

Zeolite-entrapped Osmium Carbonyl Clusters: Selective and Stable Catalysts for CO Hydrogenation

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$[\text{H}_2\text{Os}(\text{CO})_4]$ is converted in the pores of a basic form of zeolite Y (formed by treatment with NaN_3) to give entrapped Os carbonyl clusters that catalyse CO hydrogenation at 573 K and 19 bar (1 bar = 10^5 Pa) to give C_2 — C_4 hydrocarbons in high yield with only slow loss of catalytic activity and selectivity.

The practical value of hydrogenation of carbon monoxide catalysed by metals is limited by the unfavourable (Schulz-Flory) distribution of hydrocarbon products. In attempts to increase the yields of C_{2+} hydrocarbons, researchers have used zeolites as supports for the metals, attempting to impose a shape selectivity on the catalysis¹ or to control the performance through metal particle size effects.² These attempts have been successful in giving unusual distributions

of products (*e.g.*, high yields of C_3^1 or C_4^3 hydrocarbons), but the catalysts have been unstable, because the zeolite pores have been plugged with products and/or because the metal has been oxidized or migrated out of the zeolite cages to form larger aggregates,⁴ which catalyse the reaction to give the conventional product distribution.

The goal of this research was to prepare CO hydrogenation catalysts having metal clusters stably entrapped in zeolite

cages. The strategy was to introduce a small organometallic precursor into the zeolite cages and to form entrapped metal carbonyl clusters by reductive carbonylation. Precedent for this chemistry is found in the reactions of $[\text{H}_2\text{Os}(\text{CO})_4]$ on the basic surface of MgO ; condensation gives high yields of the stable $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$.^{5,6} Extension of this chemistry to a zeolite requires one with basic character.⁷

The basic zeolite support was prepared from NaY powder treated with NaN_3 in CH_3OH .^{8,9} The solid was exposed to $[\text{H}_2\text{Os}(\text{CO})_4]$ vapour at room temperature for one day. The resulting yellow solid, containing 9 wt% Os as determined by X-ray fluorescence spectroscopy, was characterized by i.r. spectroscopy before and after treatment in flowing $\text{CO} + \text{H}_2$. The fresh sample had ν_{CO} bands at 2076 w, 2046 m, 2002 vs, and 1928 vs cm^{-1} , and the sample treated in flowing $\text{CO} + \text{H}_2$ at 573 K and 1 bar had a new spectrum, with ν_{CO} bands at 2092 w, 2057m, 1988vs, and 1966s cm^{-1} ; these are suggestive of Os carbonyl clusters, but they have not been identified with known molecular species.

The sample was tested as a catalyst for CO hydrogenation in a copper-lined flow reactor operated at 573–628 K and 18–30 bar with $\text{CO} : \text{H}_2$ ratios from 0.33 to 3.0 (molar). The product distribution is markedly different from that characteristic of a conventional catalyst consisting of Os crystallites supported on $\gamma\text{-Al}_2\text{O}_3$ (Figure 1).¹⁰ The yield of $\text{C}_2\text{--C}_4$ hydrocarbons obtained with the zeolite was as high as 60% (molar). Additional data and comparisons with the literature are given in Table 1. The activity of the catalyst is relatively low (Table 1); the rate of reaction at 573 K, 19 bar, and a space velocity of 0.17 ml/(g of catalyst s) was about 4×10^{-6} mol of hydrocarbon/(mol of Os s). This activity had not declined measurably after 20 days of continuous operation under these conditions, and the selectivity changed only moderately (see Figure 1 and Table 1). The 20-day-old catalyst removed from the reactor was still yellow, suggesting the presence of the Os clusters. The i.r. spectrum of this used catalyst (ν_{CO} 2097 w, 1987 sh, 1960 vs, and 1870 sh cm^{-1}) suggests that a change in structure had occurred.

The zeolite-supported catalysts reported in the literature are much less stable (Table 1). In contrast, a Y-zeolite-

supported iron catalyst prepared from a toluene solution containing Fe introduced as the vapour lost its activity within minutes of catalytic operation.³ A catalyst prepared from zeolite A containing Co clusters formed by reduction of CoA with Cd vapour was initially selective for formation of propene and propane but lost its selectivity within hours when the temperature was increased beyond roughly 500–550 K; the loss of selectivity was attributed to migration of the Co out of pores to form larger crystallites.¹

The selectivity of the new catalyst is associated with the narrow pore structure, and its stability is attributed to the

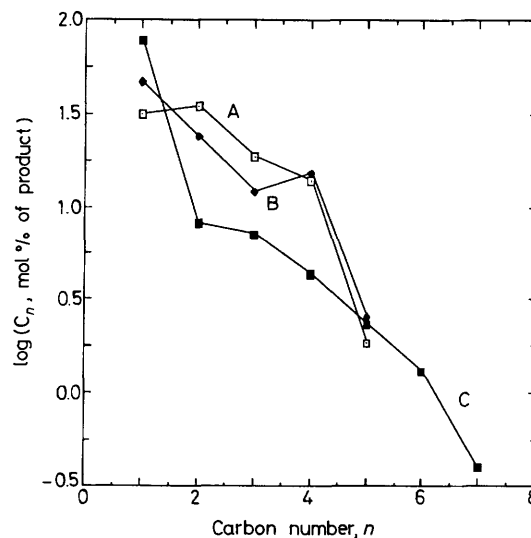


Figure 1. Hydrocarbon product distributions in CO hydrogenation catalysed by supported osmium. (A), zeolite-entrapped Os cluster catalyst prepared from $[\text{H}_2\text{Os}(\text{CO})_4]$ supported on zeolite Y treated with NaN_3 ; reaction conditions: 573 K, 19 bar, $\text{H}_2/\text{CO} = 1$ (molar), 2 days on stream, CO conversion 0.11%. (B) as in (A) except 20 days on stream. (C), Al_2O_3 -supported catalyst consisting of Os crystallites prepared from H_2OsCl_6 ; reaction conditions: 548 K, 10 bar, $\text{H}_2/\text{CO} = 1$ (molar), 20 h on stream.¹⁰

Table 1. Activities and selectivities of supported catalysts for CO hydrogenation.

