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STRUCTURE AND PROMOTION OF BIMETALLIC CATALYSTS: ACTIVITY AND SELECTIVITY

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Activity and selectivity of carbon monoxide hydrogenation can be effectively controlled by using bimetallic catalysts. There are two effects which should be taken into consideration:
(1) influencing the mode of CO chemisorption: dissociative vs associative, or
(2) affecting the amount and type of surface hydrogen: weakly vs strongly bound to the surface.

Associative CO chemisorption is controlled by two factors: either by the formation of an alloy phase as is for PtFe or PdFe where rehybridization of the Pd d-orbital results in a decreased back donation, or by an effect of a charged particles such as Fe^{3+} or RE ions which operates via a charge polarization. In highly dispersed state, e.g. inside a zeolite cage, similar effect is operative. In both cases oxygenates formation is a significant reaction pathway.

The mode of hydrogen chemisorption also affects the selectivity of the reaction. When the activated form of hydrogen is in large proportion, all the processes which require hydrogen are suppressed, consequently olefin formation is the main route of reaction.

The factors influencing both hydrogen and CO chemisorption will be considered. Here the paper will be focused on the effect of alloying, metal dispersion and shape selective environment.

1. Introduction

Large numbers of bimetallic catalysts have been investigated in CO hydrogenation processes [1–5]. The main idea was to influence the activity and selectivity of metals such as iron, nickel, cobalt, palladium, etc., being active in the $CO + H_2$ reaction by addition of a second metal. In most cases modifications were successful; catalytic activity and/or selectivity could be favourably affected and the reaction could be changed in desired directions.

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It is rather difficult to make a unified theory about the effect of second metal. Still, it is worth classifying the various effects we have to deal with, in order to be able to understand the mechanism of these changes.

Among the Group VIII transition metals some are active in CO dissociation (e.g. Fe, Co, Ni, Os, Ru), whereas others (Pt, Pd, Ir) chemisorb CO in molecular form. While selectivity of the latter group is normally high in oxygenate synthesis, on the formers only hydrocarbons are the prevailing products in the $CO + H_2$ reaction. Most interesting effects have been observed in the combination of these two groups of metals.

In early stage of the studies on $PtFe/SiO_2$ [6,7], $PtRu/Al_2O_3$ [8], $CoIr/Al_2O_3$ [9] systems indicated no oxygenate formation in the $CO + H_2$ reaction. Later, however, it turned out that under special conditions on $PtRu/Al_2O_3$ [10], $PdFe/SiO_2$ [11,12], PdFe/zeolite [13] and $PtFe/SiO_2$ [14] oxygenates were produced. Nevertheless, since the discovery of a 10–40 h induction period which is necessary for methanol formation over catalysts consisting of a variety of Group VIII noble metals promoted by Fe and Co, this proved to be a general phenomenon [15]. Whether the effect of the second metal is alloy formation, or simply an interphase effect (like metal-support interaction) helping adlineation of the chemisorbed CO molecule, the mode of CO adsorption can be altered by these bimetallic catalysts.

The second large group of the modifying factor is regarded the influence of bimetallic systems on the activated adsorption of hydrogen [16] in which the amount of weakly bound hydrogen to the catalyst is varied. Hence, again it can be influenced either by bimetallic formation, or by introducing a disperse system using the strongly interacting part of non noble metals with the support.

Finally, metal dispersion may be able to effect both the hydrogen activation and the CO chemisorption.

In the present work platinum and palladium based bimetallic systems will be followed step by step to obtain information about how the activity and selectivity of the $CO + H_2$ reactions can be changed by the different structures and morphologies of the bimetallic catalysts.

2. Results and discussion

Addition of various metal ions to Pt/Al_2O_3 [17] made platinum more active in methanol formation (e.g. the hydro-carbon/oxygenate ratio amounted to 0.9). However, the same effect could be achieved without additives, simply by changing platinum dispersion. As we proceeded from large ($D_{Pt} = 6.5$) to small particles ($D_{Pt} = 49$) the hydrocarbon/oxygenate ratio changed from 13 to 2.2 [10]. Obviously, when the interphase around the metal particle perimeter becomes larger, the linearly adsorbed CO molecules feel not only metal-metal environment, but the Al^+ may act as a promoter and finally adlineation of CO molecule occurs. This mechanism was supposed to be valid for other promoter species such as Pt-Fe^{3+} pairs on the surface [11,18–20]. Although the presence of Pt-Fe^{3+} has been supported by Mössbauer and EXAFS measurement, recently it was found that the increase in methanol activity and selectivity are due to the rising amount of FePt alloy phase [14].

