catalysts

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Supplementary Materials

The role of carbon nanotube deposit in catalytic activity of FeOx-based PECVD thin films tested in RWGS reaction

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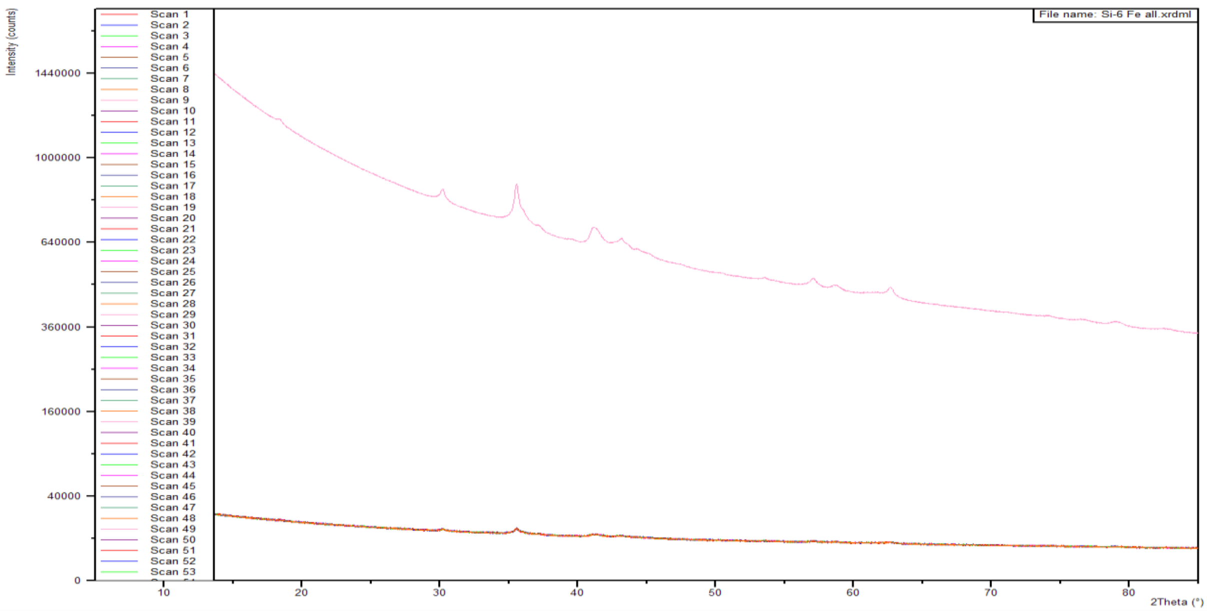
Scheme 1. X-ray diffraction (XRD)

