter evaluation can be found elsewhere [9]–[12]. The effective diffusion coefficients include a contribution from the Knudsen diffusion mechanism as well as the bulk (molecular) diffusion mechanism according to the Bosanquet formula [13]:

\[
\frac{1}{D_{IC}} = \frac{1}{\langle r \rangle \psi K_T} + \frac{1}{\alpha_{IC} \psi \phi_{IC}^{∗}}
\]

with the binary bulk diffusion coefficients of the pair C–T, \( \phi_{IC}^{∗} \), and transport parameters \( \langle r \rangle \psi \), \( \psi \) and \( \alpha \) [14] (\( \langle r \rangle \) is the integral mean transport-pore radius, and \( \psi \) is the ratio of transport-pore porosity and tortuosity). \( K_T \) is the tracer Knudsen coefficient defined as:

\[
K_T = \frac{2}{3} \sqrt{\frac{8 R_T}{\pi M_T}}
\]

with the universal gas constant, \( R_T \), temperature, \( T \), and tracer molecular weight, \( M_T \). Equation (3) can be rearranged into a form, which permits easy graphical solution:

\[
t_{0/ν} = \frac{d_p}{2} \frac{\varepsilon}{\langle r \rangle \psi} + \frac{d_p}{2} \frac{\varepsilon}{D_{IC} \psi \phi_{IC}^{∗}}
\]

where \( d_p \) denotes the equivalent sphere diameter (diameter of the sphere with the same ratio of outer surface and volume as the pellet); \( \varepsilon \) is the sample porosity.
Transport parameters $\langle r \rangle \psi$ and $\psi$ were evaluated from the slope and intercept of the straight线 $t_{\text{diff}} K_{T}$ versus $K_{T} \tau_{m}^{\infty}$, according to (5) (see Figs. 3 and 4). The obtained transport parameters and the mean transport-pore radii $\langle r \rangle \psi = \left( \langle r \rangle \psi \right)^{\psi}$ are summarized in Table III.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\langle r \rangle$</th>
<th>$\psi$</th>
<th>$\langle r \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$</td>
<td>18.5</td>
<td>0.052</td>
<td>355.8</td>
</tr>
<tr>
<td>$\text{Fe/Al}_2\text{O}_3$</td>
<td>28.2</td>
<td>0.090</td>
<td>313.3</td>
</tr>
</tbody>
</table>

As can be seen from Table III the mean transport pore radii, $\langle r \rangle$, of both $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe/Al}_2\text{O}_3$ samples are similar (355.8 nm and 313.3 nm, respectively), but the parameter $\psi$, which includes porosity of transport pores, is higher for the metal containing sample (0.090 in comparison with 0.052 for oxidic sample). Thus, $\text{Fe/Al}_2\text{O}_3$ pellets have a rather higher porosity of transport pores than $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ pellets, which is in agreement with porosity data from the textural analysis (compare Tables I and II). On the other hand, the changes of transport and texture characteristics taking place during the iron oxide reduction (see (1)) are not too high, which is quite significant for the use in the hydrogen storage process (according to the targets defined by the U.S. Department of Energy a viable method for storing hydrogen on board of a vehicle must be able to repeat hydrogen storage cycle at least 500 times [15]).
with the pore-size distribution (PSD) obtained from a high-pressure mercury porosimetry. As can be seen the mean transport pore radii are positioned approximately in the middle between the PSD peaks. It follows, that the gas diffusion transport takes place predominantly through rather wider pores.

![Figure 6](image)

Fig. 6 Comparison of the pore-size distribution curves (from high-pressure mercury porosimetry – solid line) with mean transport-pore radii (from SPSC method) for Fe/Al₂O₃ sample

IV. CONCLUSIONS

Four types of cylindrical pellets consisted from ferric oxide/aluminium oxide powders were prepared under different calcination temperatures. From the textural data it is clearly seen that the influence of calcination temperature on textural properties as well as on the mechanical stability of tablets is very significant — this fact points to the importance of the calcination temperature during the preparation of cylindrical pellets. Sample 4 prepared at the highest calcination temperature (950°C) shows the hardest solid structure of all samples. However, this sample was almost without pores due to the sintering process which takes place under these conditions. On the other hand, Sample 1 prepared at 550°C exhibited a very soft structure, which limits its use in the hydrogen storage process. Both Samples 2 and 3 possess very similar textural properties but Sample 3 reveals better mechanical stability. Therefore, Sample 3 was chosen as an appropriate testing material for hydrogen storage experiments.

Transport parameters of the Fe₂O₃/Al₂O₃ sample (Sample 3) and the Fe/Al₂O₃ sample obtained by chemical reduction were evaluated by the chromatographic technique in the single pellet-string arrangement. Owing to that, these transport parameters are material constants of porous solids and, hence, independent of the nature of used gases, as well as of temperature and pressure. They can be used for estimation of the effective diffusion coefficients for any tracer/carryer gas pairs. This fact opens the possibility of the direct utilization of the estimated transport characteristics for optimization of porous structure in materials used for hydrogen storage.

REFERENCES