

Fig. 6. Evolution of activity of FeO as function of the temperature in reducing gas atmosphere (a) 100% H_2 , (b) 80% H_2 + 20%CO, (c) 50% H_2 + 50%CO, (d) 100% CO.

Fe_3O_4 than reducing oxides such as CaO and MgO. In fact, most of the changes in average maximum activity occurred at a temperature of 950 °C in different atmospheres for Fe_3O_4 . It is noteworthy that at a certain temperature of 950 °C, the lowest average value of the maximum activity of iron, Fe_3O_4 and FeO occurs when the reduction takes place in an atmosphere of 100% H_2 . In other words, if you increase the amount of H_2 in the reduction atmosphere, the average maximum activity of iron, Fe_3O_4 and FeO at 950 °C increases. It is important to mention that at this particular temperature of 950 °C, increasing the CO content in the reduction atmosphere has a stronger influence on the increase in Fe_3C production than increasing the H_2 content.

The scatter matrix for the reduction rates can be found in Fig. 13. First of all, it is obvious that the activity of all iron oxides and pure iron is mainly influenced by the CO fraction (in direct correlation) and by the H_2 fraction (in inverse correlation). In addition, the activity of Fe_3C is mainly influenced by the CO content (in direct correlation) and by the H_2 content (in inverse correlation). As for the activity of manganite and FeO, the most important non-ferrous oxide with direct proportionality is CaO, while MgO is the one with the highest inverse proportionality. The activity of pure iron also depends strongly on CaO in direct proportionality and on MgO in inverse proportionality.

Fig. 14 shows the changes in Gibbs free energy of Eqs. (1) to (3) for

the production of Fe, FeO and Fe_2O_3 in the different reducing atmospheres including a mixture of H_2 and CO at 950°C for the pellets of 100% Fe_2O_3 . The Gibbs free energy is higher for all reduction equations with 100% CO than for the other atmospheres. It can be seen that the Gibbs free energy is reduced by increasing the amount of H_2 gas. It is known that the lower the amount of Gibbs free energy, the more spontaneous reactions can take place. It can therefore be seen that all reduction reactions of iron oxide take place spontaneously in the presence of various reducing gasses at 950 °C. The comparison of the Gibbs free energy of the three reactions shows that the reduction reaction of Fe_3O_4 has a minimum ΔG .

Fig. 15 shows the changes in Gibbs free energy for iron, iron oxide and Fe_3C in the different H_2 and CO atmospheres at 950°C with different iron pellet compounds. The Gibbs free energy (ΔG) is despite the reaction can be spontaneous. The negative ΔG (<0) shows that the process of the reaction is spontaneously and positive ΔG (>0) means that the process of the reaction is not spontaneously [reference]. As can be seen from Fig. 15, all Gibbs energies are negative, which shows that the reaction between the gas and the iron ore is spontaneous, but the different impurities have a small effect on the ΔG of the reaction. The more Fe_2O_3 in the composition of the pellets, the higher the ΔG . For this reason, the reaction requires more energy for the reduction process of the pellets.

