

Selective Formation of Lower Alkenes and Alcohols in CO + H₂ Reaction catalysed on NaY Zeolite-encapsulated Rh₆ and RhFe Bimetallic Cluster-derived Catalysts

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NaY zeolite encapsulated Rh₆ clusters characterized by EXAFS and Fourier transform i.r. spectroscopy led to the selective formation of C₂—C₄ alkenes in the reaction of CO + H₂ under atmospheric pressure, whereas RhFe carbonyl clusters synthesized in NaY showed a unique activity for formation of a mixture of ethanol and methanol.

Lack of control of product selectivity has been a major problem in the CO + H₂ reaction catalysed on transition metals. Support interactions¹ and molecular-shape control by zeolite frameworks² may influence the distribution of products such as hydrocarbons and oxygenates. It has also been reported that some electropositive metal ions exhibited a

marked promotion of CO + H₂ conversion into oxygenates catalysed on Rh, Pd, and Ir catalysts, in effectively enhancing activity with Mn, Ti, and Zr³ and selectivity towards alcohol formation with Fe, Mo, and Zn.⁴ This communication deals with the *in situ* preparation and structural characterization of Rh₆, Fe₃, and bimetallic RhFe carbonyl clusters entrapped

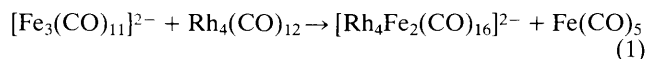
Table 1. Catalytic performance of [Rh₆]/NaY, [Rh₆] + [Fe₃]/NaY, and bimetallic RhFe/NaY in the CO + H₂ reaction, compared to the conventional Rh/SiO₂.^a

Catalyst ^b	T/K	CO conv. (%)	Hydrocarbons							Oxygenates			
			Specific rate of formation ^c							Specific rate of formation ^c			
			C ₁	C ₂	C ₃	C ₄	C ₅	C ₂ —C ₄ sel. (%)	Alkene sel. ^d	MeOH	MeCHO	EtOH	PrOH
[Rh ₆]/NaY	469	0.48	10.8	3.8	7.0	3.7	tr.	58.9	4.7	0	0.12	0	0
	498	1.96	40.0	11.9	21.1	11.9	tr.	52.9	4.0	0	2.11	0	0
	523	5.3	124	28.7	50.2	28.8	1.2	46.8	1.5	0	2.18	0	0
[Rh ₆] + [Fe ₃]/NaY	498	1.40	24.9	5.6	19.2	4.9	tr.	54.4	6.3	0	2.66	0.19	0
RhFe/NaY	469	0.26	4.3	0.6	1.0	tr.	tr.	27.1	7.8	0.88	0.76	1.4	tr.
	498	0.83	18.7	4.0	4.6	1.2	tr.	34.4	3.8	0.54	1.4	3.0	tr.
Rh/SiO ₂ ^e	498	0.42	9.2	0.8	1.2	tr.	0	18.4	0.82	0	tr.	0	0
	523	2.3	51	2.6	4.1	tr.	0	11.8	0.42	0	tr.	tr.	0

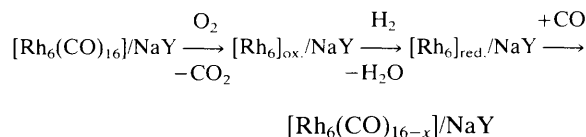
^a CO:H₂ = 1:1 (molar ratio); 1 atm pressure, flow rate 20 ml min⁻¹. ^b 0.6 g, 2 wt.% Rh. ^c Evaluated on a carbon basis. Specific rate of formation in mmol min⁻¹ (Rh mmol)⁻¹. ^d Molar ratio of propene to propane in the hydrocarbon products. ^e RhCl₃ on SiO₂ (Davison no. 57, 10–20 mesh), H₂ reduction at 673 K for 2 h. Rh distribution: CO/Rh 0.32, H/Rh 0.43.

within the NaY zeolite supercage. It is interesting that the NaY-entrapped Rh₆ clusters led to the selective formation of alkene rich C₂—C₄ hydrocarbons in CO + H₂ reactions at atmospheric pressure, whereas the bimetallic RhFe cluster in NaY showed higher selectivity for C₁—C₂ alcohol formation.

Rh³⁺/NaY (2 wt% Rh loading) was prepared from powdered zeolite NaY (Si/Al 5.6, surface area 910 m²/g, obtained from Toyo Soda Manufacturing Co.) by cation exchange of an aqueous solution of RhCl₃.⁵ Rh³⁺/NaY was heated from 300 to 393 K under an atmosphere of CO (600 Torr) and H₂O (10 Torr), resulting in the complete formation of Rh₆(CO)₁₆ inside the NaY supercage,⁶ Rh₆(CO)₁₆/NaY [I]. The reduced sample, [Rh₆]/NaY [II], was obtained by the oxidation of [I] with O₂ at 473 K, followed by H₂ reduction at 473 and 673 K. [HFe₃(CO)₁₁]⁻/NaY [III] was prepared from Fe₂(CO)₉ with hydrated NaY at 373 K.⁷ The bimetallic RhFe carbonyl cluster in NaY, RhFe/NaY [IV], was prepared by the reaction of hydrated [III] with Rh₄(CO)₁₂ at 343–393 K by analogy with reaction (1) which occurs in solution in tetrahydrofuran.⁸



