CO hydrogenation over intermetallic compounds

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Introduction
The quests for alternative sources for hydrocarbons have led to the preparation of synthetic gasoline catalytically from carbon monoxide (CO) and hydrogen mixture (synthesis gas) obtained from the gasification of coal. Considerable attention has been paid to this reaction after the successful production of hydrocarbons from synthesis gas by Fischer and Tropsch. Recent studies in this field are directed towards the understanding of the mechanism involved in the reaction of CO hydrogenation as it is a prerequisite for achieving selectivity of the reaction towards desired products. Thus a variety of hydrocarbons can be produced from CO and hydrogen mixture by choosing suitable catalysts and reaction conditions like temperature and pressure. A number of reviews dealing with different aspects of the catalytic hydrogenation of CO, such as the selectivity of the reaction for a particular product, the mechanism of the reaction and role of supports and promoters in this reaction are available in literature. In the last two decades, much interest has been generated in the study of intermetallic compounds, a novel class of catalysts, for CO hydrogenation reaction. We thought it of interest to review the developments in this field. Here a brief introduction to the widely accepted mechanism for CO hydrogenation reaction followed by properties of a few catalysts for this reaction, are presented which will help in comparing the catalytic properties of intermetallic compounds with those of the supported catalysts.

Mechanism of CO hydrogenation
Recent advances made in the field of CO hydrogenation reaction have ruled out the earlier views about the mechanism of this reaction, such as the formation of bulk carbide by the reaction of CO with the metal catalysts followed by the hydrogenation of the carbide to hydrocarbons or the CO conversion to hydroxy carbene on the catalyst surface \([M = \text{CH(OH)}]\) and the subsequent hydrogenation. Now it is widely accepted that the reaction takes place by the dissociative chemisorption of CO followed by the formation of \(\text{CH}_x\) species. The \(\text{CH}_x\) groups further polymerise to give higher hydrocarbons. Bell proposed the following reaction steps for CO hydrogenation process, based on the above mentioned mechanism:

\[
\begin{align*}
\text{CO} + S & \rightarrow \text{CO}_x (S = \text{a surface metal site}) \\
\text{CO}_x + S & \rightarrow \text{C}_x + \text{O}_x \\
\text{H}_2 + 2\text{S} & \rightarrow 2\text{H}_x \\
\text{O}_x + \text{H}_2 (\text{or } 2\text{H}_x) & \rightarrow \text{H}_2\text{S} + 2\text{S} \\
\text{O}_x + \text{CO} (\text{or } \text{CO}_x) & \rightarrow \text{CO}_2 + 2\text{S} \\
\text{C}_x + \text{H}_x & \rightarrow \text{CH}_x + \text{S} \\
\text{CH}_x + \text{H}_x & \rightarrow \text{CH}_2 + \text{S} \\
\text{CH}_2 + \text{H}_x & \rightarrow \text{CH}_3 + \text{S} \\
\text{CH}_3 + \text{H}_x & \rightarrow \text{CH}_4 + 2\text{S} \\
\text{CH}_2 \text{CH}_2 + \text{H}_x & \rightarrow \text{CH}_2 \text{CH}_2 + \text{H}_x \\
\text{CH}_3 \text{CH}_2 + \text{H}_x & \rightarrow \text{CH}_3 \text{CH}_2 + \text{H}_x \\
\text{CH}_3 \text{CH}_2 + \text{H}_x & \rightarrow \text{CH}_3 \text{CH}_2 + \text{H}_x
\end{align*}
\]

This view has been confirmed by using predeposited labelled carbon atoms on the surface and also by the incorporation of \(\text{CH}_x\) generating additives in the reactant gas mixture such as \(\text{CH}_2\text{N}_2\) or \(\text{CH}_x\text{Cl}_4-x\). From this reaction mechanism, it can be inferred that a good hydrogenation catalyst can be used for CO methanation reaction as increase in surface carbon or \(\text{CH}_x\) units is not possible on such catalysts. Hence Ni, Pd and Pt selectively produce \(\text{CH}_4\) from synthesis gas whereas Fe, Co and Ru are suitable catalysts for higher order hydrocarbons since they can dissociate CO faster and give a sufficiently high concentration of \(\text{CH}_x\) species on the surface. Unlike this, supported Pd catalysts and Cu supported on silica with suitable promoters such as lanthanum oxide, give methanol. It has been pointed out that \(\text{Pd}^{0-+} (\text{M} = \text{Pd or Cu})\) are the active centres for this reaction and the reaction proceeds via the formation of formyl radicals. The product distribution also
Table 1—Some of the surface characterisation techniques frequently utilized to determine the structure and composition of solid surface (ref. 2)

