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Characterization of Fe/C catalysts supported on Al₂O₃, SiO₂ and TiO₂

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Abstract. Structural and magnetic properties of Fe/C catalysts synthesized by ball milling and deposited onto Al₂O₃, SiO₂ and TiO₂ supports are reported. Ball milling α-Fe and C in the presence of these supports produced peculiar solid solutions in which antiferromagnetic and ferrimagnetic iron phases doped with Al, Si and Ti coexist. Mössbauer spectroscopy and powder X-ray diffraction data show no evidence of any FexC phase. Instead, oxidation took place even though carbon (graphite) was present. All the catalysts were found to exhibit strong metal-support interactions, with the strongest interactions found in the TiO₂ supported catalyst.

1. Introduction

Most commercial catalysts are made of transition metals deposited onto oxide carriers – referred to as supports, with which they interact [1]. These interactions are referred to as metal-support interactions (MSI). The interest in supports stems from the fact that transition metal-support interfaces have proven to be better catalysts than transition metals alone [1,2]. Commonly used supports include metal oxides such as Al₂O₃, CeO₂, SiO₂, MgO, TiO₂ and ZrO₂ as well as activated carbon and carbon nanotubes. The supports are primarily responsible for the stabilization of the catalysts. They affect also the performance of the catalysts during the Fischer-Tropsch synthesis (FTS) [2,3]. Hence, knowledge of the characteristics and properties of the supports is of primary importance in catalysis.

There are currently renewed interests in fundamental studies on MSI and in preparation methods driven by the need of stabilizing nanoparticles of various metals in solutions. Traditional methods of preparation of supported catalysts include impregnation, precipitation, evaporative deposition, sol-gel, etc. Recently, novel methods such as microwave synthesis [4] and ball-milling [5,6] were also used to deposit metals on various supports. In this study ball-milling is used to deposit Fe/C onto Al₂O₃, SiO₂ and TiO₂ supports. Ball milling has proven to be a powerful method to prepare metastable crystalline, amorphous phase and nanostructured alloys through solid state reactions [7,8], thus making it a valuable option for depositing metals on supports. The strengths of MSI in Fe/Al₂O₃, Fe/SiO₂ and Fe/TiO₂ and the effects of C on these interactions are investigated.

2. Experimental

The ball-milling was performed using a Spex CertiPrep 8000M mixer/mill high-energy ball mill operating at 1080 cycles/minute. Each sample was milled for 20 hours in air with a ball-to-powder weight ratio (BPR) of 20:1. The milling was done continuously for 90 minutes followed by 90 minutes of non-activity to cool the machine. The starting materials were elemental powders of α-Fe (99.99%) and carbon, as well as powders of Al₂O₃ (99.9%), SiO₂ (99.9%) and TiO₂ (99+ %). The mole ratios of Fe:C:M were 9:3:2 where M stands for Al, Si and Ti. The samples obtained were labelled Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. Characterisation methods include X-ray diffraction (XRD), Mössbauer spectroscopy (MS), magnetometry, thermogravimetric analysis (TGA) and temperature programmed reduction (TPR). MS was performed in zero-field and in an external magnetic field (B_{app}).

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of 10 T applied parallel to the γ-ray direction. Temperature and applied field dependencies of the dc-magnetization were measured using a Quantum Design SQUID MPMS XL 7AC generating magnetic fields up to 7 T.

3. Results and discussion

Figure 1 shows typical MS spectra of the samples recorded at 4.2 K in an applied magnetic field $B_{app} = 10$ T. The magnetic field dependence of the magnetization at a fixed temperature of 15 K is shown in Figure 2. The room temperature MS data (not shown) featured prominent central doublets for all the samples superimposed to distributions of the hyperfine magnetic fields ($B_{hf}$). The MS parameters of the doublets were characteristics of Fe$^{3+}$ species yielding about 15, 52 and 16 % in Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. They were ascribed to small crystallites in a superparamagnetic state. The distributions of hyperfine magnetic fields were probably caused by distributions of crystallite sizes.