The conflicting models concerning the Pt-Fe^{3+} pair site or PtFe alloy in promoting oxygenate formation can be explained by the work of Niemantsverdriet et al. [15,21]. It has been shown that most of these bimetallic combinations yield initially methane and after an induction period, once the catalyst surface has been restructured, oxygenate starts forming and levels off at around 80% selectivity. This induction period depends on the metals: for CoPt and FePt is about 1 h while for IrFe it is about 40 h. Although in the iron-iridium system the bimetallic particles are interphased to the supported highly dispersed Fe^{3+} oxide, initially no oxygenates are formed. However, after reaction iron particles are segregated to the surface and iron carbide was formed.

Bearing in mind the PtFe results our attention is now focussed to the Pd based bimetallic catalysts. After the discovery of methanol activity on palladium [22], large efforts have been spent on further development and applications of this catalyst prepared by incipient wetness method on silica [23–26].

The mechanism of iron addition to palladium has been studied by Mössbauer spectroscopy and kinetic methods [13,27,28]. When iron was added from 16 to 80 at. % to 2 wt% Pd/SiO_2 catalyst, different species were established. In fig. 1 the relative intensities of the various species formed after reduction in hydrogen, are plotted. Two types of PdFe are formed: (i) superparamagnetic PdFe particles with $IS = 0.35$ mm s^{-1} and magnetically split component with $IS = 0.41$ mm s^{-1} and MHF = 261 and 302 kOe.

Addition of 2 wt% MgO to the $PdFe/SiO_2$ system has distinct effect on the Fe^{2+} and Fe^0 components as indicated in table 1. As is demonstrated, addition of magnesia diminishes α-iron formation at the identical composition and simultaneously increases the amount of Fe^{2+}. There is also a drop in the PdFe (magnetic) to PdFe (superparamagnetic) ratio [27,28] induced by magnesia via the metal dispersion being enhanced by the magnesia spreading out on silica surface.

In contrast to some earlier work, Fe^{3+} was not observed, consequently, the effect of iron cannot be related to the presence of the neighbouring Pd-Fe^{3+} pairs. Instead, we incline to believe in the effect of PdFe alloys similarly to what was shown by other authors for PtFe system [7,14,28]. For PdFe rehybridization of the d-orbitals has been assumed in order to explain the positive isomer shift of Fe^0 species. A possible interpretation is the screening effect of the d-electrons by which s-electron density at the Fe nucleus is diminished. Rehybridization makes palladium electron deficient with a fraction of positive charge which is essential to the CO activation in molecular form.

Now, the question is why methanol activity decreases sharply at higher iron content when the amount of FePd is still high. For explanation the H/Pd ratio as

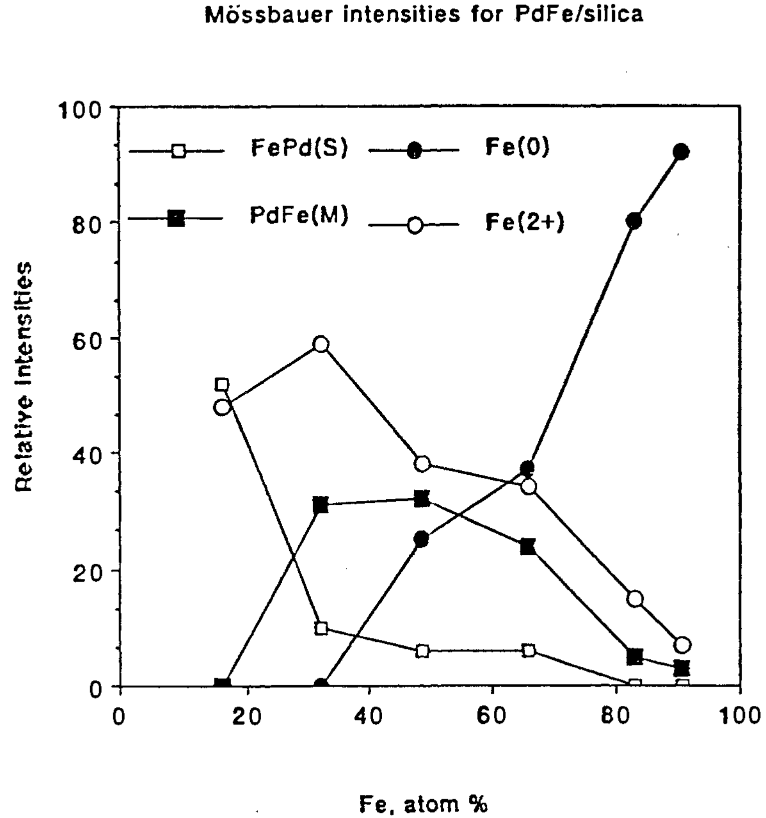

Fig. 1. Relative Mössbauer intensities of Pd_xFe (magnetic), Pd_xFe (superparamagnetic), Fe^0 and Fe^{2+} measured on $PdFe/SiO_2$ samples vs composition (from ref. [27]).

a measure of hydrogen adsorption may be considered [28]. This weakly bond hydrogen drops very fast as iron content increases, i.e. the rate of hydrogenation of the non-dissociated CO sharply decreases. On the other hand, on pure palladium, hydrogen is available but the coverage of the CO adsorbed in molecular form, is small. Superposition of the two opposite effects result in a maximum in methanol synthesis activity at around 16 at.% iron content.