<table>
<thead>
<tr>
<th>Method (Acronym)</th>
<th>Physical basis</th>
<th>Information obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low energy electron diffraction (LEED)</td>
<td>Elastic back-scattering of low energy electrons</td>
<td>Atomic structure of surfaces and adsorbates, surface composition</td>
</tr>
<tr>
<td>Auger electron spectroscopy (AES)</td>
<td>Electron emission from surface atoms excited by electron, X-ray or ion bombardment</td>
<td>Surface composition</td>
</tr>
<tr>
<td>High resolution-electron energy loss spectroscopy (HREELS)</td>
<td>Vibrational excitation of surface atoms by inelastic reflection of low energy electrons</td>
<td>Structure and bonding of surface atoms and adsorbates</td>
</tr>
<tr>
<td>Infrared Spectroscopy (IR)</td>
<td>Vibrational excitation of surface atoms by absorption of radiation</td>
<td>Structure and bonding of adsorbates</td>
</tr>
<tr>
<td>X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS, ESCA)</td>
<td>Electron emission from atoms excited by X-rays or ultraviolet light</td>
<td>Electronic structure and oxidation state of surface atoms and adsorbates</td>
</tr>
<tr>
<td>Ion scattering spectroscopy (ISS)</td>
<td>Elastic reflection of inert gas ions</td>
<td>Atomic structure and composition of solid surfaces</td>
</tr>
<tr>
<td>Secondary ion mass spectroscopy (SIMS)</td>
<td>Ion-beam-induced ejection of surface atoms as positive and negative ions</td>
<td>Surface composition</td>
</tr>
<tr>
<td>Extended X-ray absorption fine-structure analysis (EXAFS)</td>
<td>Interference effects in photoemitted electron wavefunction in X-ray absorptionsurfaces and adsorbates</td>
<td>Atomic structure of adsorbates</td>
</tr>
<tr>
<td>Thermal desorption spectroscopy (TDS)</td>
<td>Thermally induced desorption or decomposition of adsorbates</td>
<td>Adsorption energetics and composition of adsorbates</td>
</tr>
</tbody>
</table>

depends on the nature of support and promoter which are used along with the catalyst. When alkali metals are used as promoters along with Fe or Co, C₂ oxygenates are produced because the former can dissociate CO faster and give a high concentration of active carbon centres.

Research in the field of CO hydrogenation has advanced so much that catalysts can be 'tailor made' and, hence, considerable selectivity can be achieved. Thus, if Ni is used as catalyst, pure CH₄ can be obtained whereas with cobalt, a mixture of hydrocarbons can be obtained. When Cu/ZnO/Al₂O₃ or Pd/MgO promoted SiO₂ catalysts are used, CH₃OH is obtained and with Rh/V₂O₅ catalysts C₂-oxogenates are obtained. When bimetallic and alloy catalysts are employed not only selectivity, but stability of the catalyst is also achieved during hydrocarbon synthesis. In bimetallic catalysts, due to alloy formation, one of the components modifies the electronic properties of other component by virtue of which the selectivity and stability of the catalysts are enhanced. In the case of Pt-Sn reforming catalysts, Sn does the modification of the catalyst in two different ways. Firstly, it interacts with the support alumina and modifies the acidic cracking sites to olefin isomerisation sites. Secondly, it makes Pt resistant to self-poisoning by modifying the electronic properties of Pt by incorporating a part of Sn in Pt as solid solution.

