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# CARBON MONOXIDE METHANATION OVER $FeTi_{1-x}Sn_x$ INTERMETALLICS: ROLE OF SECOND PHASE

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Partial substitution of Sn in place of Ti in FeTi leads to enhanced hydrogen chemisorption and to increase in its catalytic activity for CO dissociation and methanation. Sn substitution gives rise to a dispersed second phase of $Fe_2Ti$ in the bulk and to iron cluster formation at catalyst surface. The role of secondary phase in the enhancement of catalytic activity is discussed.

## 1. Introduction

The intermetallic compounds of rare earths/actinides and of transition metals show CO methanation activity due to their decomposition into rare earth/actinide oxide and transition metal clusters [1–3]. In analogy to rare earth intermetallics, a detailed study was undertaken to evaluate the CO methanation activity of hydrogen storage material FeTi [4]. The catalytic activity of these intermetallics was found to improve on substitution of a part of iron with titanium in agreement with the ease of hydrogen activation observed over excess titanium samples. In contrast to rare earth intermetallics, no bulk decomposition was observed in the case of Fe-Ti intermetallics.

During the course of our studies on hydriding behaviour of substituted FeTi systems, it was observed that 5% Sn substitution in place of Ti facilitated the hydrogen activation though the total capacity for the hydrogen loading was found to be reduced [5]. In view of the fact that the catalytic behaviour is determined by surface characteristics and not the bulk properties, it was considered appropriate to study these Sn substituted FeTi intermetallics for CO methanation and to see the correlation between the ease of hydrogen dissociation and CO methanation activity.

## 2. Experimental

Samples of $FeTi_{1-x}Sn_x$ ($0.0 < x \leqslant 0.05$) were prepared by repeated arc melting from electrolytic grade Ti, Sn and freshly reduced Fe metal of high purity. The

ingots so prepared were annealed at about 1175 K for approximately 200 hours in evacuated and sealed quartz tubes. The ingots were crushed and sieved to get the desired particle size (between 150 and 300 mesh) for catalysis experiments. The surface area of these sieved samples was found to be $\sim 0.5$ $m^2/gm$ by nitrogen adsorption method. Three grams of a sieved sample was packed in a microcatalytic reactor to evaluate its catalytic activity for CO methanation. The catalysis experiments were conducted in two different modes. In the first mode about 40 $\mu$l pulses of CO were periodically injected into a continuously flowing hydrogen stream (25 ml/min) over the catalyst bed which was maintained at variable temperatures. In the second mode, $CO + H_2$ gas mixture (1 : 3.8 by volume) at a flow rate of 8 ml/min was continuously reacted over the catalyst. Carbon monoxide decomposition by these catalysts was studied at variable temperatures by injecting 40 $\mu$l pulses in a He stream. The effluent gases were analysed by a gas chromatograph containing a Porapak Q column and a thermal conductivity detector. The catalytic activity was also evaluated after giving successive activation/regeneration treatments to a sample. Each regeneration treatment involved heating at 625 K for two hours each in flowing oxygen and hydrogen respectively. Hydrogen absorption/desorption experiments were carried out for activated samples at variable temperature and pressure using a standard hydrogen loading apparatus [11]. Temperature programmed desorption spectra were also recorded after room temperature hydrogen exposure of the activated samples.

The catalyst samples were characterised by powder X-ray diffraction, scanning electron microscopy and $^{57}Fe$ and $^{119}Sn$ Mössbauer spectroscopy before and after catalysis experiments. Conversion electron Mössbauer spectra were also recorded to analyse the surface characteristics of these catalysts. Further details about experimental procedure etc. can be obtained from our previous publications [8,11].

