Rhodium Zeolites as Bifunctional Catalysts for the Synthesis of 2-Methylhexan-3-one and Heptan-4-one from Propylene, Carbon Monoxide, and Hydrogen

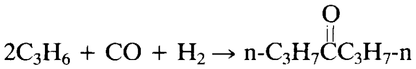
Edward Rode,[a] Mark E. Davis,*[a] and Brian E. Hanson*[b]

[a] *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, U.S.A.*

[b] *Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, U.S.A.*

RhNaX and RhNaY zeolites behave as bifunctional catalysts for the synthesis of C_7 ketones from C_3H_6, CO, and H_2 at atmospheric pressure and 120—150 °C.

The hydroformylation of olefins has long been established as a commercially important catalytic reaction.[1] The original cobalt catalysed reaction uses either $Co_2(CO)_8$ or $Co_2(CO)_8$ and $P(Bu^n)_3$ as the catalyst precursor. A large number of byproducts are observed when using cobalt catalysts for the hydroformylation of linear α-olefins; these include alkanes, internal olefins, internal branched aldehydes, and alcohols. Ketones may also be observed over cobalt catalysts and, under appropriate conditions, may even become one of the major products.[2] The reaction for ketone synthesis from propylene, CO, and H_2 is given in equation (1).



$$2C_3H_6 + CO + H_2 \rightarrow n\text{-}C_3H_7\overset{\overset{\displaystyle O}{\|}}{C}C_3H_7\text{-}n \qquad (1)$$

In the rhodium based hydroformylation process this reaction is not considered to be a source of byproducts.[3] Typically the higher molecular weight products in the homogeneous rhodium catalysed reaction arise from aldol condensation of aldehydes. However at higher temperatures and pressures than employed in the commercial rhodium hydroformylation reaction, $Rh_2(CO)_4Cl_2$ is observed catalytically to yield small quantities of ketones from cyclopropane along with many other products.[4] In a related reaction ketones are observed over ruthenium catalysts when water-gas shift conditions are used. For example, C_2H_4:CO in 1:1 mixtures react in aqueous Ru^{3+} solutions at 195—220 °C and 550—650 atm to yield pentan-3-one.[5] Palladium acetate appears to be more active for this reaction; it is reported that pentan-3-one is produced at a rate of 1—2 turnovers/hour at 50—70 °C.[6]

We have been investigating rhodium exchanged zeolites as catalysts for the hydroformylation of olefins in the gas and liquid phases.[7] For certain catalyst preparations† we observe the production of significant quantities of 2-methylhexan-3-one and heptan-4-one from propylene, CO, and H_2 in the gas phase. The synthesis of ketones in this manner is unique in that the rhodium zeolite is acting as a bifunctional catalyst for the reaction.

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† All rhodium exchanged zeolites prepared in our laboratory show activity for ketone production provided that they also show hydroformylation activity. The most active for ketone synthesis and the one for which data are provided here was prepared by cation exchange of zeolite Y with aqueous $RhCl_3$ in 0.2 M NaCl at 90 °C at pH 6. For these catalysts all of the aldehydes are converted into ketones.

Rhodium zeolites prepared *via* cation exchange have been shown to be active for the hydroformylation of olefins.[7,8] The hydroformylation reaction however is very sensitive to the temperature at which rhodium is exchanged, the presence of NaCl, and the pH at which the exchange is performed. In our laboratory some high molecular weight products have been observed for catalysts which are active for hydroformylation. Initially these were thought to be due to aldol condensation of butyraldehyde. Furthermore the higher molecular weight products are formed to the complete exclusion of aldehydes over catalysts which were exchanged in the presence of 'high' NaCl concentrations. (Sodium chloride concentration in the exchange solution was varied from 0 to 0.2 M.) It has been shown by others that NaCl may be occluded in zeolites from aqueous solutions of NaCl.[9] G.c.–mass spectroscopic analysis reveals that initially the heavy products are heptan-4-one, 2,4-dimethylpentan-3-one, and 2-methylhexan-3-one and not the expected aldol condensation products. After several hours on line only heptan-4-one and 2-methylhexan-3-one are formed. Significantly, these are formed in a 2 : 1 ratio with the linear ketone as the major product. This is the same linear/branched ratio observed for butyraldehyde synthesis over Rh-zeolites which gives very little ketone product.[7a] Over RhNaY and RhNaX catalysts ketone synthesis is only observed once the catalyst has been activated for aldehyde synthesis. Typical reaction conditions are 150 °C, 1 atm, 1.25 s residence time of reactant gases over a fixed catalyst bed containing *ca.* 0.8 g of 3.5 wt.% RhNaY catalyst. The rate of ketone production is 0.25 turnovers/hour based on the total rhodium content of the reactor. For catalysts prepared with low NaCl concentrations, the rate for butyraldehyde synthesis is also in the range 0.2 to 0.3 turnovers/hour for total rhodium in the reactor. Separate *in situ* i.r. experiments suggest that most of the rhodium present on the zeolite is inactive for hydroformylation.[10]

Although it is well established that transition metals may catalyse the synthesis of ketones from olefins, CO, and H_2,[2–6] in the case of Rh-zeolites the zeolite may be responsible for ketone synthesis. Thus the following control experiment was performed: Propylene saturated with butyraldehyde vapour (normal/iso, 1 : 1) was passed over a zeolite Y sample which had first been treated with 0.2 M NaCl at 90 °C. At 150 °C significant quantities of both heptan-4-one and 2-methylhexan-3-one are produced. Thus the zeolite is responsible for converting butyraldehydes and propylene into ketones.

The role of the NaCl in modifying the selectivity of these catalysts appears to be the promotion of the zeolite catalysed reaction of aldehyde and propylene to ketone. The total rate of product formation (C_4 aldehydes + C_7 ketones) is not changed significantly with increasing NaCl concentration. Thus NaCl does not appear to be blocking active hydroformylation sites on the catalyst.

This observed bifunctional catalytic reaction should be general for a wide range of olefins.

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