Alloying group VIII metals with group IB metals modifies the electronic nature of both the metals which in turn affects the chemisorption behaviour. It has been reported that when the Cu content in Ni-Cu alloy is greater, selectivity to C₂ and C₃ hydrocarbons is observed, whereas when the Cu content is low, selectivity to CH₄ is observed. Ru-Fe alloy catalyst gave a marked increase in the yield of olefins as compared to the paraffins when the Ru content was in the range of 35-65%. On unsupported Fe-Ru, a surface enrichment of Fe was found to occur and as the Fe content in Fe-Ru increased, selectivity for olefins was observed to increase.

Experimental methods

Intermetallic compounds and alloys are prepared by repeated melting of the constituent metals in the desired ratio followed by annealing the sample at suitable temperature. Supported bimetallic catalysts are prepared by impregnation using a solution of the constituent metals in the form of chloride or nitrate and the subsequent reduction of the compound to the respective metals. Intermetallic compound with particle size in the range of 150-300 mesh have been used without any support.

Activity of a catalyst is studied by determining the concentration of the reactants and products as a function of temperature, pressure or time. The identification and quantitative evaluation of the composition of the effluents from the catalyst reactor
can be carried out using a gas chromatograph or a mass spectrometer. Reaction over the catalyst can be carried out in two different ways. (i) A continuous flow mode in which the reactants flow continuously through the catalyst and the composition of the product is analysed periodically by sampling the effluent to a gas chromatograph. By this method, the change in the activity of the catalyst over a period of time and the poisoning effect of the reactants on the catalysts are studied. (ii) In pulse injection mode, pulses of reactant gases are injected to the catalysts followed by the analysis of the effluent. A quantitative study of the activity of catalyst can be carried out over a range of temperatures by this method.

The physico-chemical characterisation of the catalyst surface is an important aspect in the catalytic reaction as it has a large influence on the catalytic activity. Many cells have been designed for in situ studies of the catalyst in which facilities are available for carrying out reaction at high temperature and pressure along with the simultaneous characterisation of the catalyst by different techniques. Thus, for a particular experimental condition, the reaction parameters can be correlated with the surface structure, composition and the oxidation state of the catalyst. Some of the frequently used techniques for surface characterisation and the type of information obtained from them are given in Table 1.

### Rare earth-transition metal intermetallic compounds

A novel class of catalysts which have been studied for CO hydrogenation reaction in the last two decades are the intermetallic compounds of rare earth and transition metals. Many of these intermetallic compounds having general formulae RM$_2$, RM$_3$, R$_2$M$_7$, and RM$_5$ (R = a rare earth metal like Gd, Tb, Er, Dy or Ho and M = a transition metal like Fe, Co or Ni) absorb large quantities of hydrogen per unit volume of the compound, often exceeding the density of liquid hydrogen. Most of these compounds can be hydried at room temperature even at less than one atmosphere H$_2$ pressure. From the observation that the hydrogen absorbed per unit mass of the metal is directly proportional to the square root of hydrogen pressure, it has been concluded that hydrogen is absorbed dissociatively. Surface studies of these intermetallics have revealed that the rare earth metal is in the form of oxide thereby leading to the segregation of transition metal over the surface. Hydrogen absorption process involves the chemisorption and dissociation of hydrogen on these transition metal centres followed by its diffusion into the bulk matrix through the transition metal-rare earth oxide interface.

The fact that monatomic hydrogen is present on the surface of these intermetallics due to the dissociative absorption of hydrogen led researchers to think that these intermetallics can be used for hydrogenation reactions. Thus, a number of studies like ethylene hydrogenation and ammonia synthesis and hydrocarbon synthesis have been carried out using rare earth intermetallic compounds as catalysts. Because of the selectivity of rare earths towards oxygen, when these intermetallics are exposed to CO + H$_2$ mixture, the intermetallics transform to rare earth oxides and transition metals, which act as the centres for hydrogen and CO dissociation. The same effect can also be produced by exposing the catalyst to oxygen. These transformed intermetallic compounds are the active catalysts for CO hydrogenation reaction and often their activity is found to be better than that of supported metal catalysts made by wet impregnation method.

Another advantage of this type of catalysts is that they are self-generative in nature as they continuously transform when exposed to oxidising environment, creating fresh metal sites dispersed on rare earth oxide.