## 3. Results

Figure 1(a–c) show the methanation efficiency of freshly crushed $FeTi_{1-x}Sn_x$ samples with different values of $x$ when CO pulses were injected into $H_2$ carrier gas flowing over the catalyst bed at different temperatures. The repeated regeneration of the catalyst improved their efficiency significantly. Figure 1(d–f) show similar observations for the activated samples of $FeTi_{1-x}Sn_x$ samples recorded after third cycle of regeneration treatment. From this figure it is clear that like rare earth intermetallics the Fe-Ti-Sn intermetallics are also capable of CO methanation and almost complete conversion of CO to methane occurs at about 600 K for the activated sample of $FeTi_{0.95}Sn_{0.05}$. A comparison of these data also shows that the catalytic activity is significantly improved by Sn substitution. In fact the catalytic activity of $FeTi_{0.95}Sn_{0.05}$ is found to be much higher as compared to that of $FeTi_{1.15}$ reported by us earlier [4]. The formation of higher

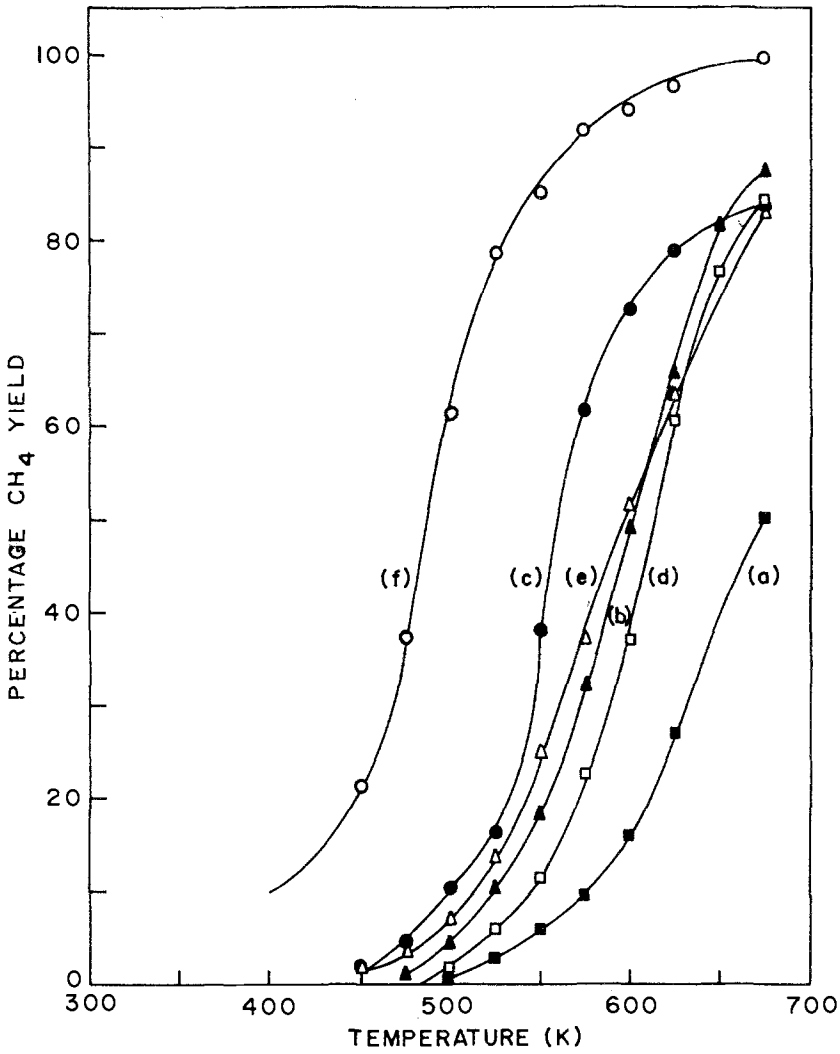


Fig. 1. Catalytic activity for CO methanation of original samples of (a) FeTi, (b) $FeTi_{0.98}Sn_{0.02}$, (c) $FeTi_{0.95}Sn_{0.05}$ and for regenerated samples of (d) FeTi, (e) $FeTi_{0.98}Sn_{0.02}$ and (f) $FeTi_{0.95}Sn_{0.05}$.

hydrocarbons such as ethane etc. if at all occured in these experiments, was below the detection limit of the gas chromatographic technique used in this study. The behaviour of $FeTi_{1-x}Sn_x$ based catalysts for CO methanation and the temperature of complete reaction are quite comparable to the results reported for supported catalysts and the rare earth intermetallics. However when a mixture of CO and $H_2$ was continuously reacted over these catalysts the activity for CO methanation was found to decrease within few minutes of time to a small value which was then sustained for long durations as was also observed in our previous study using $FeTi_{1+x}$ intermetallics.