0.1FeOx



0.3FeOx

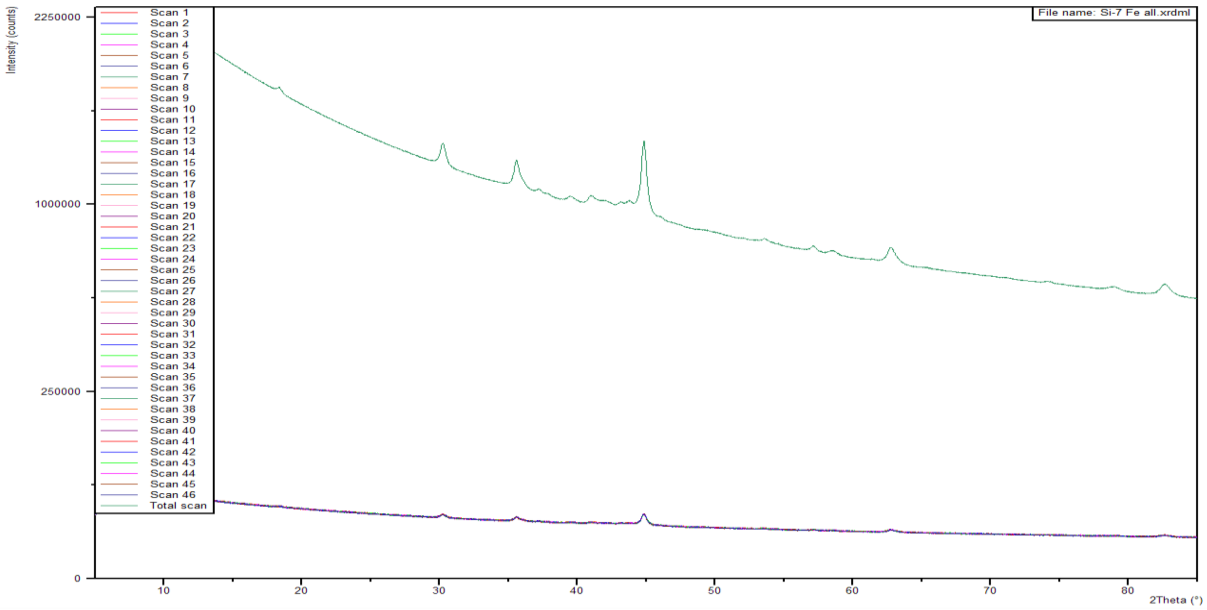


Figure S1. Raw XRD patterns for 0.1FeOx and 0.3FeOx films indicate, in both cases, the possible presence of an amorphous fraction containing nanocrystalline structures.These structures are analyzed in the article.

Scheme 2. RWGS reaction – thermodynamic analysis.

In this study, we conducted a thermodynamic analysis of the reverse water gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$) to determine the equilibrium CO_2 conversion (X_{CO2}). The analysis employed the total Gibbs free energy minimization method, whichallows for the calculation of equilibrium composition based on the initial reactants' composition and the operating conditions.

For this calculation, two reaction substrates, CO_2 and H_2, were fed to the reactor in a ratio of 1:4. In modeling the RWGS reaction, the following reagents were considered: CO_2, H_2, H_2O,and CO. The equilibrium composition of the outlet stream was determined under a constant pressure of 0.1 MPa while varying the temperature within the range of 423 to 773 K. The results of the analysis are presented in Figure S2, showing the mole fractions of the components as functions of temperature and the calculated equilibrium CO_2 conversion.

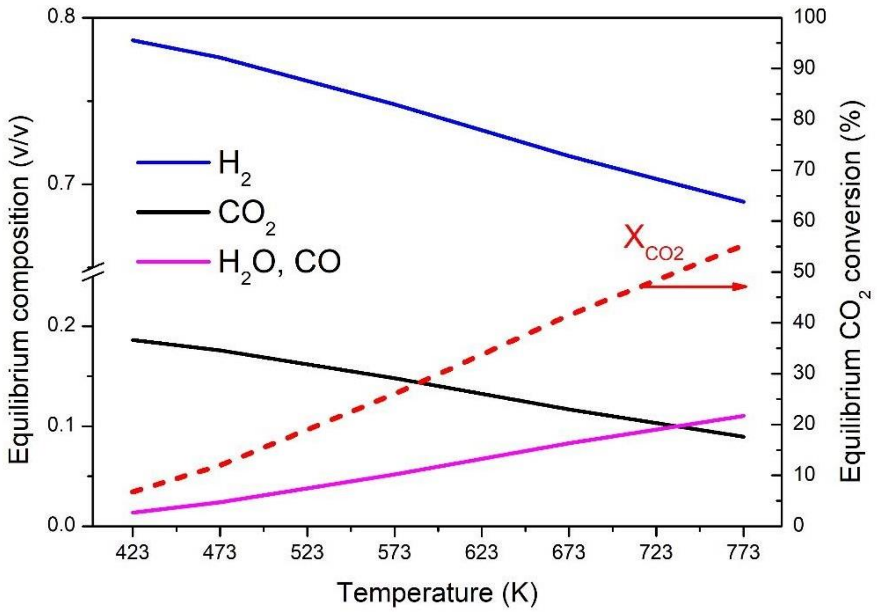


Figure S2. The equilibrium composition and CO_2 conversion as a function of temperature for RWGS reaction (0.1 MPa; H_2/CO_2=4).

As can be seen from the calculated data, the production of CO is favored at high temperatures due to the endothermic nature of the RWGS reaction. At 673 K, which isthe highest reaction temperature applied in catalytic tests, the equilibrium conversionis 41.5%.

Scheme 3. Calculation of composition of core–shell iron nanoparticle.

