# DIRECT CONVERSION OF SYNGAS TO AROMATICS ON FePd/$SiO_2$ CATALYST

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## 1. Introduction

Reactions of a $CO + H_2$ mixture can be conducted either to yield hydrocarbons e.g. over iron, nickel and ruthenium, or alcohols such as on conventional copper-zinc catalysts and on La doped Pd catalysts [1]. It is, however, well known that $C_6$ fraction of hydrocarbon can be directly produced via methanol using ZSM-5 zeolites [2]. On the other hand, Chang et al. [3] first reported a bifunctional or hybrid catalyst on which aromatics could be produced in two steps combining a CO hydrogenation catalyst with cyclization catalyst.

In the present work a FePd catalyst is introduced which produces aromatics in one step with high efficiency. This silica supported FePd bimetallic catalyst favourably combines the Fischer Tropsch (FT) activity of iron and the hydrogenation activity of palladium.

## 2. Experimental

Catalysts were prepared by impregnation of $SiO_2$ (surface area 200 $m^2$ $g^{-1}$) with aqueous solutions containing $Fe(NO_3)_3$ and $Pd(NO_3)_2$. After drying at 390 K the samples were calcined at 570 K. The palladium content was kept constant, 2 wt%, and the amount of iron varied in the samples (1, 2, 5, 10 wt%). The palladium free sample contained 10 wt% Fe. All samples were reduced in situ at 470 K for 0.5 h and at 670 K for 1 h in a stream of purified hydrogen.

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CO hydrogenation was studied in a continuous flow reactor using 0.5 g catalyst and a 2 : 1 $H_2$ to CO mixture with a flow rate of 0.75 $dm^3/h$ in a temperature range between 570 and 670 K.

For catalyst characterization TPR experiments were applied using a 5% $H_2/Ar$ mixture. Initially, the sample was cooled down to 193 K and after reaching room temperature the TPR profile was recorded [4].

Samples for Mössbauer measurements were prepared using $^{57}Fe$ isotope. Experiments were performed in an in-situ measuring cell and the experimental details have been described elsewhere [5].

## 3. Results and discussion

In table 1 and in fig. 1 the effect of alloying on the formation of aromatics from syngas is demonstrated. A very specific effect for addition of palladium is the dramatic decrease in methane and ethylene formation at the expense of production of aromatics exhibiting a maximum at 17 at% Pd in the iron-palladium bimetallic catalyst. As the iron content is further decreased production of aromatics is dropped and iron becomes a modifier to palladium in methanol formation [6].

This unique behavior of iron-palladium bimetallic catalysts can be interpreted by using the structural changes revealed from their TPR and Mössbauer spectra.

Table 1
Products of CO hydrogenation at 620 K with 1% conversion of CO obtained on Fe and FePd catalysts

| Product<br>% | Catalyst | |
|---|---|---|
| | 10 wt% Fe | 10 wt% Fe 2 wt% Pd |
| $CH_4$ | 38 | 8.9 |
| $C_2$ | 12 | 12.4 |
| $C_2^=$ | 35 | 3.4 |
| $C_3$ | 0 | 6.1 |
| $C_3^=$ | 13 | 16.1 |
| $C_4$ | 0 | 3.2 |
| $C_4^=$ | 2 | 18.5 |
| $C_5$ | 0 | 0.9 |
| benzene | 0 | 2.3 |
| toluene | 0 | 14.6 |
| m-, p-xylene | 0 | 7.0 |
| o-xylene | 0 | 2.7 |
| ethylbenzene | 0 | 3.9 |
| sum of olefins | 50 | 38.0 |
| sum of aromatics | 0 | 30.5 |

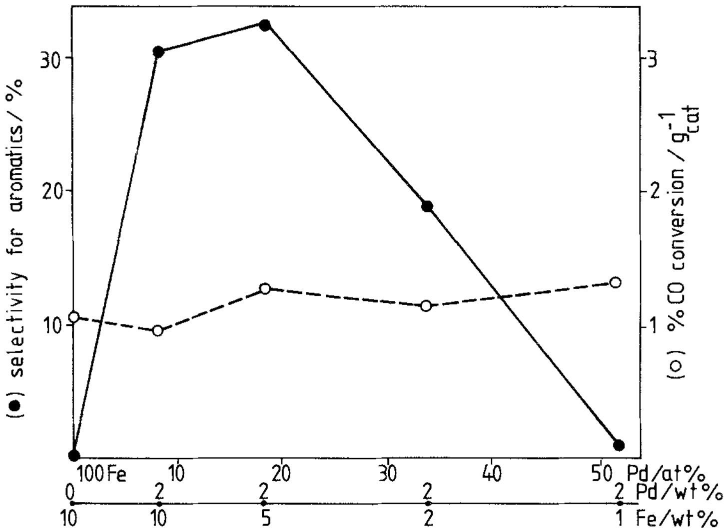

Fig. 1. Selectivity of aromatics (●) and CO conversion (o) in the CO hydrogenation over FePd/$SiO_2$ catalyst at different compositions.