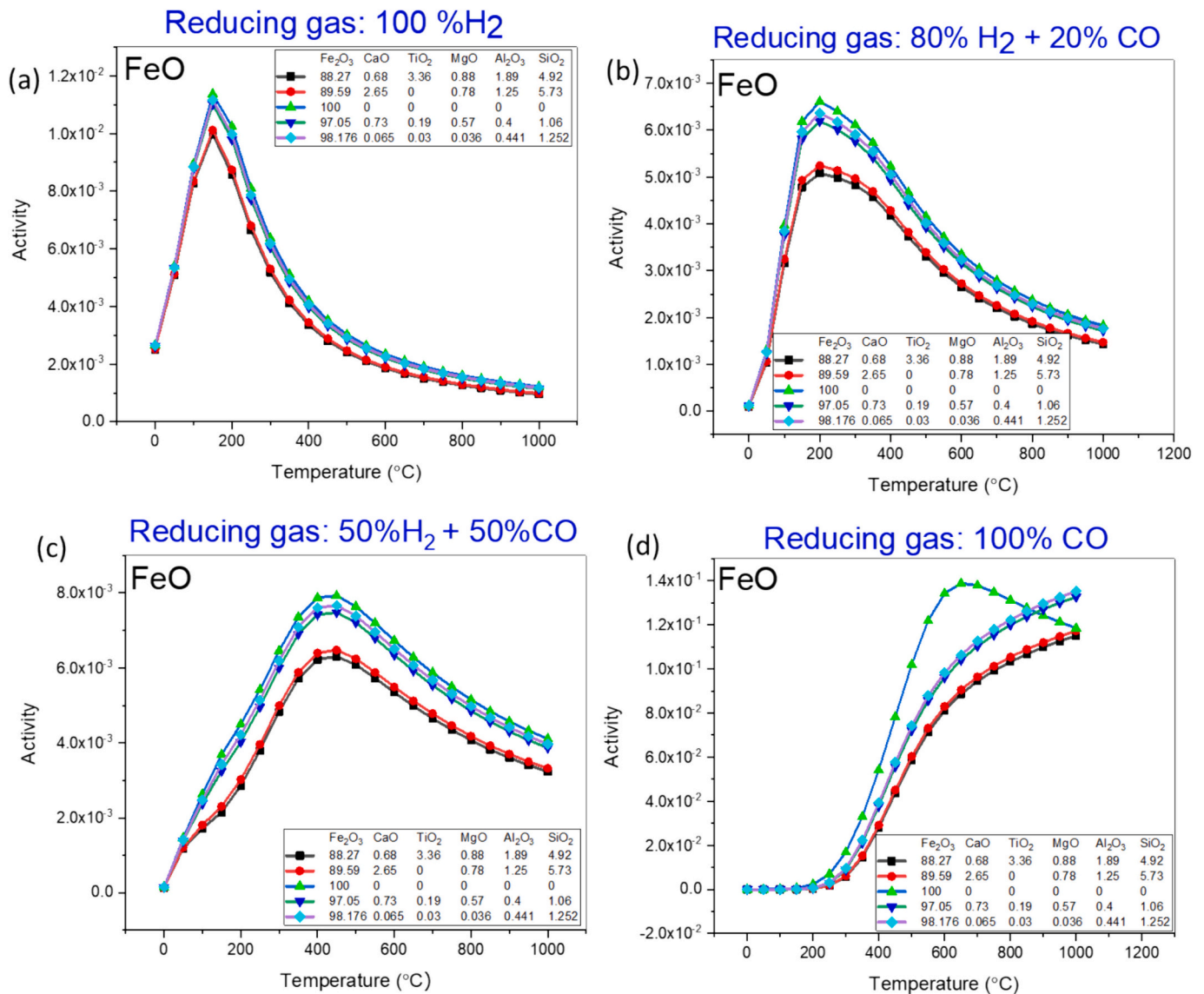


Fig. 7. The effect of CaO impurity on the evolution of FeO activity as function of the temperature in reducing gas atmosphere (a) 100% H₂, (b) 80% H₂ + 20% CO, (c) 50% H₂ + 50% CO, (d) 100% CO.

Another important factor that affects the free Gibbs energy of the different pellet compositions is the gas atmosphere. The 100% H₂ gas used for the reduction of the iron oxide is lower than 100% CO and the composition of the H₂ + CO gasses. From Figs. 9 and 15, it can be seen that the Fe₃O₄ is more stable when 100% CO gas is used for the reduction of the iron pellets, and the same condition can be seen in the ΔG when the atmosphere is changed to CO for the reduction, which increases the ΔG . This shows that the reduction process requires more energy because the stability of the Fe₃O₄ is increased by using 100% CO gas. The same results can be seen for the FeO reduction when using 100% CO for the reduction. The reduction of the iron pellets in the different atmospheres with the composition H₂ + CO and CO produces Fe₃C. The stability of Fe₃C is high at 100% CO and with increasing H₂ in the gas composition of H₂ + CO the stability of Fe₃C decreases.

3. Discussion

Considering that the presence of non-ferrous oxides in iron ore and subsequently in Fe₂O₃ pellets is unavoidable for geographical and geological reasons, the study of the effects of these impurities, especially in the direct regeneration process, is a necessity of today's technologies.

