

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

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[H₂Os(CO)₄] is converted in the pores of a basic form of zeolite Y (formed by treatment with NaN₃) to give entrapped Os carbonyl clusters that catalyse CO hydrogenation at 573 K and 19 bar (1 bar = 10⁵ Pa) to give C₂—C₄ 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 C₂₊ 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 C₃¹ or C₄³ 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

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

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

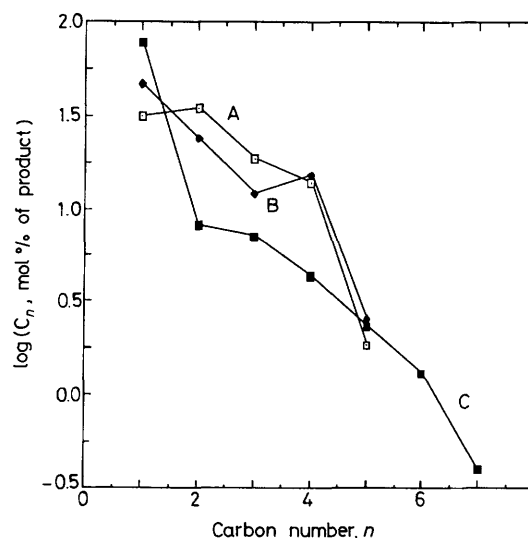


Figure 1. Hydrocarbon product distributions in CO hydrogenation catalysed by supported osmium. **(A)**, zeolite-entrapped Os cluster catalyst prepared from $[\text{H}_2\text{Os}(\text{CO})_4]$ supported on zeolite Y treated with NaN_3 ; *reaction conditions*: 573 K, 19 bar, $\text{H}_2/\text{CO} = 1$ (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		[H ₂ Os(CO) ₄] Os/Y ^a		[H ₂ Os- (CO) ₄] [H ₃ Os- (CO) ₁₂] ⁻ /MgO		CoY ^b Co ⁰ /CdAc ^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- (NH ₃) ₅ ⁻ Cl ₃		H ₂ OsCl ₆	
Catalyst														Ru/NaY		Ru/LaY		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	5.0	5.0	5.0
Reaction conditions	<i>T</i> , K	573	628	548	424	455–473	560	455	527	573	520	563	525	525	525	548	583	583	
	<i>P</i> , bar ⁱ	19	19	10	6	6.2	6.4	6.5	1	1	1	1	14.2	14.2	10	10	10	10	
	H ₂ /CO mol ratio	1	1	3	1	1	1	1	2	2	2	2	1.5	1.5	1	1	1	1	
CO conversion, %		0.11	0.11	1.82	<0.7	~1	—	>15	0.15	0.10	0.02	0.04	12	25	<7	<7	<7	<7	
Reaction rate ⁱ		3.7	4.1	1.21	1.5	~1.3	—	—	—	—	—	—	—	—	6.7	2.1	—	—	
		×10 ⁻⁶	×10 ⁻⁶	×10 ⁻⁴	×10 ⁻⁴	×10 ⁻⁴	—	—	—	—	—	—	—	—	×10 ⁻⁴	×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	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	—	—	—	trace	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	20	20	20	
Hydrocarbon product range		C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₅	C ₁ –C ₄	—	C ₃	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	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-Flörv 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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References

- 1 D. Fraenkel and B. C. Gates, *J. Am. Chem. Soc.*, 1980, **102**, 2478.
- 2 P. A. Jacobs and H. H. Nijs, *J. Catal.*, 1980, **65**, 328.
- 3 L. F. Nazar, G. A. Ozin, F. Hugues, J. Godber, and D. Rancourt, *J. Mol. Catal.*, 1983, **21**, 313.
- 4 Th. Bein, G. Schmiester, and P. A. Jacobs, *J. Phys. Chem.*, 1986, **90**, 4851.
- 5 H. H. Lamb and B. C. Gates, *J. Am. Chem. Soc.*, 1986, **108**, 81; H. H. Lamb, T. R. Krause, and B. C. Gates, *Proc. 9th Int. Congr. Catal.*, 1988, **3**, 1378.
- 6 H. H. Lamb, B. C. Gates, and H. Knözinger, *Angew. Chem.*, 1988, **27**, 1127.
- 7 P. Fejes, I. Kiricsi, I. Hannus, T. Tihanyi, and A. Kiss, in 'Catalysis by Zeolites,' eds. B. Imelik *et al.*, Elsevier, Amsterdam, 1980, 135.
- 8 L. R. M. Martens, P. J. Grobet, and P. A. Jacobs, *Nature (London)*, 1985, **315**, 568.
- 9 L. R. M. Martens, P. J. Grobet, W. J. M. Vermeiren, and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, 1986, **28**, 935.
- 10 E. O. Odebunmi, B. A. Matrana, A. K. Datye, L. F. Allard, Jr., J. Schwank, W. H. Manogue, A. Hayman, J. H. Onuferko, H. Knözinger, and B. C. Gates, *J. Catal.*, 1985, **95**, 370.
- 11 H. H. Nijs, P. A. Jacobs, and J. V. Uytterhoeven, *J. Chem. Soc., Chem. Commun.*, 1979, 180; 1979, 1095.