Catalyst precursor Catalyst	$[\text{H}_2\text{Os}(\text{CO})_4]$ Os/Y ^a		$[\text{H}_2\text{Os}(\text{CO})_4]$ $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ /MgO	CoY ^b Co ⁰ /CdA ^c	CoA ^b Co ⁰ /CdY ^c	Fe ^d Fe ⁰ /NaY ^e	Co ^f Co ⁰ /NaY ^g		Ru(NH ₃) ₆ Cl ₃ Ru/NaY	Ru- (NH ₃) ₆ Cl ₃ Ru/LaY	H ₂ OsCl ₆ Os/ γ -Al ₂ O ₃							
	T, K	P, bar ⁱ					Co _n ⁰ /NaY ^g	Ru/NaY	Ru/LaY	Os/ γ -Al ₂ O ₃	Os/ γ -Al ₂ O ₃	Os/ γ -Al ₂ O ₃						
Metal content, wt %	8.9	8.9	ca. 1	—	—	0.5	0.5	2.4	2.4	5.79	2.0	5.0	5.0					
Reaction conditions	573	628	548	424	455–473	560	455	527	573	520	563	525	525	548	583			
	19	19	10	6	6.2	6.4	6.5	1	1	1	1	14.2	10	10	10			
	1	1	3	1	1	1	1	2	2	2	2	1.5	1	1	1			
CO conversion, %	0.11	0.11	1.82	<0.7	~1	—	>15	0.15	0.10	0.02	0.04	12	<7	<7	<7			
Reaction rate ^j	3.7	4.1	1.21	1.5	~1.3	—	—	—	—	—	—	—	6.7	2.1	—			
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	—	—	—	—	—	—	—	$\times 10^{-4}$	$\times 10^{-3}$	—			
Product distribution, mol %	C ₁	31.4	46.8	67.4	90	—	80.5	56.6	19	50	25	68	—	34	74	77	82	
	C ₂	34.7	23.8	18.5	>0.2	—	12.8	4.3	2	8	0	19	—	5	9	8	6.5	
	C ₃	18.5	11.8	7.3	1.8	—	100	5.5	3.8	9	5	9	—	6	8.2	7	5.3	
	C ₄	13.6	14.9	5.3	0.09	—	—	1.3	18.3	47	15	70	3	20	5	4.3	2.8	
	C ₅	1.9	2.6	1.4	—	—	tracc	11.0	23	18	0	1	—	34	2.3	2.3	1.6	
	C ₆	—	—	—	—	—	—	5.0	—	—	—	—	—	—	1.2	1.3	1.0	
	C ₇	—	—	—	—	—	—	0.9	—	—	—	—	—	—	0.5	0.4	0.3	
Alkene/alkane molar ratio	C ₂	3.5	7.4	4.0	—	—	0.44	0.43	—	—	—	—	—	—	0.46	0.45	0.19	
	C ₃	6.3	5.1	4.8	—	—	7	1.2	0.58	—	—	—	—	—	0.94	1.2	1.3	
	Total	1.45	0.94	0.38	—	—	0.08	0.05	—	—	—	—	—	—	—	—	—	
Time on stream, h	48	480	200	5	—	<5	—	≤0.1	≤0.1	60	60	1	1	1	20	20	20	
Hydrocarbon product range	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₄	—	C ₃ only	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₄	C ₁ –C ₅	C ₁ –C ₁₁ ^h	C ₁ –C ₅	C ₁ –C ₇	C ₁ –C ₇	C ₁ –C ₇
Ref.	This work	—	—	5	1	1	1	3	3	3	3	11	11	10	10	10	10	

^a Osmium in zeolite Y containing Na clusters prepared from NaN_3 . ^b Cobalt-exchanged zeolite A. ^c Cobalt in zeolite A reduced with Cd vapour. ^d Fe in toluene made from metal vapour. ^e Fe in sodium-form zeolite Y. ^f Co in toluene made from metal vapour. ^g Co in sodium-form zeolite Y. ^h Schulz–Flory distribution. ⁱ 1 bar = 10^5 Pa. ^j Rate = mol hydrocarbon/(mol of metals).

stabilisation of anionic Os clusters associated with (i) the strength of the Os–Os bonds, (ii) the CO (and possibly H) ligands provided by the gas-phase reactants, (iii) the basic character of the zeolite cages, and (iv) the geometry of the zeolite pores, with relatively large cages (diameter = 1.2 nm) and small apertures (diameter = 0.8 nm) which entrap the clusters and hinder their sintering into large, unselective Os particles. These results suggest broader opportunities for synthesis of metal clusters in zeolites and for application of encaged metal clusters as catalysts for shape-selective reactions of synthesis gas and CO.

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