The TPR profiles are shown in fig. 2. Pure iron is reduced in a very broad temperature range between 520 K and 920 K, where the reduction is still incomplete. This behaviour is similar to that of unsupported Fe [7]. Pure Pd is

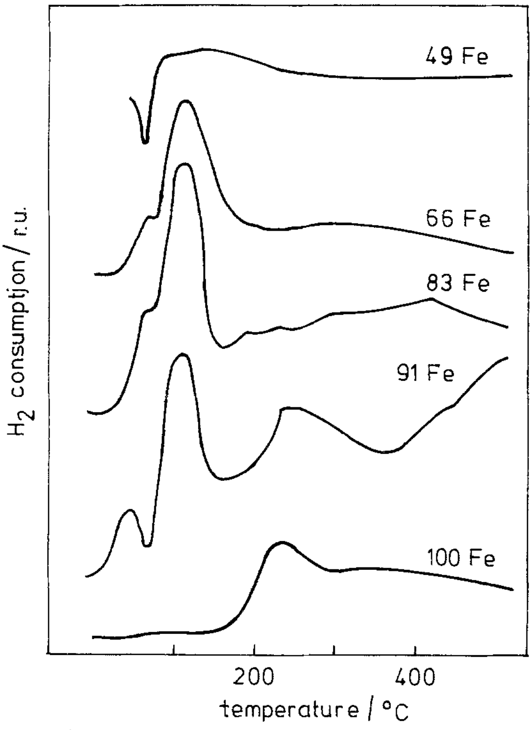

Fig. 2. TPR curves of FePd/$SiO_2$ catalysts.

mainly reduced below room temperature and only a small rest is reduced at about 370 K [4]. The present TPR profiles of the Pd modified Fe catalysts are characterized by the appearance of a very pronounced peak at the temperature of 370 K. Moreover, this peak is accompanied by a shoulder or a small peak.

This indicates a strong interaction between Fe and Pd. Obviously, Pd facilitates reduction of iron. Since the product of reduction is inhomogeneous, it could contain metallic iron as well as bimetallic alloy. With increasing iron content the interaction between Pd and Fe becomes more complicated as pure Fe is reduced less easily than the alloy. This could explain the appearance of the shoulder or the small separate peak attributable for the alloy. In addition, the sample with the highest amount of Fe (91 at%) exhibits a separate reduction peak nearly at the same temperature as the sample, containing pure iron only. This indicates the decreasing influence of Pd on the reducibility of iron with increasing iron content.

In Mössbauer spectra of samples three iron containing species were found on each catalyst after hydrogen reduction at 670 K: metallic $\alpha$-iron, PdFe alloy and ionic $Fe^{2+}$. The value of the average magnetic hyperfine field obtained for the PdFe alloys from the 80 K spectra of the different samples were close to 30.0 T. Thus, we had concluded that the alloys have a disordered structure and their composition was between the ratios of $2 < Pd : Fe < 3$ [5]. These results are summarized on fig. 3, where the relative spectrum absorption areas of the different components are plotted after multiplying them by the total iron content of the samples, thus, the resulting quantity is proportional to the given component present in the sample. (It should be mentioned that comparison among the

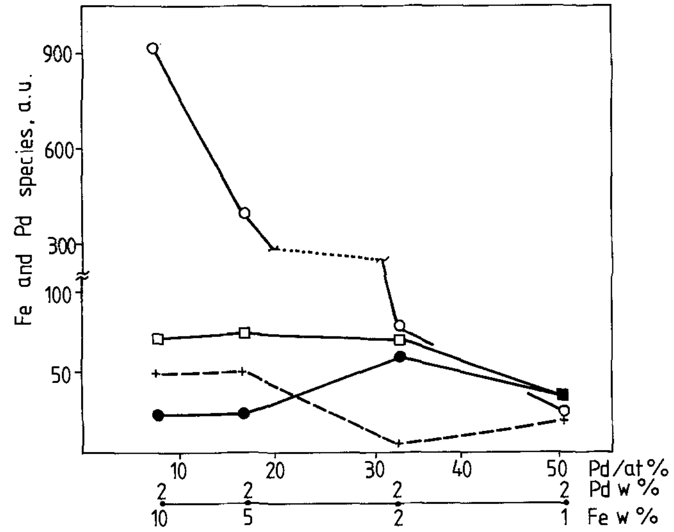

Fig. 3. Relative amounts of $\alpha$-iron (○), $Fe^{2+}$ (□), $Pd_xFe$ alloy (●) and non-alloyed Pd (+) estimated from room temperature Mössbauer spectra.

different components may contain 20–30 per cent uncertainty, since the probability of the Mössbauer effect may vary for the different components. On the other hand the shape of the curves is exact for each component separately.) Taking into account that the composition of $Pd_xFe$ alloys formed does not significantly depend on the composition of samples and Pd : Fe ratios found for alloys are between 2 and 3, a rough estimation can be given for the amount of non-alloyed Pd, too. This is also shown in fig. 3, assuming $x = 2$. As it is seen, surprisingly, presence of significant amount of non-alloyed Pd can be assumed in Fe-rich samples.