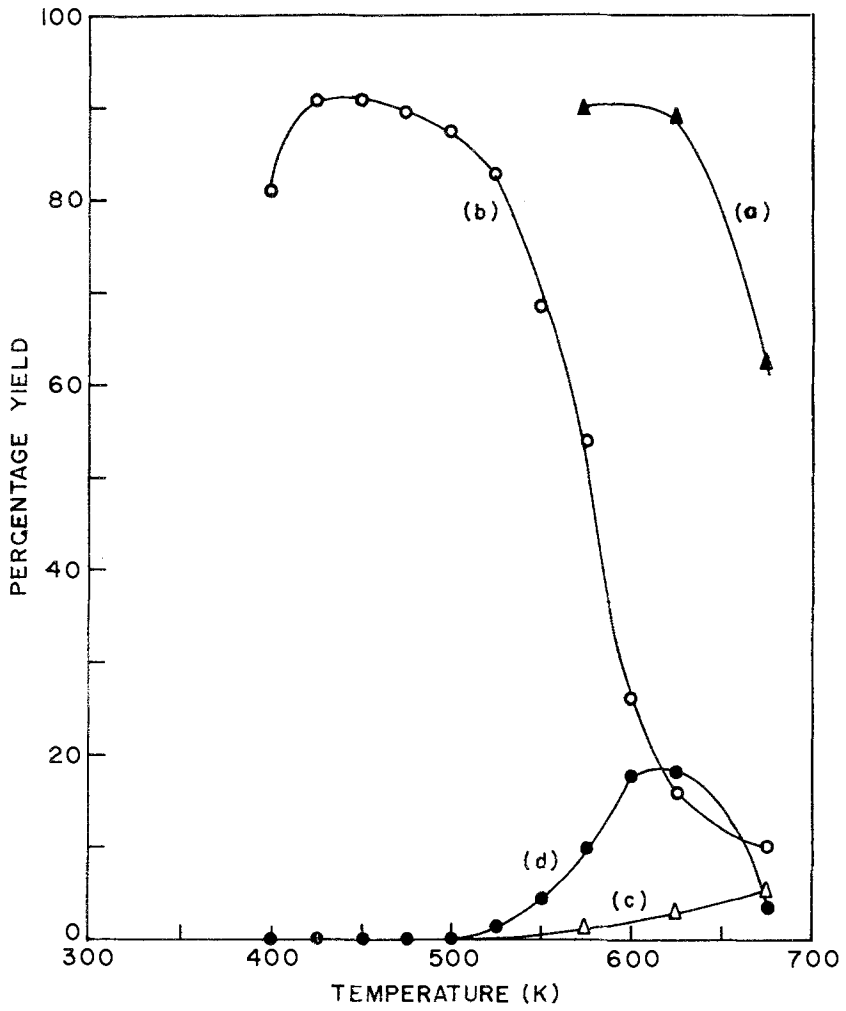


Fig. 2. CO disproportionation over activated $FeTi_{1-x}Sn_x$ samples. Amount of CO eluted for (a) FeTi and (b) $FeTi_{0.95}Sn_{0.05}$. Amount of $CO_2$ formed (c) FeTi and (d) $FeTi_{0.95}Sn_{0.05}$.

In fig. 2 the results of CO disproportionation experiment conducted at variable temperature in He stream, are reported for activated samples of FeTi and $FeTi_{0.95}Sn_{0.05}$. From this figure it is clear that the activity of $FeTi_{0.95}Sn_{0.05}$ for CO disproportionation is much higher than that of FeTi measured under identical conditions. The behaviour for $FeTi_{0.98}Sn_{0.02}$ was found to be intermediate to these two compositions which is in agreement with the CO methanation activity of these samples. The other two important inferences drawn from these studies are (i) the amount of $CO_2$ evolved is much less than the amount of CO consumed suggesting that the carbon deposition and oxygen reactions occur at the surface of the catalyst samples (ii) for $FeTi_{0.95}Sn_{0.05}$, the amount of $CO_2$ evolved above 600 K was found to be reduced appreciably (viz. fig. 2(d)) suggesting further