MS data recorded at 4.2 K in $B_{app} = 10$ T revealed the presence of hematite ($\alpha$-Fe$_2$O$_3$) in all the samples yielding about 34, 18 and 40% of Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. Ti-doped hematite, $\alpha$-Fe$_{2-x}$Ti$_x$O$_3$, was found to be a major phase (53%) in Fe/C/Ti. Both $\alpha$-Fe$_2$O$_3$ and $\alpha$-Fe$_{2-x}$Ti$_x$O$_3$ exhibited typical antiferromagnetic responses to $B_{app}$ parallel to γ-rays. A decrease in $B_{hf}$ was observed for $\alpha$-Fe$_{2-x}$Ti$_x$O$_3$ caused by the substitution of Fe by Ti. The XRD data (not shown) showed the presence of residual Al$_2$O$_3$ in Fe/C/Al and Ti$_2$O$_3$ in Fe/C/Ti. Spinels in the form of Al-doped magnetite Fe$_{3-x}$Al$_x$O$_4$, Si-doped magnetite Fe$_{3-x}$Si$_x$O$_4$ and Ti-doped maghemite γ-Fe$_{2-x}$Ti$_x$O$_3$ were found in Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. Their relative contents amounted to 66, 82, and 17% for Fe$_{3-x}$Al$_x$O$_4$, Fe$_{3-x}$Si$_x$O$_4$ and γ-Fe$_{2-x}$Ti$_x$O$_3$, respectively. They exhibited typical ferrimagnetic responses to $B_{app}$. XRD data showed that $x \approx 0.04$ for Fe$_{3-x}$Si$_x$O$_4$. The substitution of Fe by Al, Si and Ti resulted in a noticeable decrease of $B_{hf}$ on the octahedral (B) sites. Similar results were also previously reported for Al-doped Fe$_3$O$_4$ [9] and Ti- and Sn-doped γ-Fe$_2$O$_3$ [10]. No divalent iron component was detected in Fe/C/Ti. The MS parameters of γ-Fe$_{2-x}$Ti$_x$O$_3$ were consistent with those previously reported at 10 K for γ-Fe$_2$O$_3$ doped with 8% Ti in $B_{app} = 8$ T parallel to γ-rays [10]. Small deviations from the ideal behavior were however observed: the lines 2 and 5 cancelled out on the tetrahedral (A) sites only, while small residual intensities persisted for the lines 2 and 5 on the B sites. It is believed that they were caused by spin canting effects preventing a complete alignment of the spins on $B_{app}$ as previously reported for Ti- and Sn-doped γ-Fe$_2$O$_3$ with the effects occurring on both A and B sites [10].
The formation of either inverse or mixed spinels of composition \( A_{(1-\delta)}B_{\delta}[A_{\delta}B_{(2-\delta)}]O_4 \), where A and B represent cations on the A and B sites, respectively, is usually interpreted as an indication of interactions between the active and substituting metals [11]. In spinels active metal ions can dissolve in the lattice of the support thus yielding strong cation-cation interactions via a suitable overlap of d-orbitals [1,3,11]. In addition, the electronic bonding of metal particles with oxygen atoms through M-O linkage does influence the electronic nature of the surface metal atoms and thus the catalytic behaviors [3]. The presence of Al-, Si- and Ti-doped spinels \( \text{Fe}_{3-x}\text{Al}_x\text{O}_4 \), \( \text{Fe}_{3-x}\text{Si}_x\text{O}_4 \) and \( \gamma-\text{Fe}_{2-x}\text{Ti}_x\text{O}_3 \) observed in Fe/C/Al, Fe/C/Si and Fe/C/Ti could be indicative of strong MSI.

The M vs. H curves in Figure 2 feature hysteresis effects for all the samples. Their shapes appeared to be consistent with the coexistence of antiferromagnetic and ferrimagnetic phases in the samples. Fe/C/Al and Fe/C/Si had relatively large saturation magnetization \( M_s \approx 23 \) and 19 emu/g, respectively. Saturation was not reached for Fe/C/Ti in the range of the magnetic field of the experiments \((-3 \text{ T to } +3 \text{ T})\) and the highest magnetization measured at 3 T amounted to about 1.3 emu/g. The remanence amounted to \( M_r \approx 14, 10 \) and 0.5 emu/g for Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. These gave reduced-remanence \( M_r/M_s \approx 0.6 \) for Fe/C/Al and \( M_r/M_s \approx 0.5 \) for both Fe/C/Si and Fe/C/Ti. \( M_r/M_s \approx 0.5 \) is of the order of magnitude of the value expected for an assembly of randomly oriented, single-domain particles with uniaxial anisotropy [12]. Fe/C/Al had a coercivity \( H_c \approx 0.4 \) T, Fe/C/Ti had \( H_c \approx 0.25 \) T, while Fe/C/Si had negligible coercivity \( (H_c \approx 0) \). The absence of coercivity in Fe/C/Si is due to the magnetization changing its direction almost instantaneously on the application of a reverse field. This corroborates the superparamagnetic behavior in Fe/C/Si as inferred from MS data.