Conversion of synthesis gas to hydrocarbons was studied using systems such as RM$_5$, RM$_3$ and RM$_2$ (R = La, Er, Th, Ce, Ho and M = Co, Fe, Ni, Al). Among these systems ThNi$_5$ and LaNi$_5$ have been studied very extensively. The transformed ThNi$_5$ was found to show unusually high activity for CO hydrogenation. The reason suggested for this was that Th in ThO$_2$ is quadripositive whereas La in La$_2$O$_3$.

### Table 2—Comparison of the catalytic activity of catalysts formed by decomposition of intermetallic compounds with those made by wet chemical methods (ref. 22)

<table>
<thead>
<tr>
<th>Precursor intermetallic compound</th>
<th>Catalyst type</th>
<th>Turn over no. x $10^3$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi$_5$</td>
<td>I</td>
<td>2.7</td>
</tr>
<tr>
<td>LaNi$_2$</td>
<td>I</td>
<td>9.8</td>
</tr>
<tr>
<td>CeNi$_5$</td>
<td>II</td>
<td>3.8</td>
</tr>
<tr>
<td>Th$_x$Ni$_y$</td>
<td>II</td>
<td>2.8</td>
</tr>
<tr>
<td>ThNi$_2$</td>
<td>II</td>
<td>2.9</td>
</tr>
<tr>
<td>ThNi$_5$</td>
<td>I</td>
<td>4.7</td>
</tr>
<tr>
<td>ThNi$_5$</td>
<td>II</td>
<td>10.6</td>
</tr>
<tr>
<td>Ni/ThO$_2$-impregnation</td>
<td></td>
<td>~0.0</td>
</tr>
<tr>
<td>Ni/SiO$_2$-impregnation</td>
<td></td>
<td>~1.0</td>
</tr>
</tbody>
</table>

I-catalyst made by exposing to synthesis gas at elevated temperatures (transforms to rare earth oxide and Ni)

II-catalyst made by oxidising the intermetallic with O$_2$
is tripositive which considerably changes the acidity of the support. These catalysts were found to be selective for methanation reaction. The Co containing intermetallics were found to be similar to the Ni system except that these needed higher temperatures to get oxidised to form the active catalyst. When Fe systems were employed, the catalyst was found to get deactivated with the passage of time due to the formation of higher molecular weight waxes which got deposited on the catalyst. Unlike this, the RAl₂ compounds were found to be inactive for CO methanation which implied that the catalytic activity is associated with the formation of transition metal centres.

The activity of a few rare earth intermetallic compounds for CO hydrogenation is listed in Table 2 (ref. 17) along with that of commercial catalysts to show their relative merits.

**Intermetallic compounds of Fe and Ti**

Another class of intermetallic compounds which has been studied very extensively for hydrogen storage properties comprises FeTi and related systems. Eventhough the hydrogen absorbing capacity of FeTi is very impressive, it needs an elaborate activation process before it can start absorbing hydrogen. Some authors relate the problem of activation to the surface segregation of Fe and Ti, whereas others relate it to the diffusion of hydrogen through the bulk. The details regarding the activation of FeTi for hydrogen absorption have been reported by many authors. The general opinion is that it is difficult to activate as prepared single phase FeTi. However, if FeTi contains excess Ti in it or if Fe is partly substituted by Mn, V, Cr, Ni, etc., an ease of activation is observed. As FeTi-based intermetallics are also good hydrogen storage materials like rare earth intermetallics, they are expected to be potential catalysts for CO hydrogenation. Kulshreshtha and coworkers have investigated the CO hydrogenation reaction over these systems and an attempt has been made to correlate the ease of activation observed for substituted intermetallic compounds for hydrogen absorption with their catalytic activity for CO hydrogenation.

These authors have prepared a number of intermetallic compounds of FeTi with different compositions of Fe and Ti as well as partly substituted FeTi by substituting with Mn, Sn and Ni. All these intermetallics were found to be active catalysts for CO hydrogenation.
nation and the only product detected was CH₄, apart from CO₂. The activity of these intermetallics was found to be composition-dependent and the presence of a second phase in FeTi was found to enhance the catalytic activity.