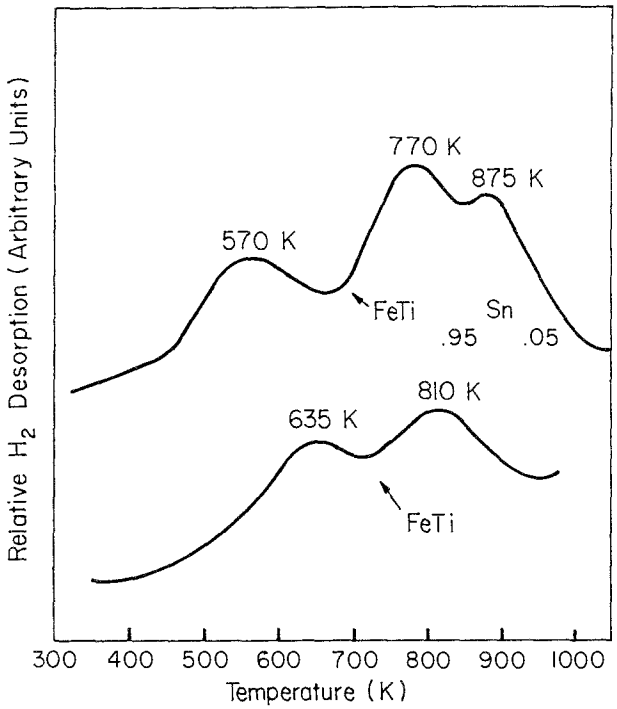


Fig. 3. Temperature programmed desorption curves for activated $FeTi_{1-x}Sn_x$ samples.

decomposition of $CO_2$. From this figure it is clear that at lower temperatures a part of CO is chemisorbed on the surface of these samples and the effect is more pronounced for Sn substituted sample.

From hydrogen storage experiments conducted on these samples, it was observed [5] that unlike FeTi which needed about twelve or thirteen cycles of activation before attaining the saturation composition of $FeTiH_{\sim 2.0}$, the $FeTi_{0.95}Sn_{0.05}$ sample attained the saturation value after second cycle of activation itself with a saturation composition of $FeTi_{0.95}Sn_{0.05}H_{\sim 1.4}$. Thus the kinetics of hydrogen dissociation and absorption is significantly improved by Sn substitution.

The results of temperature programmed desorption studies of hydrogen from the surface of activated $FeTi_{0.95}Sn_{0.05}$ are shown in fig. 3. From this figure it is clear that the total quantity of hydrogen released from $FeTi_{0.95}Sn_{0.05}$ is significantly larger than that of FeTi. The volume of hydrogen desorbed for FeTi and $FeTi_{0.95}Sn_{0.05}$ was found to be approximately 2.0 and 6.2 ml/gm respectively, which is much larger than the volume required for monolayer adsorption of hydrogen suggesting that a part of the hydrogen is coming out of the bulk $\alpha$ hydride phase of the material particularly for $FeTi_{0.95}Sn_{0.05}$. Furthermore, the desorption peaks for Sn substituted sample have shifted to lower temperatures and an additional peak is visible on higher temperature side at about 875 K suggesting the presence of additional $H_2$ adsites as has been discussed in [6].