As many of these impurities are in the form of oxide compounds with low free oxide formation energies at standard reduction conditions, they tend to remain in their original state. These non-ferrous oxides, which are inherently stable due to their high melting point, can affect the overall reactivity and efficiency of the iron compounds during the reduction process. In addition, the presence of some of these non-ferrous oxide compounds has a significant impact on the metallization and efficiency of the DR process.

In general, the Blast Furnace-Basic Oxygen Furnace (BF-BOF) uses less pure iron ore, as most of the impurities are removed with the BF slag, whereas in the DR process, impurities remain in the DRI, resulting in a high slag load in the EAF. For this reason, the DR-EAF process requires the highest quality pellets with an impurity level of <5% [35]. The reducibility of iron ores depends on their composition and structure. In general, Fe₂O₃ is easier to reduce than Fe₃O₄. The solid structure of Fe₃O₄ with dense iron shells hinders rapid reduction by solid diffusion and favors slower gas diffusion. It should also be mentioned at this point that the reduction of Fe₂O₃ to pure iron is not possible even at high reduction rates, as intermediate products of iron oxides must be taken into account to accommodate practical scenarios. This is particularly important during the first stages of the reduction of Fe₃O₄, FeO and pure

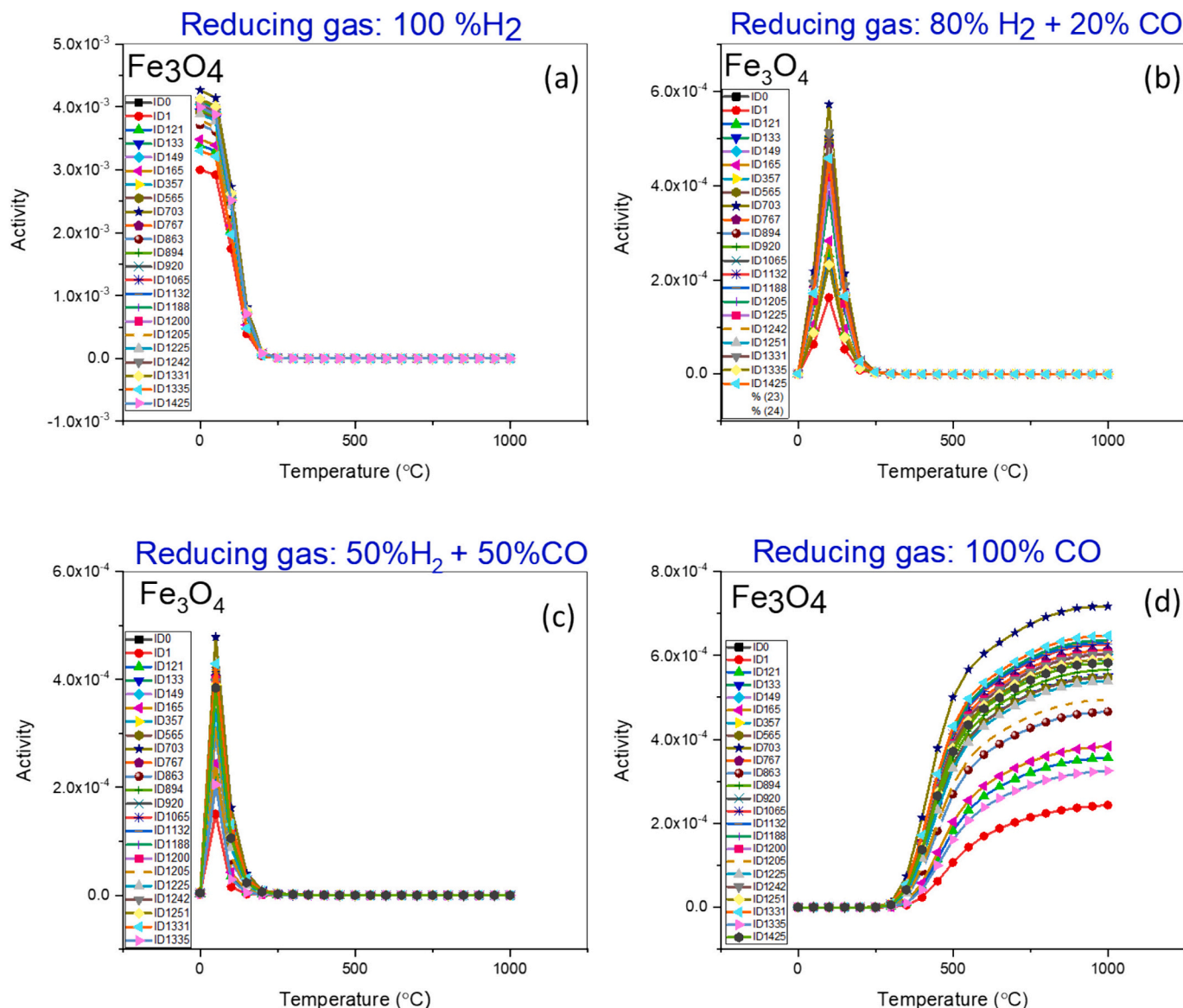


Fig. 8. Evolution of activity of Fe_3O_4 as function of the temperature in reducing gas atmosphere (a) 100% H_2 , (b) 80% H_2 + 20%CO, (c) 50% H_2 + 50%CO, (d) 100% CO.