Hirata⁴⁶-⁴⁷, while studying the effect of gaseous impurities such as CO and O₂ on the hydrogen absorption properties of FeTi₁₋₀.₉O₀.₀₃, observed that the hydrogen absorption capacity degraded significantly in the presence of above mentioned impurities and the analysis of residual gas revealed the presence of hydrocarbons like CH₄, C₂H₄, C₃H₄ and n-butane. Also, a high catalytic activity was observed for such a surface of hydrogen absorbing material, where the activation of hydrogen was easy.

In the case of FeTi₁₋₀ₓ (₀.₀ < x < ₀.₁₅) intermetallics⁴⁸, the catalytic activity was found to increase with increase in Ti content as shown in Fig. 1. This feature is also reflected in the activation energy required for CO methanation reaction which is 25.₂ kJ for FeTi and 2₁.₀ kJ for FeTi₁₋₀.₁₅. The improved activity is attributed to the presence of a second phase, namely, suboxide of FeTi, whose concentration increases with the increase in concentration of Ti in FeTi. The second phase present in it helps in creating fresh surface by creating microcracks as a result of the difference in the thermal expansion of the two phases during activation process. Thus, these compounds exhibited a parallelism between the ease of hydrogen absorption and catalytic activity for CO hydrogenation.

Pretreatment given to these intermetallic compounds such as oxygen heating for one hour at 62₅ K followed by hydrogen heating for two hours at the same temperature improved the catalytic activity. Surface studies by conversion electron Mössbauer spectroscopy³⁸-⁴¹ (Fig. 2) have revealed the presence of Fe clusters over the surface after the activation process. These clusters are believed to be the active centres for CO methanation. The mechanism proposed was the dissociative chemisorption of CO and hydrogen on Fe sites and the hydrogenation of nascent carbon to methane.

The hydrogenation of surface carbon can proceed in two different ways (i) and (ii).

(i) Stepwise addition of hydrogen to carbon as shown below:

\[
\begin{align*}
C_{(ad)} + H_{(ad)} & \rightarrow CH_{(ad)} \\
CH_{(ad)} + H_{(ad)} & \rightarrow CH_{2(ad)} \\
CH_{2(ad)} + H_{(ad)} & \rightarrow CH_{3(ad)} \\
CH_{3(ad)} + H_{(ad)} & \rightarrow CH_{4(ad)}
\end{align*}
\]

(ii) Simultaneous addition of more than one hydrogen atom:

\[
C_{(ad)} + xH_{(ad)} \rightarrow CH_{x(ad)} \quad (1 < x \leq 4)
\]

Kim and Lee³⁰ have suggested that the presence of metals of high oxide stability can protect the Fe clusters of FeTi from deactivation and, hence, make the activation process easier. In order to verify this aspect, Fe was partially substituted by Mn or Ni in FeTi and its catalytic activity was investigated³⁶. The expe-
ments of CO methanation on Mn substituted FeTi have shown that up to \( x = 0.10 \) in Fe\((1-x)\)Mn\(_x\)Ti, the catalytic activity increases considerably; however, for higher values of \( x \), the activity decreases slightly as compared to that of FeTi (Fig. 3). The conclusion drawn from this study was that the presence of Mn stabilizes the metallic state of Fe which in turn promotes the catalytic activity. The comparatively lower activity at higher concentration of Mn is attributed to the decreased concentration of Fe clusters. But in the case of Fe\((1-x)\)Ni\(_x\)Ti, the activity was found to be less than that of FeTi up to a concentration of \( x = 0.30 \), but when \( x = 0.50 \), the activity was restored (Fig. 4), possibly due to the Ni segregates which are known to be good hydrogenation catalyst. The decrease in catalytic activity observed with Ni substitution is ascribed to its low oxygen affinity as compared to that of Fe. The \( \text{O}_2 \) and \( \text{H}_2 \) pretreatment given to these catalysts did not lead to significant improvement in the activity for Fe\((1-x)\)Mn\(_x\)Ti, whereas considerable improvement was observed in the activity of Fe\((1-x)\)Ni\(_x\)Ti which further supports the view that in Mn substituted samples, Fe clusters are predominantly in metallic state whereas in Ni substituted samples it is not so before activation.