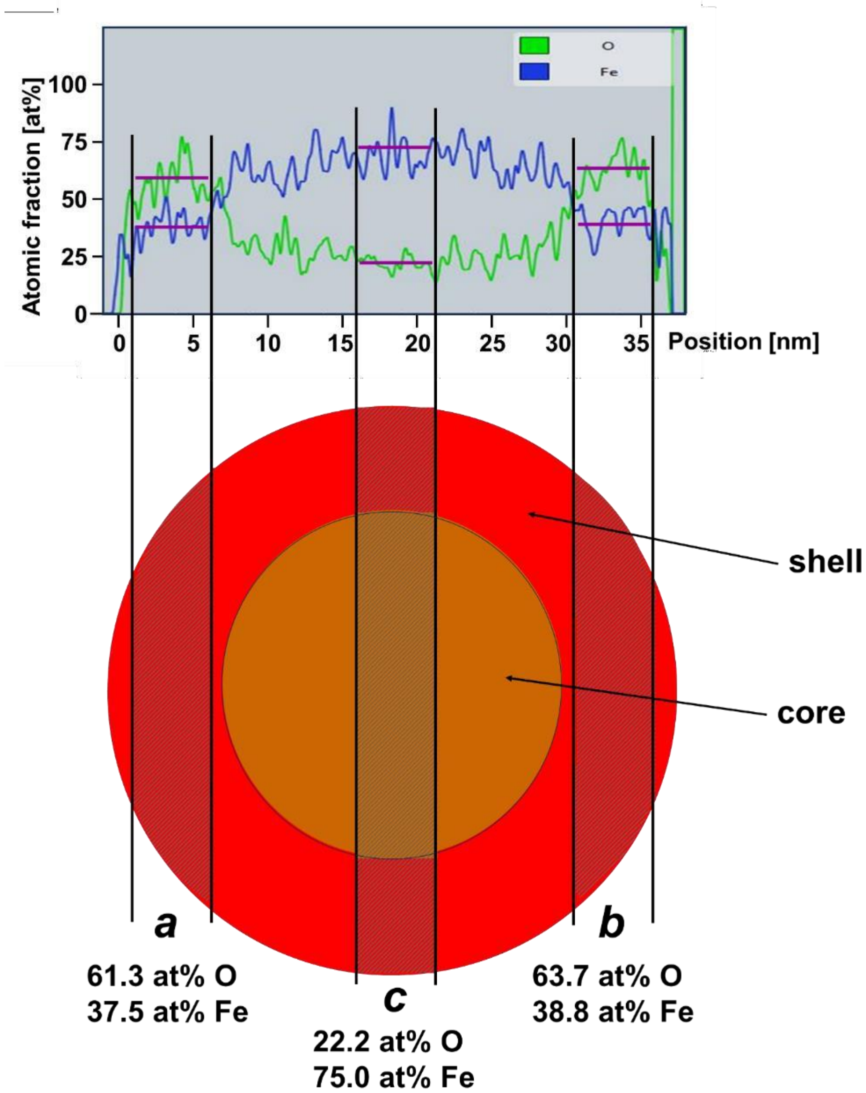


Figure S3. Nano-XRD results: atomic intensity profile of iron and oxygen along thediameter of the nanoparticle and its model with analyzed zones.

The nano-EDX measurements presented in the paper's Figures 7(a-e) reveal that the nanoparticles accompanying the carbon nanotubes are composed of an iron-rich core and an oxygen-rich shell. To precisely determine the composition of the shell andcore, an analysis was performed based on the atomic intensity profiles of iron and oxygen across the nanoparticle's diameter (Figure S3). The examined area was5 nm x 10 nm, which allowed us to measure only the shell volume (zones ***a*** and ***b***) as wellas the core volume plus two fragments of the shell volume (zone ***c***). The average ratioof oxygen and iron in the shell, approximately 1.6, aligns well with the O/Fe ratio in iron oxide Fe_2O_3, theoretically 1.5. This suggests that the shell is composed of Fe_2O_3.

Regarding zone ***c*** and assuming the shell consists of Fe_2O_3, the oxygen content determined there (22.2 at%) would correspond to 14.8 at% of iron within two fragments of the Fe_2O_3 shell (top and bottom). In this case, the iron contribution in thecore of the studied nanoparticle is 75.0 – 14.8 = 60.2 at%, which constitutes 80.3 % of alliron present in zone ***c***.

By assuming that the core and shell consist of pure iron and Fe_2O_3, respectively, the absolute number of moles of Fe within the core and shell in zone ***c*** can be calculated. The diameter of the core in the investigated nanoparticle is around 23 nm, and the thickness of the shell is about 6 nm. The volumes tested in zone ***c*** are therefore as follows:

- for the shell (top and bottom): 2 x 6 nm x 5 nm x 10 nm = 600 nm^3.
- for the core: 23 nm x 5 nm x 10 nm = 1150 nm^3.

Using the density of iron (7.66 g/cm^3), the density of Fe_2O_3 (5.34 g/cm^3), the atomic weight of iron (56 g/mol), and the molecular weight of Fe_2O_3 (160 g/mol), calculationswere performed to find that the analyzed core volume contains 1.57×10^{-19} mol of Fe, while both regions of the shell contain 0.4×10^{-19} mol of Fe. This calculation demonstrates that the core comprises 79.7 % of the iron present in zone ***c***, closely matching the nano-EDX measurements (80.3 %), thereby confirming the hypothesis that the core of the nanoparticle is composed of pure iron.