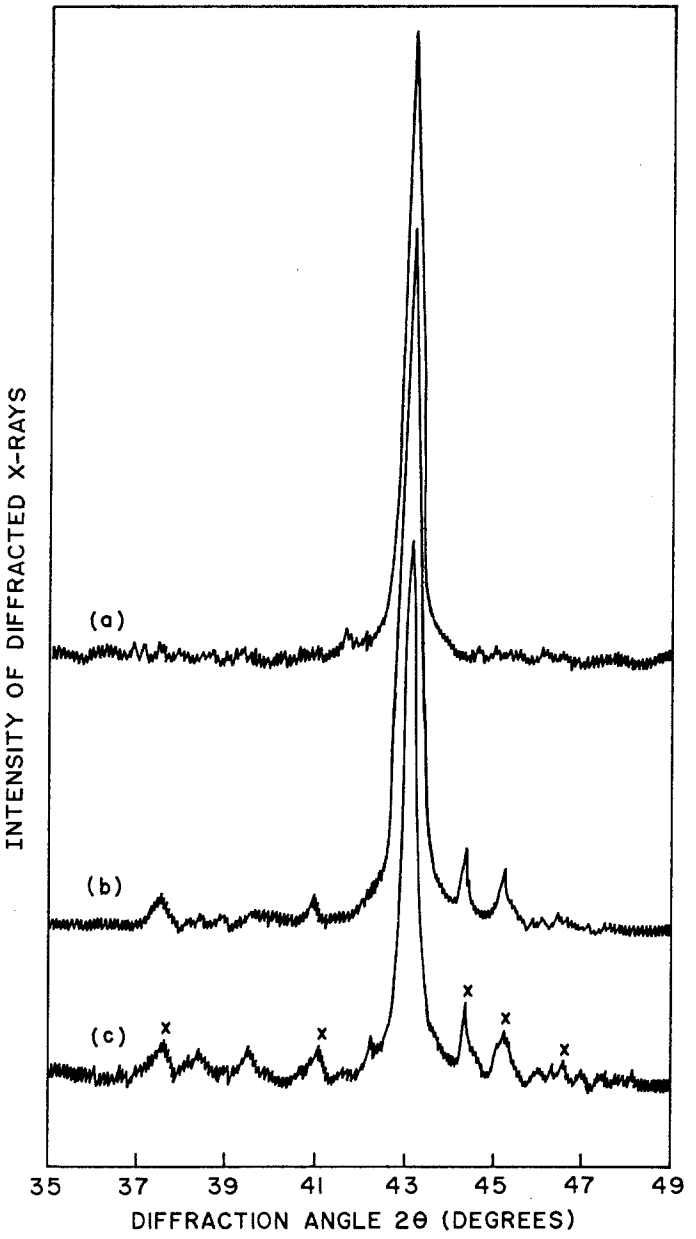


Fig. 4. Selective region of X ray diffraction patterns for (a) FeTi, (b) $FeTi_{0.98}Sn_{0.02}$ and (c) $FeTi_{0.95}Sn_{0.05}$. Additional peaks due to $Fe_2Ti$ have been marked by ×.

In fig. 4, a selective region of the X-ray diffraction pattern of $FeTi_{1-x}Sn_x$ samples is displayed. From this figure it is clear that on Sn substitution some additional lines appear in the X-ray diffraction pattern and their intensity increases with increase in Sn content. Most of these lines can be indexed in terms

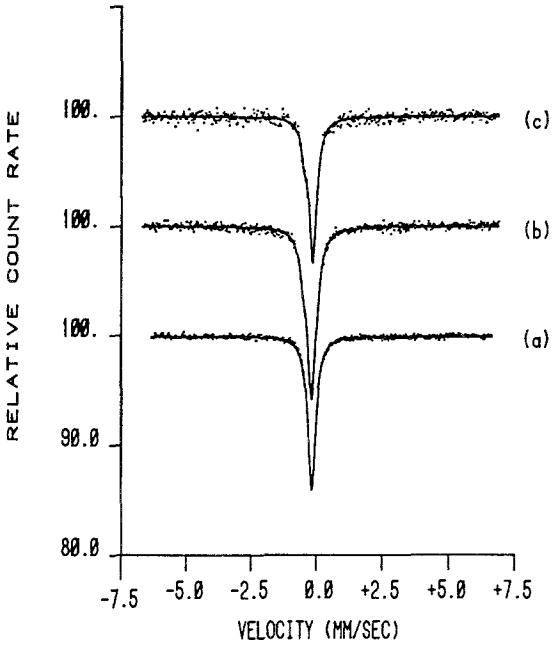


Fig. 5. Room temperature $^{57}$Fe Mössbauer spectra of (a) FeTi(b) $FeTi_{0.98}Sn_{0.02}$ and (c) $FeTi_{0.95}Sn_{0.05}$.

of $Fe_2Ti$ phase [7]. Electron micrograph of a finely polished surface showed that the second phase is randomly distributed in the bulk matrix with no specific size. Furthermore, the particles of the original crushed samples, had random shape with average size of about $75 \pm 20$ $\mu$m. The existence of $Fe_2Ti$ is also apparent from the $^{57}$Fe Mössbauer spectra of these samples shown in fig. 5. The intense single line with isomeric shift $\delta = -0.13$ mm/sec with respect to Fe metal at room temperature corresponds to FeTi and the Less intense doublet with $\delta = -0.27$ mm/sec and $\Delta E_q = 0.36$ mm/sec corresponds to $Fe_2Ti$. $^{119}$Sn Mössbauer spectra of these samples, as have been reported earlier [5], showed two single lines having isomeric shift values as $\delta_1 \sim 1.45$ mm/sec and $\delta_2 \sim 2.32$ mm/sec (w.r.t. $SnO_2$ at room temperature). These two lines are arising due to the Sn substitution at both Fe and Ti sites. The intensity of these two lines was found to be composition dependent.