iron, where gas diffusion acts as a rate-limiting step. In the final stages of reduction, which essentially take place at higher temperatures, where the process is usually governed by two mechanisms, namely gas diffusion and chemical reactions at the interfaces, the equilibrium quantity values for pure iron increase with increasing H_2 concentration in the reducing gas. In high temperature CO reduction processes, the presence of non-iron oxide impurities can impair and reduce the activity of reduced pure iron. These impurities can act as catalyst poisons or enter into competing reactions that can reduce the effectiveness of the reduction process and the activity of the pure iron.

The results showed a large difference in the activity efficiency of the various reduced iron compounds in the different reducing gasses above RT up to 1000 °C. From a thermodynamic point of view, the reduction of iron oxide Fe_2O_3 or Fe_3O_4 to pure iron is basically an endothermic process. In addition, CO can also react exothermically with iron oxides, producing iron and carbon dioxide.



On the other hand, H_2 is also a reducing agent but less favorable thermodynamically. The reduction of iron oxide with H_2 consumes more heat as compared to CO.



This difference in thermodynamics makes CO more effective in reducing iron oxide, resulting in a higher activity of reduced iron in a CO-rich atmosphere. As can be seen in Fig. 16, it is immediately clear how strongly the iron activity is influenced by the addition of H_2 to CO. Nevertheless, the basicity index is more influential in the case of CO reduction than in the case of H_2 reduction (Fig. 18). The presence of non-ferrous oxides in the iron pellets, such as gangue or impurities, could strongly influence the reduction behavior. The reduction of these non-ferrous oxides can also consume some of the reducing agents. CO, with its stronger thermodynamic driving force, may be more effective than H_2 in reducing iron and non-ferrous oxides. Nevertheless, H_2 has a smaller molecular size and lower viscosity compared to CO [36], which can influence mass transfer phenomena even in the presence of non-

