

## Hydroformylation of Propene with Zeolite-supported Rhodium Phosphine Complexes

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Rhodium phosphine complexes synthesized *in situ* on zeolite NaY are active for propene hydroformylation at 150 °C and 1 atm; the catalysts are not stable yet show an enhancement in linear vs. branched products with an increased production of alcohols compared to rhodium zeolites without phosphines.

Rhodium exchanged zeolites have been investigated as heterogeneous catalysts for a number of gas phase reactions including olefin hydroformylation.<sup>1-4</sup> It is postulated that binary or zeolite modified rhodium carbonyls are formed in these reactions. For hydroformylation with homogeneous catalysts it is well known that rhodium phosphine complexes are more selective towards the production of linear compounds than binary rhodium carbonyls.<sup>5</sup> Also, it is well documented that reduction of rhodium in zeolites yields rhodium carbonyls,<sup>2</sup> and that they react with small phosphines to give zeolite-supported rhodium phosphine complexes.<sup>6</sup> Here we present preliminary results for propene hydroformylation over zeolite-supported rhodium phosphine complexes. Rhodium zeolite catalysts (RhNaY) were prepared by dropwise addition of aqueous RhCl<sub>3</sub> to 0.1 M aqueous NaCl slurries of zeolite NaY at 90 °C. It has been suggested that this type of exchange most probably locates the rhodium mainly within the zeolite.<sup>7</sup> This is the material from which all the phosphinated catalysts were derived. The RhNaY catalyst without added phosphine gave an n-butyraldehyde production rate of  $5 \times 10^{-3}$  mol (g Rh)<sup>-1</sup> h<sup>-1</sup> (150 °C, 1 atm, 3:3:2:1 C<sub>3</sub>:H<sub>2</sub>:N<sub>2</sub>:CO, 45 ml/min S.T.P. total flow) with a normal/isobutyraldehyde ratio (Pr<sup>n</sup>CHO/Pr<sup>i</sup>CHO) of 1.8.<sup>1</sup> These catalysts were active for more than one week with no noticeable deactivation.

Since it has been shown that dimethylphenylphosphine (DMP) forms intrazeolitic complexes with rhodium carbonyls on zeolites,<sup>6</sup> this phosphine was chosen as the initial modifying ligand for the gas phase hydroformylation reaction. Five experiments have been performed in which DMP was added to the catalyst. In each case approximately a three-fold excess of phosphine was injected over the catalyst. For these

experiments, the gas mixture and flow rate were the same as for the RhNaY catalyst above. Table 1 summarizes the experimental conditions and includes a brief statement of the results, while Table 2 gives typical reaction rate data.

In experiment A, a precarbonylated (30 psig CO, at 120 °C for 12 h) catalyst was allowed to reach a steady state at 150 °C. Following DMP injection, the reactor heated up by 2 °C for 3 min. A sample taken 10 min later showed an order of magnitude increase in the rate of aldehyde production with only a slight enhancement of the n/iso ratio. After 40 min, the catalyst had lost over 90% of its activity prior to DMP injection; 55 min after injection no hydroformylation activity was observed. Further injections of DMP failed to reactivate the catalyst.

Experiments B and C show the effect of a constant partial pressure of DMP on the activity of a precarbonylated catalyst. In B, DMP was injected only at the time at which reactant flow was initiated. The first sample showed mainly n-butanol production, with only trace quantities of aldehyde present. Catalyst B was deactivated in 6 h. Experiment C shows that the constant partial pressure of DMP alters the catalyst selectivity to yield 2-methylhexan-3-one (Pr<sup>n</sup>COPr<sup>i</sup>) and heptan-4-one (Pr<sup>n</sup><sub>2</sub>CO) in a 1:2.3 ratio. Ketone synthesis over RhNaY catalysts has been observed previously.<sup>8</sup> Catalyst C is deactivated in 24 h.

Experiments D and E probe the effect of DMP on an untreated RhNaY catalyst. In experiment D, DMP was injected simultaneously with reactants at 25 °C. After heating to 150 °C for 1 h, n-butanol was the only product observed. n-Butanol production decreased steadily from its initial rate while iso- and n-butyraldehyde production increased. Maximum rates were observed after 5 h with n/iso ~1.0. This

Table 1. Effect of addition of dimethylphenylphosphine to RhNaY on activity.

Catalyst	T/°C <sup>a</sup>	Precarbonylated	Steady state	Injection or partial pressure of DMP	Results	Deactivation time/h
A	150	Yes	Yes	Injection	10-fold rate increase; slight selectivity increase	1
B	150	Yes	No	Injection	n-Butanol with trace of aldehydes	6
C	150	Yes	No	Partial pressure	Ketones only	24
D	25	No	No	Injection	n-Butanol initially; n/iso aldehydes ~1:1 later	24
E	25	No	No	Partial pressure	C <sub>4</sub> aldehydes and n-butanol; n/iso increases with time	36

<sup>a</sup> Temperature at which DMP first contacts the catalyst.

**Table 2.** Reaction rate data for experiments listed in Table 1.

Catalyst	Time	Rate of formation/mmol (g Rh) <sup>-1</sup> h <sup>-1</sup>					
		Pr <sup>i</sup> CHO	Pr <sup>n</sup> CHO	Pr <sup>i</sup> CH <sub>2</sub> OH	Pr <sup>n</sup> CH <sub>2</sub> OH	Pr <sup>n</sup> COPri	Pr <sup>n</sup> <sub>2</sub> CO
A	Steady state prior to DMP injection	5.0	8.8	—	3.7	—	—
	10 min after DMP	62.0	120.0	3.67	65.7	—	—
B	75 min after DMP	trace	trace	—	8.3	—	—
	225 min after DMP	—	—	—	1.9	—	—
C	45 min	—	—	—	—	2.5	5.7
	7 h	—	—	—	—	0.5	1.1
D	90 min after DMP	—	—	—	4.8	—	—
	11 h after DMP	1.5	1.6	—	—	—	—
E	6.5 h	3.0	1.7	—	0.6	—	—
	14 h	1.3	1.5	—	0.7	—	—
	27 h	0.8	1.5	—	0.5	—	—

catalyst was completely deactivated within 24 h. In experiment E, the reactant stream was continuously contacted with a partial pressure of DMP at 25 °C. After several hours at 150 °C, both butyraldehydes were present as was n-butanol. Deactivation slowly took place over 36 h. During the deactivation period the n/iso ratio increased owing to the faster decline in activity for isobutyraldehyde formation.

In general, the addition of DMP shifts the catalytic activity to favour the production of linear compounds. n-Butanol is the major product formed initially in experiments B and D. Experiments C and E show that a continuous feed of DMP slows the deactivation process more than that shown for catalysts B and D. These reactions have been performed at 150 °C to allow direct comparison with previous work.<sup>1-4</sup> However, it is possible that catalyst deactivation may be related to phosphine decomposition over the zeolite at these temperatures. Lower reaction temperatures may lead to better catalyst stability with retention of higher production of linear compounds.

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