Both X-ray diffraction and transmission Mössbauer spectra recorded for $^{57}$Fe and $^{119}$Sn did not show any measurable change for the samples used in catalysis experiments. Also, the particle size and the shape of the used catalyst samples remained almost unaltered as was revealed by SEM studies. These results thus suggest that no bulk decomposition of intermetallics takes place during the catalytic process under the experimental conditions used in these studies and the total surface area is not altered appreciably. This is unlike what has been observed for most rare earth/actinide intermetallics where decomposition of the

bulk into rare earth/actinide oxide and transition metal has been observed during the catalytic reaction. Conversion electron $^{57}Fe$ Mössbauer spectra recorded for these samples after catalysis experiments showed very weak additional signal for Fe clusters on the surface which is in conformity with the results reported earlier for FeTi and related systems [4,8] by us as well as by other authors for activated FeTi system [9,10]. It can thus be suggested that only surface modifications are occuring during these catalysis experiments.

## 4. Discussion

The data presented in this paper clearly indicate that Sn substitution significantly improves the catalytic activity of $FeTi_{(1-x)}Sn_x$ for CO methanation and facilitates the dissociation of $H_2$. TDS study (fig. 3) clearly shows that larger amount of desorbed hydrogen is available for CO methanation in case of Sn substituted samples at relatively much lower temperatures. Furthermore, the catalytic activity is affected by regeneration treatments which are found to result in the formation of Fe metal clusters on the catalyst surface as has been observed from conversion electron Mössbauer experiments. Depending upon the heat treatment different competing processes such as the formation of Fe clusters and $Fe_2Ti$ and oxidation of Fe or Ti may take place on the surface of crystallites according to the following routes [10–12].

$$FeTi + O \rightarrow TiO_x + FeTi + Fe$$

$$FeTi + Fe \rightarrow Fe_2Ti$$

$$Fe + O \rightarrow FeO_x$$

On hydrogen treatment iron is found to exist in metal form at the surface as has been reported by several authors [4,12,13]. However, during CO methanation reaction, both the hydrogen and oxygen (due to decomposition of CO) are available insitu, giving rise to surface modifications and to the formation of Fe clusters over surface as has been demonstrated in our earlier studies [4,8]. It can thus be argued that the catalytic activity for CO methanation is arising due to Fe clusters produced over the surface of FeTi. The increase in catalytic activity after successive $O_2/H_2$ regenerations can also be understood in the light of above mechanism. As discussed in [4], the Fe centres help in dissociation of CO and the active carbon thus formed is an essential precursor to methane formation.

The role of dispersed second phase in the easy activation of FeTi for hydride formation has been emphasised by a number of workers [14,15] and a variety of substitutions both of Fe and Ti sites have been attempted to achieve this objective. Nagai et al. [16,17] have made a detailed study of Cu, Mn and Nb substitution in FeTi and it was concluded that the interfaces between the FeTi and second phase act as centres for hydrogen dissociation and its easy diffusion

into the bulk. Furthermore, they suggested that the composition of the second phase is also an important factor in facilitating the easy activation. The importance of $Fe_2Ti$ as second phase has been emphasised by Nagai et al. [16,17] as well as by Khatamian [18] for easy activation of $H_2$ over FeTi. In the present study the substitution of Sn in FeTi has also lead to the formation of $Fe_2Ti$ as a second phase. This dispersed second phase could contribute to the enhancement of catalytic activity because of following possible reasons.

(i) The difference in the thermal expansion of FeTi and $Fe_2Ti$ may lead to the formation of microcracks in the matrix during regeneration process, thereby creating fresh surface and some additional centres for CO methanation.

(ii) The formation of $Fe_2Ti$ will create some Ti metal which acts as a getter for oxygen thereby helping in the preservation of Fe in the metallic state on the surface [6].

In conclusion we would like to state that the partial Sn substitution in FeTi has led to the formation of $Fe_2Ti$ as second phase which helps in the generation of large number of segregated Fe centres which are primarily responsible for catalytic activity.

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