Table 1
Relative intensities of $FePd_x$, Fe^{2+} and α-iron as a function of composition

Fe (at.%)	$FePd/SiO_2$			$FePd/SiO_2/MgO$		
	PdFe	Fe^{2+}	Fe^0	PdFe	Fe^{2+}	Fe^0
16	52	48	–	61	28	11
32	41	59	–	63	25	11
49	38	38	25	51	49	–
66	30	34	37	43	49	9
83	5	15	80	13	49	37

Table 2
Relative intensities of the different iron species in the PdFe/zeolite samples after reduction and $CO+H_2$ reaction

component	after 720 K H_2	after $CO+H_2$ at 570 K
PdFe/NaHX	Pd/Fe ratio is 5	
	Fe^{2+}_{tet}	32 –
	Fe^{2+}_{oct}	32 43
	Pd_xFe	36 24
	Fe(C)	– 13
PdFe/NaHX	Pd/Fe ratio is 14	
	Fe^{2+}_{tet}	12 –
	Fe^{2+}_{oct}	39 56
	Pd_xFe	49 44
PdFe/ZSM5	Pd/Fe ratio is 5	
	Fe^{2+}_{tet}	– –
	Fe^{2+}_{oct}	84 48
	Pd_xFe	15 15
	Fe(C)	– 37

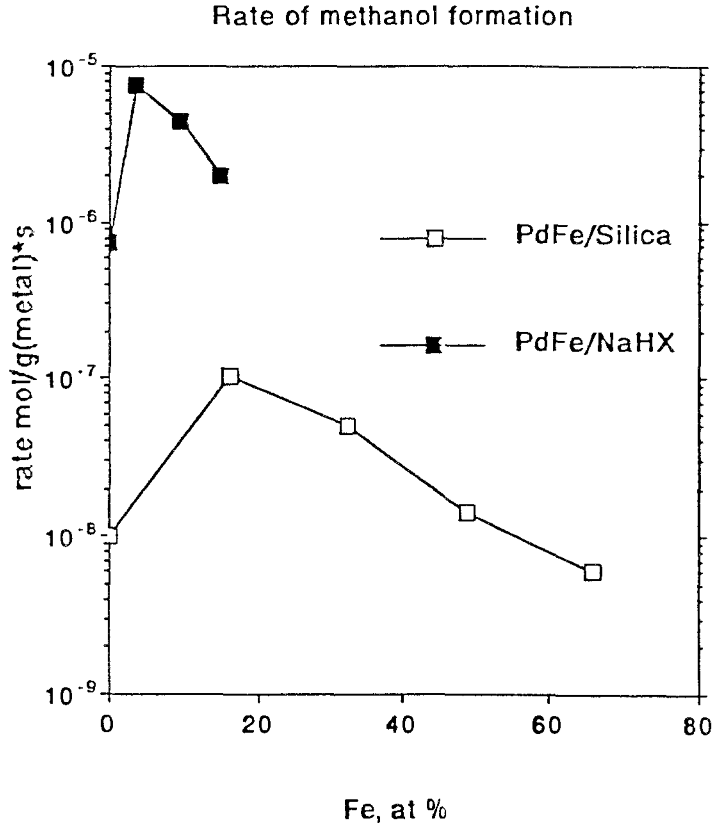

Fig. 2. Rate of methanol formation (mol g^{-1}_{metal} s^{-1}) on $PdFe/SiO_2$ (lower curve) and PdFe/NaHX-zeolite (upper curve) vs composition (from ref. [28 and 31]).

As was previously shown, MgO appeared to be beneficial for the optimum size of the bimetallic particles. We may expect, therefore, further improvement when metal particle size is further diminished and its growth geometrically confined when iron and palladium placed into zeolite cages [13,29,30].

There are two problems when the 2 wt% Pd ion exchanged into NaHX-zeolite or NaH ZSM5 and promoted by iron, are studied. First, it is to be proven whether or not bimetallic particles are formed and if so, they are formed in zeolite cages and not at the external surface. Second, whether or not these particles have better performance in the CO hydrogenation than the conventionally supported ones.