To gain more information on the composition of alloys 1120 K reductions were also carried out. The average magnetic hyperfine field obtained for the $Pd_xFe$ alloy from the 80 K measurement was around 30 T even at the 66 at% Fe sample indicating that the Pd content of the alloy formed is still between 66 and 75 at%. In contrast, the average magnetic field measured after the reduction of a corresponding unsupported sample was 38 T pointing to the presence of FePd alloy with considerably lower (40 at% or less) Pd content. These latter measurements provided an additional evidence for that the PdFe alloys formed on silica have high Pd content even if the average Pd content of the samples is low.

In a third series of the measurements the reduced catalysts were treated under the conditions of catalytic experiments in flowing syngas at 650 K. As it can be expected all metallic iron was transformed into $\varepsilon$ and $\chi$ iron carbides. The maximum of the detected amount of $\varepsilon$ carbide coincides with the maximum of selectivity found at 17 at% Pd content. $\chi$ carbide is the main component of the two $Fe/SiO_2$ samples. The amount of ionic $Fe^{2+}$ remained more or less unaffected. Remarkably, the amount of the PdFe component remained also unchanged in the $CO + H_2$ reaction.

Iron is known as a typical Fischer-Tropsch catalyst which converts syngas to paraffins and partially to olefins. Carbon, formed by dissociation of CO molecules, may either take part in the construction of different active surface species, or may form different bulk iron carbides, which still possess various catalytic activity [8,9]. Surprisingly, addition of a small amount of Pd significantly shifts the selectivity towards the formation of aromatics. As far as we know this is the first bimetallic Fe catalyst, which produces a considerable amount of aromatics.

As the presented TPR and Mössbauer studies of $FePd/SiO_2$ catalysts revealed the activated bimetallic system consists of three, more or less separable components: (i) $\alpha$-iron, (ii) $Pd_xFe$ alloy ($2 < x < 3$), and (iii) non-alloyed Pd. As it was also proved the Pd rich alloy is resistant to carbidization, while $\alpha$-iron was converted to iron carbides by syngas reaction.

From these starting points we propose a model of a bifunctional catalyst. Paraffins and olefins are formed on the $Fe(Fe_xC)$ component of the bimetallic catalyst. In a second step aromatics are formed by subsequent dehydrogenation and dehydrocyclization. Probably, this proceeds on the PdFe alloy since Pd is known as a good reforming catalyst producing aromatics from paraffins. In the present case the Pd alloy is even more suitable, because Pd alone should produce predominantly methane directly from syngas at higher temperatures.

The model of a bifunctional catalyst can explain the observed maximum of aromatization. Fe($Fe_xC$) as well as pure Pd would be monofunctional catalysts. The condition of bifunctionality would only be fulfilled by the combination of two different species, as given in bimetallic samples. Hence the appearance of an alloy upon addition of small amounts of palladium strongly increases the selectivity of iron toward aromatization. As it was shown, a surplus of non-alloyed iron is necessary in the bimetallic system to exhibit this bifunctional character. As this surplus of non-alloyed iron is lost in samples containing 50 and more at% Pd the catalytic activity is dropped significantly.

It should be mentioned that in Pd rich $PdFe/SiO_2$ systems another drastic shift of the selectivity in CO hydrogenation has been observed recently. Pd itself is known as a catalyst, producing methanol from CO and $H_2$. Addition of a small amount of Fe enhances the methanol formation by one order of magnitude [6]. Altogether, the system Fe-Pd displays a surprising variability in the CO hydrogenation and alloy formation seems to play a crucial role at both edges of the composition range.

## References

[1] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1983) 26.
[2] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[3] C.D. Chang, W.H. Lang and A.J. Silvestri, J. Catal. 56 (1979) 268.
[4] H. Lieske, G. Lietz, W. Hanke and J. Völter, Z. anorg. allg. Chem. 527 (1985) 135.
[5] K. Lázár, M. Nimz, G. Lietz, J. Völter and L. Guczi, Hyperfine Interactions 41 (1988) 657.
[6] T. Fukushima, K. Araki and M. Ichikawa, J. Chem. Soc., Chem. Commun. (1986) 148.
[7] I.S.C. Hughes, J.O.H. Newman and G.C. Bond, Appl. Catal. 30 (1987) 303.
[8] J.W. Niemantsverdriet, A.M. van der Kraan, W.L. van Dijk and H.S. van der Baan, J. Phys. Chem. 84 (1980) 3363.
[9] M. Pijolat, V. Perrichon and P. Bussiere, J. Catal. 107 (1987) 82.