Iron or Lanthanum Promoters on the Selectivity of Palladium Zeolites in Methanol Synthesis

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The first example that demonstrates the distinct shift in selectivity towards methanol formation on the addition of Fe or La to Pd zeolite catalysts, together with enhanced activity, is reported.

There has been intensive research on the selective synthesis of methanol by the hydrogenation of carbon monoxide using palladium catalysts, since the pioneering work of Poutsma *et al.*, in view of its industrial application.[1,2] Recent studies indicate that the addition of Fe or La to Pd on SiO_2 enhances the activity for methanol formation.[3,4]

We now report the promoting effect of La or Fe addition to Pd zeolites that leads to enhanced selectivity for methanol formation, in addition to increased activity at atmospheric and elevated pressures. In addition, PdFe bimetallic particles are identified by *in situ* Mössbauer spectroscopy.

La and Fe promoted 2 wt% Pd zeolites were prepared from NaY or NaX zeolites by a successive exchange method. The slurry of the zeolite was treated for 24 h with a solution of $Pd(NH_3)_4Cl_2$, then, after filtration, the Pd zeolite was washed several times to remove any chlorides present in the support. After drying at 80 °C the sample was treated in the same manner with a solution of $Fe(NO_3)_3$ or $LaCl_3$. The partial

Table 1. Kinetic data on oxygenate formation on Fe and La containing PdNa zeolite.

					Selectivity (%)				
Run	Catalyst[a]	Atomic ratio, Pd : promoter	*P*/atm	*T*/°C	Methane	C_2—C_6 alkanes	Oxygenates[b]	Methanol	Activity[c]
1	PdNa(H)X		1	235	52			48	0.3
2	PdNa(H)X		10	235	100			—	0.8
3	PdLaNa(H)X	1 : 0.25	1	235	10			90	1.3
4	PdLaNa(H)X	1 : 0.25	10	235	15		45	40	6.4
5	PdLaNa(H)X	1 : 0.5	1	235	7			93	1.5
6	PdLaNa(H)X	1 : 0.7	1	235	7			93	3.2
7	PdLaNa(H)X	1 : 0.7	10	235	7	3		90	7.3
8	PdLaNa(H)X	1 : 1	1	235	11		1	88	1.5
9	PdFeNa(H)X	1 : 0.33	1	235	22			78	0.6
10	PdFeNa(H)X	1 : 0.33	10	235	62	10		28	1.9
11	PdFeNa(H)X	1 : 0.2	1	235	11			89	1.1
12	PdFeNa(H)X	1 : 0.07	1	235	8			92	1.7
13	PdFeNa(H)X	1 : 0.07	10		7	5		88	3.0
14	PdNa(H)Y		1	235	77			23	0.1
15	PdLaNa(H)Y	1 : 1	1	235	40		6	54	2.1
16	PdLaNa(H)Y	1 : 1	1	200	19		3	78	0.9

[a] Pd (2 wt%) for all samples. [b] Majority of the product is dimethyl ether. [c] $10^7\times$ Number of CO moles converted on 1 g of catalyst in 1 second.

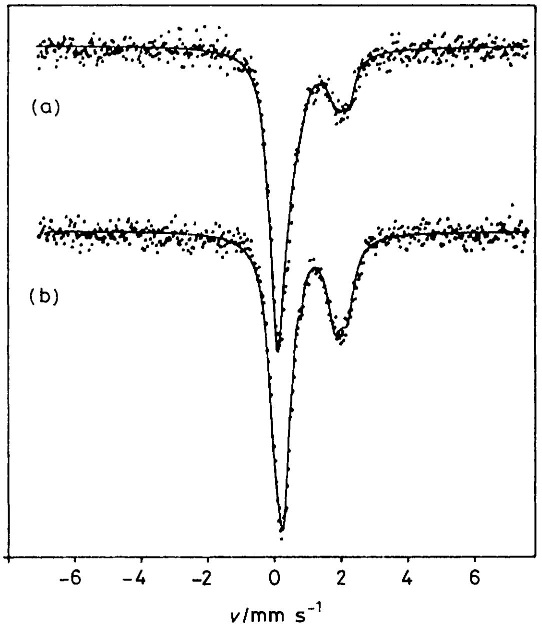

Figure 1. Room temperature Mössbauer spectra of PdFe (1 : 0.07) NaX samples: (a) after reduction at 450 °C in hydrogen for 5 h; (b) after reaction at 235 °C in CO + H_2 for 8 h.