The partial substitution of Ti by Sn in FeTi had profound effect on the hydriding kinetics of these intermetallics as well as on the catalytic activity. In these intermetallics also, a second phase (Fe\(_2\)Ti) was seen whose concentration increased with increasing Sn content. The role of second phase in enhancing the catalytic activity of these intermetallic compounds has already been discussed earlier. Moreover, the presence of Fe\(_2\)Ti can create some Ti centres which can easily get oxidised and can prevent Fe clusters from oxidation.

The role of activation of FeTi intermetallics in the surface dissociation of hydrogen has also been reported by studying the \( \text{H}_2/\text{D}_2 \) isotope scrambling after different types of pretreatments. The results indicate that an oxygen pretreatment followed by hydrogen treatment of FeTi at 625 K gives more HD as compared to that formed on the catalyst heated only in \( \text{H}_2 \). A similar behaviour was exhibited in CO methanation reaction also by these catalysts. These results further support the view that the Fe clusters generated during the activation process are the active centres for this reaction. Another evidence for the presence of Fe/TiO\(_x\) type species on the surface of FeTi after activation has been reported from the investigation of the hydrogen adsorbed on these intermetallics by thermal desorption spectroscopy (TDS). On the basis of the oxide stability of Ti, Mn, Fe and Ni and the activation energy values for hydrogen desorption, the low temperature peaks (300-750K) were assigned to the hydrogen bound to Fe/TiO\(_x\) type species whereas the high temperature peak (> 700K) was assigned to the hydrogen desorbed from the interstitials of these intermetallics.

Thus, like rare earth intermetallic compounds, FeTi also undergoes a surface segregation process. But unlike the rare earth intermetallic compounds, the segregation process is confined only to the surface in FeTi intermetallics. The lack of continuous transformation results in the deactivation of these intermetallics with time due to the deposition of inactive carbon on the surface. The activity is restored by heat treatment in \( \text{O}_2 \) and \( \text{H}_2 \) at 625 K.

Hydrogen storage materials such as intermetallic compounds of rare earths and transition metals, iron and titanium, etc., are active catalysts for hydrogenation reactions. The rare earth intermetallics, which reversibly absorb hydrogen at low pressures, readily catalyse the CO hydrogenation reaction. When exposed to synthesis gas, they continuously transform to rare earth oxide and transition metal clusters and, hence, they are self-generative in nature. The transition metal clusters are the active centres for CO and \( \text{H}_2 \) dissociation. FeTi intermetallics also absorb large quantities of hydrogen, but many cycles of absorption-desorption are needed to get the saturation hydride composition of FeTiH\(_{1-2}\). Substitution of a part of Fe or Ti by another metal such as Mn, Sn, Cr or V and presence of excess Ti in FeTi facilitate the activation of FeTi and, just in a few cycles, the saturation hydride composition is obtained. Such substitution in FeTi is found to enhance the catalytic activity for hydrogenation reaction also. Thus, a similarity is seen in their behaviour towards the ease of activation for hydrogen absorption and in the enhancement of catalytic activity for hydrogenation reaction. The second phase present in FeTi\(_{(1+x)}\) and substituted intermetallics is believed to play an important role in improving the catalytic activity. It is suggested that when a second phase is present in FeTi, microcracks are created in the matrix during activation, due to the difference in the thermal expansion of the two phases which create fresh surface. However, unlike rare earth intermetallics, FeTi and related intermetallics do not continuously transform because of their better stability towards oxygen and show relatively poor catalytic activity in comparison to the rare earth intermetallics. The surface segregation of transition metal clusters, which is found to take place during activation, helps in increasing the number of metallic centres which in turn improves the catalytic activity.

Based on the results reported in the literature, it has been observed that some of the intermetallics of rare
earth and first transition series initially show very high activity for CO hydrogenation. However, their behaviour for continuous flow experiments has not been found to be encouraging for extended use. The reason for this is that after complete transformation, the deactivation of transition metal centres takes place and it is difficult to regenerate them in comparison to noble metal catalysts. It is desirable to do similar experiments with rare earth and noble metal intermetallics, where such problems may be overcome. Similarly, for FeTi and related intermetallics attempts should be made to have suitable substitutions so that bulk transformation of FeTi is facilitated and iron centres are preserved on the surface during catalytic process.

References
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