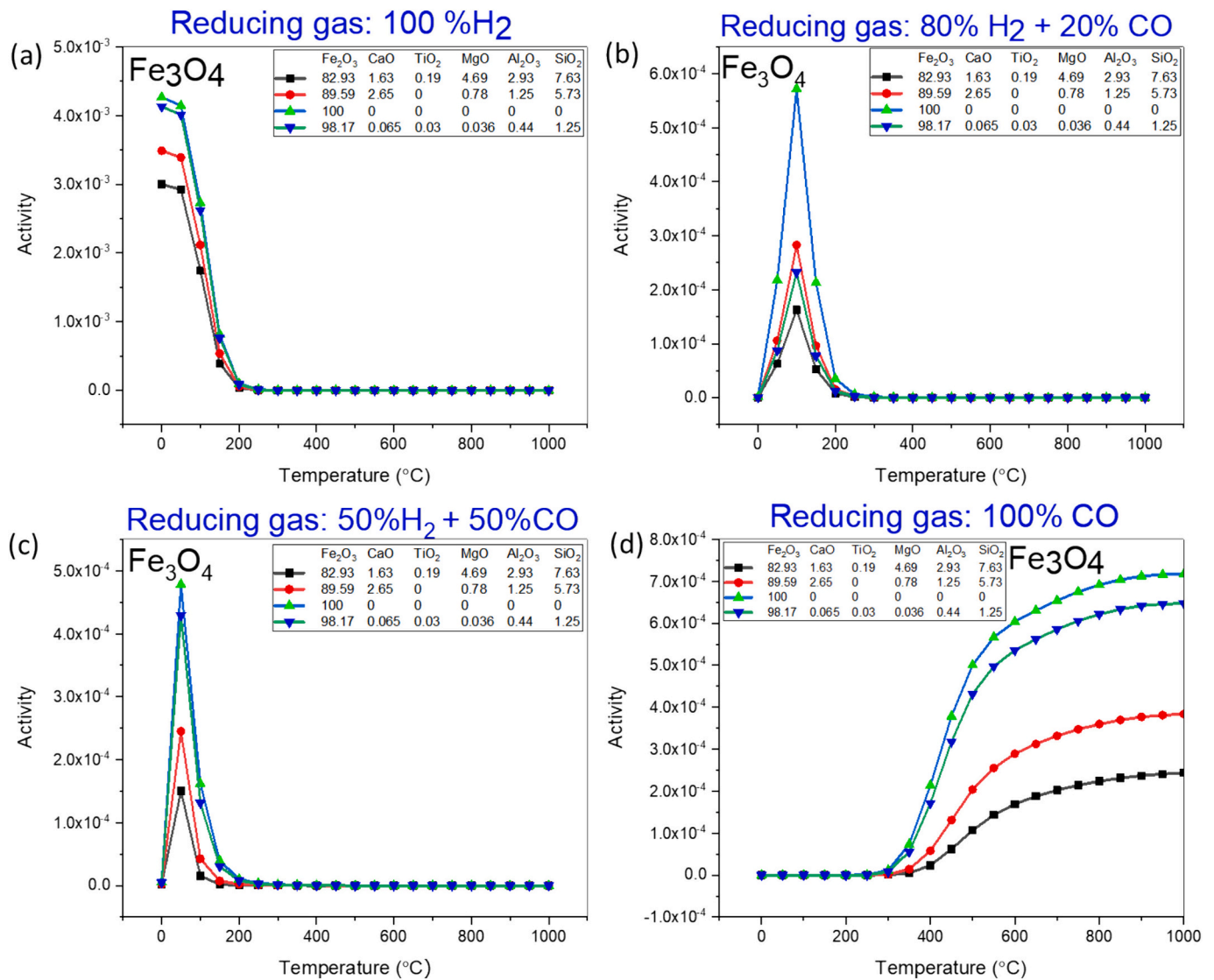


Fig. 9. The effect of oxidic impurity on the evolution of Fe_3O_4 activity as function of the temperature in reducing gas atmosphere (a) 100% H_2 , (b) 80% H_2 + 20CO, (c) 50% H_2 + 50%CO, (d) 100% CO.

ferrous oxides. Smaller molecules such as H_2 can diffuse more easily through porous materials, resulting in better penetration and contact with the iron ore particles. This can lead to efficient mass transfer during H_2 -based reduction. (See Fig. 17.)

The behavior of the reduction process seems to have a complex and nuanced relationship with the basicity index. However, when the basicity index decreases, the iron activity in the CO atmosphere increases with minimal addition of H_2 . This is in contradiction with the result reported in [37]. The reason for this behavior is that the material becomes more acidic with decreasing basicity. In the context of reduction reactions, a slightly acidic environment can promote the reduction of iron oxides. In addition, a decrease in basicity enhanced the reduction of iron catalysts, leading to the formation of metallic iron [38]. The increased acidity can facilitate the interaction between CO and iron oxides, leading to improved reduction kinetics. From a thermodynamic point of view, a decrease in basicity often correlates with an increase in the redox potential of the system. This means that iron ions are more prone to accept electrons and reduce to metallic iron. In addition, a decrease in basicity can increase the reactivity of CO so that it can reduce iron oxides more effectively to metallic iron.