Ball-milling of \( \alpha-\text{Fe} \) and C powders is known to produce iron carbide species [8] and to induce reduction of iron oxides in the presence of carbon [7]. However, the data reported in this study show that oxidation had prevailed during ball-milling. No Fe\(_x\)C phase had formed. It appears as though C was not reactive under the ball milling conditions used in this study. To assess the role played by carbon TGA analyses were performed (Figure 3) complemented with isothermal TPR (Figure 4).

**Figure 3.** TGA profiles of a) Fe/C/Al, (b) Fe/C/Si and (c) Fe/C/Ti featuring the weight profiles (blue) and the heat flow (black)

**Figure 4.** TPR profiles of a) Fe/C/Al, (b) Fe/C/Si and (c) Fe/C/Ti.

TGA curves indicated that the samples underwent two-step weight loss process and were thermally stable up to at least 300 °C. The onset temperatures of the weight losses were approximately 310, 320 and 350 °C for Fe/C/Al, Fe/C/Si and Fe/C/Ti, respectively. The decomposition process was completed
at approximately 800 °C for all samples. The observed thermal stability could be attributed to strong MSI in the samples analyzed. MS and magnetisation measurements revealed that the degree of Fe\textsuperscript{3+} substitution in Fe/C/Ti was significantly higher compared to Fe/C/Al and Fe/C/Si leading to lower magnetisation (Figure 2). The substitution could have led to the delay of the onset of the reduction.

The TPR profiles (Figure 4) featured three reduction peaks for each sample. The origin of the first peak occurring after about 50 minutes is not well known. The second peak between 100 and 120 minutes corresponds to the reduction of Fe\textsubscript{2}O\textsubscript{3} – Fe\textsubscript{3}O\textsubscript{4} and the third much broader peak at about 145 – 300 minutes is due to the reduction of Fe\textsubscript{3}O\textsubscript{4} to Fe. The onset of the third reduction peak for Fe/C/Si was more delayed as compared to Fe/C/Al and Fe/C/Ti most probably due to the presence of small iron crystallites. Fe/C/Si exhibited the most broad 3\textsuperscript{rd} reduction peak, Fe/C/Ti was the most difficult to reduce (higher H\textsubscript{2} uptake) and Fe/C/Al the easiest (lower H\textsubscript{2} uptake). The degree of reducibility of oxides is determined to a certain extent by MSI [2]. Hence, it is speculated that the reducibility of the samples is indicative of the strength of MSI and that Fe/C/Ti had the strongest MSI followed by Fe/C/Si, while Fe/C/Al appeared to have weaker MSI. This is consistent with previous studies reporting that TiO\textsubscript{2} exhibits stronger MSI as compared to Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, it interacts strongly with most transition metal elements [1,11].

4. Conclusion
In this study, the ball milling technique was used to deposit α-Fe and C onto Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2} and TiO\textsubscript{2} supports. This produced peculiar solid solutions in which antiferromagnetic and ferrimagnetic (spinsels) iron phases doped with Al, Si and Ti coexisted. However, the data reported in this study show oxidation had prevailed during the ball-milling process. No Fe\textsubscript{3}C phase had formed. It appears as though C was not reactive under the ball milling conditions used in this study. The catalysts were found to exhibit strong metal-support interactions, with the strongest interactions found in the TiO\textsubscript{2} supported catalyst. The formation of spinsels, together with the presence of vacancies and defects expected to be generated during the ball milling process, make this technique suitable for adding active metal(s) onto supports. Interest in spinsels arises also from the fact that the near-surface position of the A sites and low coordination of Fe\textsuperscript{3+} increase the activity of the catalyst in FTS [1].

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