

Preliminary communication

SUPPORTED $(\eta\text{-C}_5\text{H}_5)\text{NiOs}_3(\text{CO})_9(\mu\text{-H})_3$ AS A HYDROGENATION CATALYST. METHANATION OF CARBON MONOXIDE AND DIOXIDE AT ATMOSPHERIC PRESSURE

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Summary

The title complex, supported on γ -alumina has been shown to be a very efficient catalyst for the hydrogenation of a variety of substrates; in particular its use permits high-efficiency methanation of CO and CO₂ at atmospheric pressure.

Hydrogenation of carbon monoxide to give methane has been accomplished with a variety of homogeneous and heterogeneous systems operating under various sets of conditions [1a,1b,2]. In contrast, there are only a few examples of the methanation of CO₂, a reaction which is of interest as providing an alternative source of natural gas [3]. The nickel complex $\text{Ni}(\text{NO}_3)\cdot\text{H}_2\text{O}$ adsorbed on SiO₂ has been used as catalyst [4] as have supported Fe—Ru, Co—Ru or Ru clusters [5].

We now describe some preliminary results on the activity of the cluster $(\eta\text{-C}_5\text{H}_5)\text{NiOs}_3(\text{CO})_9(\mu\text{-H})_3$ (complex 1) supported on $\gamma\text{-Al}_2\text{O}_3$. Complex 1 has been characterized by spectroscopy [6] and by X-ray techniques [7]; its structure is depicted in Fig. 1. It has been shown to be a very stable, though low efficiency catalyst in the selective hydrogenation of alkynes and alkenes in homogeneous conditions [6]. We have used 1 on γ -alumina as a catalyst for hydrogenation of alkynes, alkenes, CO and CO₂.

The heterogeneous catalytic system was prepared by evaporating to dryness in

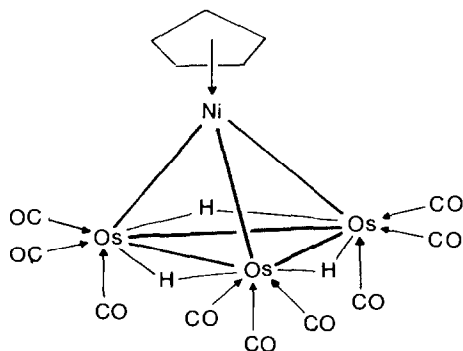


Fig. 1. Structure of complex 1. Spectroscopy in ref. 6; X-ray study in ref. 7.

a rotating flask a solution of complex 1 in CHCl_3 in the presence of $\gamma\text{-Al}_2\text{O}_3$ in a stream of nitrogen at room temperature. The supported cluster, which contained ca. 2% by weight of the metals, was then usually activated by heating to 200°C in a stream of hydrogen (1 atm) for 4 h.

Catalytic activity tests were performed by injecting into a pulse reactor containing 0.3–0.4 g of the catalyst, 0.1–1 ml of the selected reagent in a stream of hydrogen (pressure ca. 1 atm, space velocity ca. 2400 h^{-1}) at a temperature of $20\text{--}350^\circ\text{C}$. The effluent products were quantitatively determined by passage through a gas chromatograph equipped with a thermal conductivity detector. The results obtained can be summarized as follows:

(i) Complex 1 supported on $\gamma\text{-Al}_2\text{O}_3$ is a very efficient catalyst for the hydrogenation of alkynes to alkenes and alkanes (see Table 1). However, a good selectivity in this process can be only obtained if the catalyst is activated at temperatures below 180°C ; after activation at higher temperatures its use leads to quantitative conversion of acetylene to ethane even at room temperature. By comparison, the homogeneous reaction shows a much lower activity with higher selectivity.

(ii) Ethylene and propylene are converted into ethane and to propane, respectively, at room temperature. Under the same conditions benzene is mainly converted into cyclohexane.

(iii) Carbon monoxide is converted in high yield to methane at temperatures above 250°C (see Table 2), with small amounts of carbon dioxide and C_2 hydrocarbons as by-products; at lower temperatures carbon monoxide can be hydrogenated to give oxygenated compounds.

(iv) Carbon dioxide undergoes methanation in high yield (see Table 3) at temperatures comparable with those used either for “pure heterogeneous” systems [4] or for “cluster based heterogeneous” systems [5]. The process occurs at atmospheric pressure and, in general, the efficiency is higher than that in the above systems.

Complex 1 is thus one of the most effective “cluster based” catalysts for the methanation of CO_2 , and its efficiency is much higher than that of catalysts containing only nickel. Attempts to characterize the supported species are in progress, as well as studies on the related cluster $(\eta\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{Os}_3(\text{CO})_9$ [8,6] on the same support.

TABLE 1

HYDROGENATION OF C_2H_2 OVER $(\eta-C_5H_5)NiOs_2(CO)_9(\mu-H)_3$ SUPPORTED ON $\gamma-Al_2O_3$

Activation temperature (°C)	Reaction temperature (°C)	Moles of C_2H_2 converted g.atom of metals (Ni + Os)	Percentage of C_2H_2 converted into	
			C_2H_4	C_2H_6
100	40	0.003	43	57
	80	0.013	73	27
	90	0.020	68	32
	100	0.039	61	35
180	150	0.490	47	53
	165	0.545	45	55
	180	0.655	45	55
200	20	0.918	2	98
	50	0.927	2	98

TABLE 2

METHANATION OF CARBON MONOXIDE^a

Reaction temperature (°C)	Moles of CO converted g.atom of metals (Ni + Os)	Percentage of CO converted into			
		CH_4	C_2H_4	C_2H_6	CO_2
180	0.235	75.3	—	—	—
200	0.311	78.9	—	6.9	—
250	0.381	96.8	—	2.5	0.7
275	0.420	95.9	0.2	3.2	0.7
300	0.555	92.6	1.0	5.1	1.3
325	0.769	95.2	0.1	1.8	0.2
350	0.821	93.6	—	0.9	1.1

^a The catalyst was activated at 200°C.

TABLE 3

METHANATION TESTS OF CARBON DIOXIDE^a

Reaction temperature (°C)	Moles of CO_2 converted g.atom of metals (Ni+Os)	Percentage of CO_2 converted into		
		CH_4	C_2H_6	CO
200	0.155	76.0	—	3.2
225	0.215	89.5	—	4.0
250	0.338	91.2	0.2	6.9
275	0.376	93.6	0.2	5.3
300	0.415	95.1	0.3	4.5
325	0.444	95.2	0.3	4.5
350	0.459	95.6	0.1	4.3

^a Catalyst activated at 200°C.

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