From kinetic point of view, H_2 reduces pellets faster and more rapidly than CO [23,39]. In the direct reduction of Fe_2O_3 pellets, the

reduction rates of the first two reductions from Fe_2O_3 to Fe_3O_4 and from Fe_3O_4 to FeO are high, while the reduction of FeO to pure iron is extremely slow [36]. After the formation of the product phase during the heterogeneous gas–solid reactions, the reducing gas must be transported through this phase in order to reach the reacting interface. This is due to the formation of a dense iron shell in which the unreacted oxides are trapped. Consequently, the further reaction takes place via the solid-state diffusion of oxygen ions to the outer surface [40]. Both Fe_2O_3 and Fe_3O_4 can be completely reduced to Fe by a continuous injection of H_2 . This was attributed to the effect of impurities that promote the reduction kinetics by accelerating mass transfer due to the formation of liquid slag phases at high temperatures. Both Fe_2O_3 and Fe_3O_4 can be completely reduced to elemental Fe by the continuous injection of H_2 gas. This transformation is primarily accompanied by the influence of impurities that act as catalysts such as SiO_2 and accelerate the kinetics of the reduction process. This acceleration occurs by promoting efficient mass transfer mechanisms, which are facilitated by the formation of liquid slag phases at elevated temperatures [5,41].

At elevated H_2 flow rates, CaO and, to a somewhat lesser extent, MgO were found to promote the local formation of porous Fe nuclei [42]. However, the introduction of SiO_2 and Al_2O_3 additives had no discernible effect on the formation of porous Fe nuclei. This observation