exchange of sodium by hydrogen cannot be excluded since the solutions are slightly acidic. After thorough drying all catalysts were calcined at 300 °C in flowing oxygen for 18 h to expel ammonia, and evacuated *in vacuo* for 2 h. The catalysts were then transferred into a flow reactor, reduced for 5 h at 450 °C in flowing hydrogen, and then treated with CO + H_2 (1 : 2). The activity and selectivity were measured under the conditions listed in Table 1. (For the measurements the feed was kept constant, so the conversion of CO varied between 0.2 and 5.5% at 1 atm and between 1 and 9% at 10 atm.)

For Mössbauer studies, the calcined catalyst samples (^{57}Fe was used for the exchange) were pressed into wafers and placed in the *in situ* cell described elsewhere.[5] Room temperature Mössbauer spectra of the samples were obtained after reduction in hydrogen at 450 °C for 5 h (Figure 1a). The influence of the reaction on the catalysts was studied by recording their room temperature spectra after 8 h at 235 °C in flowing CO + H_2 (Figure 1b).

The selectivity of the CO + H_2 reaction is markedly affected by temperature, pressure, the type of reactor, and the carriers employed to disperse the Pd metal particles. Pd on SiO_2 is known to give methanol selectively at high pressure,[1] methane below atmospheric pressure in a flow reactor,[6] and methanol in a recirculation reactor.[7] Zeolite supported Pd gave only methane at elevated pressure,[8] but at atmospheric pressure the proportion of methane dropped to one fifth of the products and no methanol was produced.[9] This anomaly is probably due to changes in the Pd morphology. The acidity of the zeolite influences the product selectivity; dimethyl ether can be formed from methanol on acidic sites.[10] Partial hydrolysis of hydrated ions, *e.g.* $La(H_2O)^{3+}$, can also generate Brönsted acidity.[11]

In our results, there is a distinct shift in methanol selectivity from 0 to 92% at high pressures and 50 to 93% at atmospheric pressure caused by the addition of Fe or La. The results indicate that the catalysts at the optimum ratio of Pd to La (1 : 0.7, runs 6 and 7) and of Pt to Fe (1 : 0.07, runs 12 and 13), which exhibited the highest selectivity and activity, behaved almost identically at elevated and atmospheric pressures except in the formation of a small percentage of hydrocarbons and oxygenates.

In the case of the iron promoter the enhanced selectivity can be attributed to the formation of PdFe bimetallic particles. In fact, the presence of PdFe particles was detected by Mössbauer studies. The spectra in Figure 1 are very similar to those obtained on PdFe bimetallic alloys supported on silica[12,13] with characteristic isomer shift values of 0.17—0.20 mm/s for the PdFe component. The second component in the spectra is due to Fe^{2+} which exhibits at least two doublets. The parameters and relative intensity of PdFe do not change in the CO + H_2 reaction, but the quadrupole splittings of Fe^{2+} doublets are altered. Namely, the splitting of the outer doublet decreases from 2.46 to 2.22 mm/s and that of the inner one increases from 1.48 to 1.75 mm/s. This change can be related to co-ordination of water molecules to the Fe^{2+} lattice cations.[14]

On increasing the iron content (run 10) iron carbide was identified along with PdFe particles in the Mössbauer spectra, and this might be responsible for low methanol activity. The catalysts are stable, methanol being generated even after 38 h on stream (runs 6 and 11).

The promoting mechanism of La is probably different from that observed with iron and is probably related mainly to the modification of the zeolite. An indication of this is the presence of oxygenates among the products of La-promoted catalysts (although oxygenates were not found with each La-promoted catalysts). The increase of acidity and also further factors may play a more important role, since significant enhancement of metal–support interactions has been found on Pd/La_2O_3[15] and Pd/ZSM-5 systems on addition of La_2O_3 promoter.[16]

In conclusion, addition of iron or lanthanum helped to stabilize and increase the number of Pd sites that give methanol selectively thus resulting in enhanced methanol selectivity and activity.

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