Sample [I] showed i.r. terminal carbonyl bands at 2096s, 2046w, and 2022w cm⁻¹, and a band at 1760m cm⁻¹ due to the triply bridging CO interacting with Al³⁺ (or Na⁺) located on the wall of the NaY supercage.⁶ *In situ* EXAFS was conducted for samples [I] and [II] at SOR beam line 10B of the National Laboratory for High Energy Physics (KEK-PF). Rh K-edge EXAFS analysis of the first neighbour Rh–Rh, Rh–C, and Rh–O distances for sample [I] provided direct evidence for the stoichiometric formation of a hexanuclear Rh carbonyl within the zeolite framework; an Rh–Rh C.N. (co-ordination number) of 3.1 and an atomic distance *R* of 2.74 Å are in good agreement with those observed for crystalline Rh₆(CO)₁₆ (C.N. 4.0, *R* 2.76 Å). Additionally, a small contribution of Rh–O bonding with the oxide wall of the supercage (Rh–O: C.N. 1.9, *R* 2.06 Å) was observed for sample [I]. The EXAFS data for the reduced sample [II] also support the retention of the original Rh₆ framework (Rh–Rh: C.N. 4.6, *R* 2.70 Å), with a small Rh–O bonding contribution (Rh–O: C.N. 0.7, *R* 2.09 Å). Sample [II] (reduced with H₂ at 473 or 673 K) chemisorbed CO and H₂ at 298 K with stoichiometries CO/Rh = 2.0 and H/Rh = 0.6. The results of the EXAFS

**Scheme 1**

measurements and Fourier transform i.r. studies in CO chemisorption suggest that irrespective of the treatment and temperature, hexanuclear Rh clusters with sizes in the <10 Å region are accommodated within the zeolite framework cavities (13 Å inner radii) without the formation of large crystallites on the external surface through the redox processes in Scheme 1.

The CO + H₂ reaction was performed at atmospheric pressure on both samples [I] and [II] at 423–523 K. As shown in Table 1, they showed higher activities for formation of alkene-rich C₂—C₄ hydrocarbons (45–60% CO base selectivity) even at the higher CO conversions of 2–5%, compared with those on conventional Rh/SiO₂ catalysts. A small amount of acetaldehyde was also obtained. The CO conversion and selectivity for formation of lower alkenes were maintained for long (40 h) time-on-stream reactions of CO + H₂ on both [I] and [II]. *In situ* Fourier transform i.r. studies suggested that [II] was completely converted into [I] under the atmosphere of CO–H₂ at 373–423 K. The pattern of alkene and alkane products in the C₁—C₅ range studied did not show a typical Schulz–Flory distribution. Products with chain lengths >C₄ were drastically diminished, and there was a sharp maximum at C₃ on samples [I] and [II]. The higher selectivities for formation of C₂—C₄ alkenes on the cluster-zeolite samples are proposed to be associated not only with the molecular-shape control properties of the zeolite supercage, but also with the limiting of the size of the Rh particles to <10 Å. We assume that the small Rh particles inside the zeolite depress the hydrogenation activity, because they chemisorb CO strongly but H₂ relatively weakly in the CO + H₂ reaction. This is reflected in the higher alkene/alkane ratios of the hydrocarbons, and promotion of the chain propagation which leads to formation of longer hydrocarbons on the [Rh₆]/NaY catalysts. In this connection, it has been reported previously that Ru crystallites⁹ derived from Ru carbonyls and Co (and

Fe) particles¹⁰ of size <12 Å inside NaY gave a distribution of lower alkenes centred on C₄ in the reaction, although at a very low conversion (<1%).

The bimetallic RhFe carbonyl cluster, inferred to be RhFe/NaY [IV] gave characteristic i.r. carbonyl bands (2078s, 2020m, 1958w; and 1741m, 1711s, 1689w cm⁻¹), which resembled those of [Rh₄Fe₂(CO)₁₆][NMe₃(CH₂Ph)]₂ deposited on NaY (2093s, 2044w; and 1811w, 1754m, 1705s cm⁻¹). It is interesting that a sample of [IV] after oxidation followed by H₂ reduction at 473 K regenerated the RhFe carbonyl species in CO (600 Torr) + H₂O (10 Torr) at 390 K, this sample showing i.r. carbonyl bands similar to those of the original [IV]. A Mössbauer study at 298 K indicated that the iron remains in a higher oxidation state even after the H₂ reduction of RhFe/NaY at 473 K, suggesting that the cationic Fe anchors Rh clusters in the NaY supercage. As also shown in Table 1, it is of interest that the bimetallic RhFe/NaY sample provided a good yield of oxygenates, mainly consisting of EtOH and MeOH, at the expense of a decrease in yields of CH₄ and higher hydrocarbons in the CO + H₂ reaction. To rationalize the origin of the promotion for alcohol formation on RhFe/NaY, a sample consisting of a physical mixture of Rh₆ and Fe₃ carbonyl clusters entrapped inside NaY cages, [Rh₆] + [Fe₃]/NaY [V], was prepared by the reaction of [Rh₆(CO)₁₆]/NaY and Fe₂(CO)₉ in CO + H₂O at 343 K. The resulting sample preferentially gave alkene-rich C₂—C₄ hydrocarbons with a trace of MeCHO in the CO + H₂ reaction, a product pattern which was almost the same as that for [Rh₆]/NaY [II]. The results suggest that Fe-promotion in the RhFe/NaY catalyst for C₁—C₂ alcohol formation is related to the existence of adjacent Rh—Fe bimetallic sites in a NaY supercage which activate CO in enhancing migrating CO insertion into Rh—H and Rh—alkyl bands, forming MeOH and higher oxygenates, as has previously been reported for alkene hydroformylation catalysed on SiO₂-supported RhFe bimetallic carbonyl cluster-derived catalysts.¹¹

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