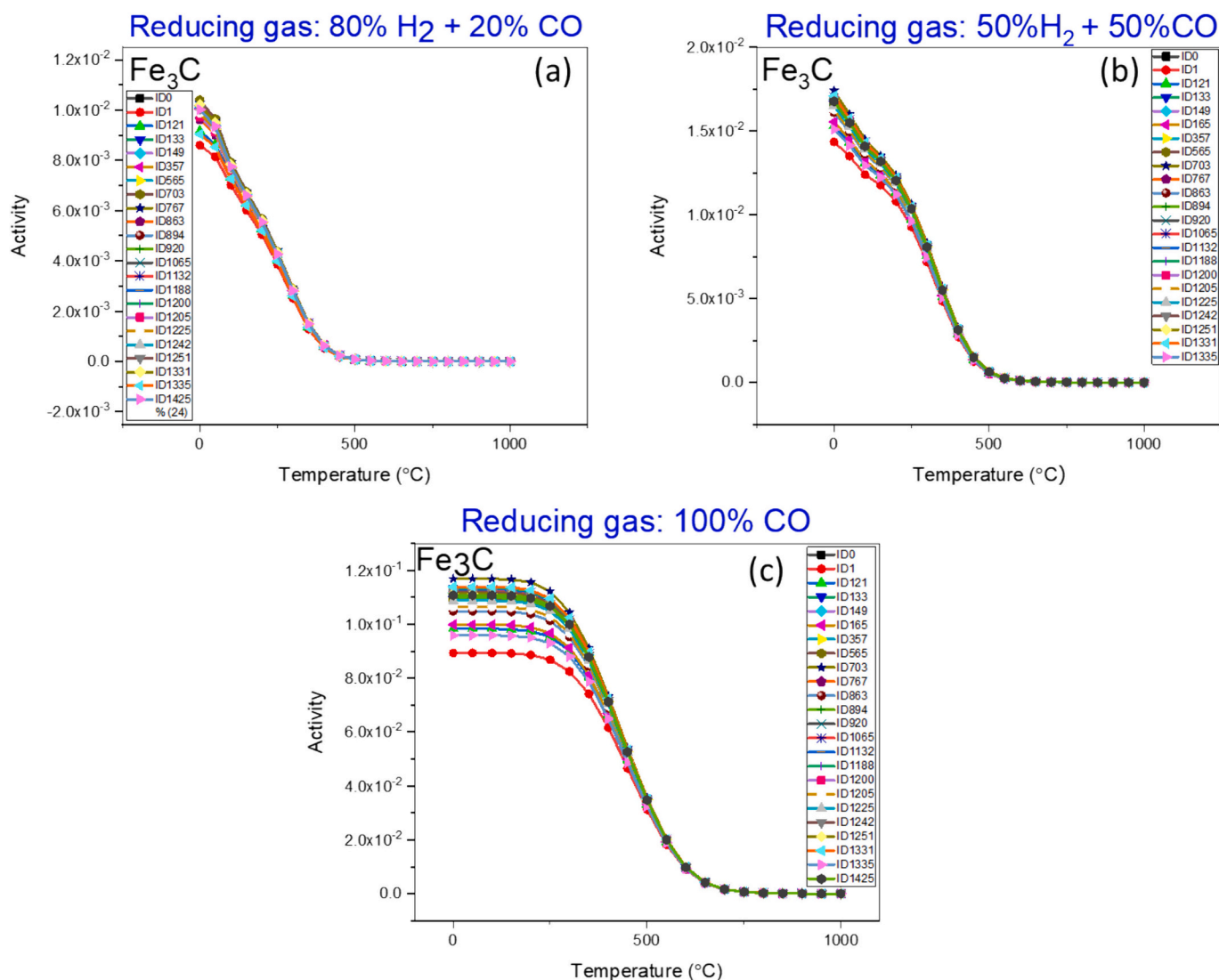


Fig. 10. Evolution of activity of Fe_3C as function of the temperature in reducing gas atmosphere (a) 80% H_2 + 20% CO , (b) 50% H_2 + 50% CO , (c) 100% CO .

suggests that CaO and MgO play a notable role in promoting the formation of porous Fe nucleus formation under high H_2 flux conditions, while SiO_2 and Al_2O_3 appear to have only a minimal effect on this particular aspect of the process.

The presence of TiO_2 as a non-ferrous oxide in the iron oxide pellets is more likely to play a role as a catalyst in the reduction of iron oxide, as it can enhance the reduction reaction by promoting the formation of CO and H_2 gasses, which are the reducing agents in this process. TiO_2 can also help prevent the reoxidation of reduced iron by reacting with the oxygen that may be present in the system. One study suggests that the presence of TiO_2 oxide can increase the reduction rate of iron oxide by promoting the formation of a liquid phase during the reduction process. This liquid phase can help to transport the reducing gasses to the surface of the iron oxide particles where they can react and reduce the iron oxide [43]. In addition, the presence of TiO_2 oxide can also increase the surface area of the iron oxide particles, which can enhance the reduction reaction as there are more active sites for the reducing gasses to react with. Overall, the exact mechanism behind the effect of TiO_2 oxide on the activity of reduced iron is not clear. However, it is hypothesized that TiO_2 oxide may enhance the reduction reaction by promoting the formation of reducing gasses, preventing reoxidation and increasing the surface area of iron oxide particles, which in turn increases the activity of reduced iron [44]. It should be mentioned that the effect of the

presence of TiO_2 together with other non-iron oxides on the direct reduction process is a complex phenomenon, so the presence of one can affect the others directly or indirectly.

With increasing temperature, using different gas compositions, including 100% H_2 , 80% H_2 + 20% CO , 50% H_2 + 50% CO and 100% CO , it was found that an increase in the silica content leads to a decrease in the activity of the FeO , Fe_3O_4 and Fe_3C compounds and consequently the reduction rates, which is also reflected in a decrease in the corresponding activity. This in turn leads to an increase in the activity of the reduced pure iron, in direct proportionality to the CO content in the reducing gas. These results were in agreement with the results reported in [45]. This decrease in the reduction rate was attributed to a decrease in pellet porosity due to the formation of iron silicates during the reduction process, as suggested in [6]. In addition to porosity, tortuosity is a critical parameter in the HyDR process that influences the diffusion and flow of gasses in porous media such as iron oxide pellets. It characterizes the complexity of the path that the gasses must take through the pellet structure, which becomes increasingly tortuous as the tortuosity increases. When temperatures rise, structural changes in the pellets can lead to increased tortuosity [6,46]. This change affects gas diffusion by increasing the length of the diffusion path and introducing more obstacles. Consequently, gas flow is impeded and permeability is reduced, which in turn reduces the uniformity of gas distribution in the