In table 2 the relative intensities of the various species are compared. As shown in the table, the Fe^{2+} in tetrahedral coordination located in the sodalite- and super-cage plays vital role in formation of Pd_xFe bimetallic particles (compare e.g. Fe^{2+}_{tet} to Pd_xFe conversion for Pd/Fe = 5 and Pd/Fe = 14, which is 32 to 36 and 12 to 49, respectively), that is, PdFe bimetallic particles are indeed formed inside the zeolite matrix.

The catalytic activity for the zeolite supported PdFe bimetallic particles is somewhat higher than what has been measured on SiO_2 support as shown in fig. 2. The activity of methanol formation passes through a maximum in both cases nearly at identical composition.

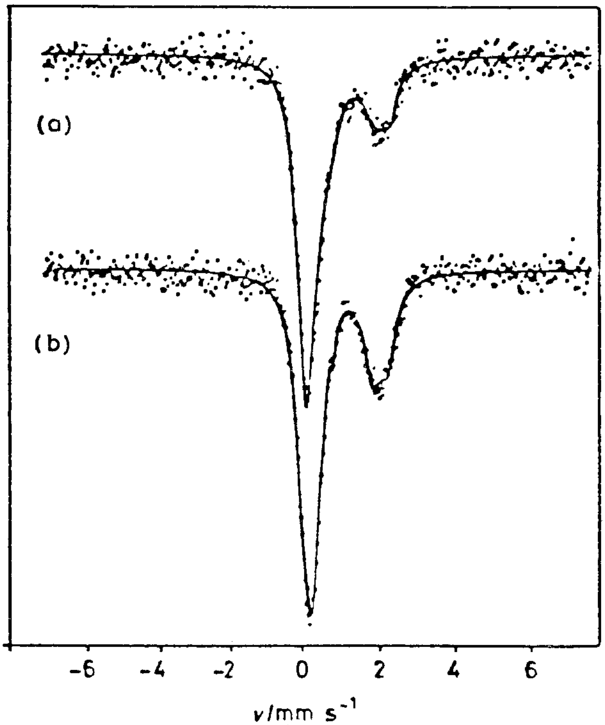

Fig. 3. Mössbauer spectra of PdFe/NaHX-zeolite (with 3.5 at.% Fe) measured at RT (a) after reduction at 720 K in H_2 for 5 h and (b) after $CO+H_2$ reaction at 508 K for 8 h (from ref. [13]).

Stability of the various samples is different. The most stable proved to be the PdFe/NaHX with Pd/Fe = 14 ratio because no carbide formation has been observed and the Mössbauer spectra before and after 8 h reaction time in $CO + H_2$ are the same (see fig. 3). On the other hand, PdFe/ZSM5 is the least stable sample because the PdFe particles cannot be stabilized in the zig-zag channels thus, the largest amount of carbide is formed (compare lines 4 and 11).

However, the metal-oxide interphase influences not only the mechanism of CO activation, but also the ratio of strongly to weakly held hydrogen on the surface. As is well know, hydrogen is adsorbed over various supported metals in activated form, i.e. higher adsorption temperature is required to fill up the adsorption sites bonding hydrogen strongly. It is also known [32] that by increasing metal dispersion the number of kink and step sites increases and thereby opening strongly bonding sites for hydrogen adsorption. Futhermore, when the number of neighbours of a metal adsorption site decreases, the metal-hydrogen bond strength increases [33]. This is also a way to control selectivity via the amount of surface hydrogen available for hydrogenation.

3. Conclusions

It has been established in the present work that activity and selectivity in $CO + H_2$ reactions over multimetallic catalysts are controlled by various factors:

(i) bimetallic catalysts may influence the dissociative vs associative CO adsorption. The exact mechanism is still not known: it is basically determined by the nature of metals, but metals which adsorb CO in molecular form (e.g. Pt, Pd, Ir), can be activated by addition of a second metal. Here alloy formation or non-reducible oxide-metal interface serve as activating species in CO activation even in molecular form. The effect is twofold; either the adsorption of non dissociated CO is enhanced at the metal-support interface by creating more adsorption sites or the linearly adsorbed CO is further activated.

(ii) Activity and selectivity is further influenced by the dispersion induced hydrogen adsorption. If the activated form of hydrogen on the surface is increased, i.e. high temperature is required for hydrogen adsorption, the amount of hydrogen available for hydrogenation of the surface species is depleted, consequently, the selectivity is shifted toward olefins. As a secondary effect of the hydrogen depletion, deactivation of the catalyst may result from formation of inactive carbide.

Generally, metallic dispersion is the factor which may affect the selectivity in both directions. Large metallic particles which dissociate CO may be drastically changed when they are in form in highly dispersed metal particles. The same is valid for hydrogen adsorption: the activated form of hydrogen appears only when the metal is in disperse form.

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