Selective Formation of Lower Alkenes and Alcohols in CO + H_2 Reaction catalysed on NaY Zeolite-encapsulated Rh_6 and RhFe Bimetallic Cluster-derived Catalysts

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NaY zeolite encapsulated Rh_6 clusters characterized by EXAFS and Fourier transform i.r. spectroscopy led to the selective formation of C_2—C_4 alkenes in the reaction of CO + H_2 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 + H_2 reaction catalysed on transition metals. Support interactions[1] and molecular-shape control by zeolite frameworks[2] 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 + H_2 conversion into oxygenates catalysed on Rh, Pd, and Ir catalysts, in effectively enhancing activity with Mn, Ti, and Zr[3] and selectivity towards alcohol formation with Fe, Mo, and Zn.[4] This communication deals with the *in situ* preparation and structural characterization of Rh_6, Fe_3, and bimetallic RhFe carbonyl clusters entrapped

Table 1. Catalytic performance of $[Rh_6]/NaY$, $[Rh_6] + [Fe_3]/NaY$, and bimetallic RhFe/NaY in the CO + H_2 reaction, compared to the conventional Rh/SiO_2.[a]

			Hydrocarbons							Oxygenates			
		CO	Specific rate of formation[c]					C_2—C_4	Alkene	Specific rate of formation[c]			
Catalyst[b]	*T*/K	conv. (%)	C_1	C_2	C_3	C_4	C_5	sel. (%)	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] $CO:H_2 = 1:1$ (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] $RhCl_3$ on SiO_2 (Davison no. 57, 10—20 mesh), H_2 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 Rh_6 clusters led to the selective formation of alkene rich C_2—C_4 hydrocarbons in CO + H_2 reactions at atmospheric pressure, whereas the bimetallic RhFe cluster in NaY showed higher selectivity for C_1—C_2 alcohol formation.

Rh^{3+}/NaY (2 wt% Rh loading) was prepared from powdered zeolite NaY (Si/Al 5.6, surface area 910 m^2/g, obtained from Toyo Soda Manufacturing Co.) by cation exchange of an aqueous solution of $RhCl_3$.[5] Rh^{3+}/NaY was heated from 300 to 393 K under an atmosphere of CO (600 Torr) and H_2O (10 Torr), resulting in the complete formation of $Rh_6(CO)_{16}$ inside the NaY supercage,[6] $Rh_6(CO)_{16}/NaY$ [I]. The reduced sample, $[Rh_6]/NaY$ [II], was obtained by the oxidation of [I] with O_2 at 473 K, followed by H_2 reduction at 473 and 673 K. $[HFe_3(CO)_{11}]^-/NaY$ [III] was prepared from $Fe_2(CO)_9$ 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 $Rh_4(CO)_{12}$ at 343—393 K by analogy with reaction (1) which occurs in solution in tetrahydrofuran.[8]

$$[Fe_3(CO)_{11}]^{2-} + Rh_4(CO)_{12} \rightarrow [Rh_4Fe_2(CO)_{16}]^{2-} + Fe(CO)_5 \quad (1)$$

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 Al^{3+} (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 stoicheiometric 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 $Rh_6(CO)_{16}$ (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 Rh_6 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 H_2 at 473 or 673 K) chemisorbed CO and H_2 at 298 K with stoicheiometries CO/Rh = 2.0 and H/Rh = 0.6. The results of the EXAFS 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 accomodated 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.

$$[Rh_6(CO)_{16}]/NaY \xrightarrow[-CO_2]{O_2} [Rh_6]_{ox.}/NaY \xrightarrow[-H_2O]{H_2} [Rh_6]_{red.}/NaY \xrightarrow{+CO} [Rh_6(CO)_{16-x}]/NaY$$

Scheme 1

The CO + H_2 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 C_2—C_4 hydrocarbons (45—60% CO base selectivity) even at the higher CO conversions of 2—5%, compared with those on conventional Rh/SiO_2 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 + H_2 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–H_2 at 373—423 K. The pattern of alkene and alkane products in the C_1—C_5 range studied did not show a typical Schulz–Flory distribution. Products with chain lengths >C_4 were drastically diminished, and there was a sharp maximum at C_3 on samples [I] and [II]. The higher selectivities for formation of C_2—C_4 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 H_2 relatively weakly in the CO + H_2 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 $[Rh_6]/NaY$ catalysts. In this connection, it has been reported previously that Ru crystallites[9] derived from Ru carbonyls and Co (and

Fe) particles[10] of size <12 Å inside NaY gave a distribution of lower alkenes centred on C_4 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 $[Rh_4Fe_2(CO)_{16}][NMe_3(CH_2Ph)]_2$ deposited on NaY (2093s, 2044w; and 1811w, 1754m, 1705s cm^{-1}). It is interesting that a sample of [IV] after oxidation followed by H_2 reduction at 473 K regenerated the RhFe carbonyl species in CO (600 Torr) + H_2O (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 H_2 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 CH_4 and higher hydrocarbons in the CO + H_2 reaction. To rationalize the origin of the promotion for alcohol formation on RhFe/NaY, a sample consisting of a physical mixture of Rh_6 and Fe_3 carbonyl clusters entrapped inside NaY cages, $[Rh_6]$ + $[Fe_3]$/NaY [V], was prepared by the reaction of $[Rh_6(CO)_{16}]$/NaY and $Fe_2(CO)_9$ in CO + H_2O at 343 K. The resulting sample preferentially gave alkene-rich C_2—C_4 hydrocarbons with a trace of MeCHO in the CO + H_2 reaction, a product pattern which was almost the same as that for $[Rh_6]$/NaY [II]. The results suggest that Fe-promotion in the RhFe/NaY catalyst for C_1—C_2 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 SiO_2-supported RhFe bimetallic carbonyl cluster-derived catalysts.[11]

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