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Preliminary communication

WATER GAS SHIFT REACTION CATALYZED BY OSMIUM CARBONYLS SUPPORTED ON ACID ZEOLITE

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Summary

$Os_3(CO)_{12}$ supported on acid zeolite (HX) reacts at high temperature with hydroxyl groups of the support to give a variety of compounds which are active catalysts for the water gas shift reaction. The catalytic activity depends on the thermal treatment.

The water gas shift reaction (WGSR)

$$H_2O + CO \rightleftarrows CO_2 + H_2 \quad (1)$$

has received growing interest because of its possible industrial relevance for CO removal or for adjusting the hydrogen content in synthesis gas for production of methanol or for methanation or the Fischer—Tropsch reaction [1,2]. The WGSR is catalyzed in the heterogeneous phase by several metals under a range of conditions. For example, Ru metal supported on zeolite was found to be superior to the conventional copper based catalyst [3]. Metal carbonyl clusters heterogenized on polymeric supports also catalyze the reaction [4]. The same type of carbonyl clusters also catalyze the WGSR in the homogeneous phase, but in this case a cocatalyst is usually needed [5].

$Os_3(CO)_{12}$ was adsorbed on acidic zeolite (HX), prepared by conventional methods from 13X type zeolite [6] to give $[Os_3(CO)_{12}HX]$. Under the conditions used, no formation of $[HOs_3(CO)_{12}]^+$ was indicated by the IR spectrum [7]. After heating $[Os_3(CO)_{12}HX]$ for six days up to 180°C, with a temperature increment of 5°C per hour, a carbonyl compound was detected by IR spectroscopy, having bands in the carbonyl region at 2120w, 2080s, 2068s, 2015s, 1980(sh) cm^{-1}.

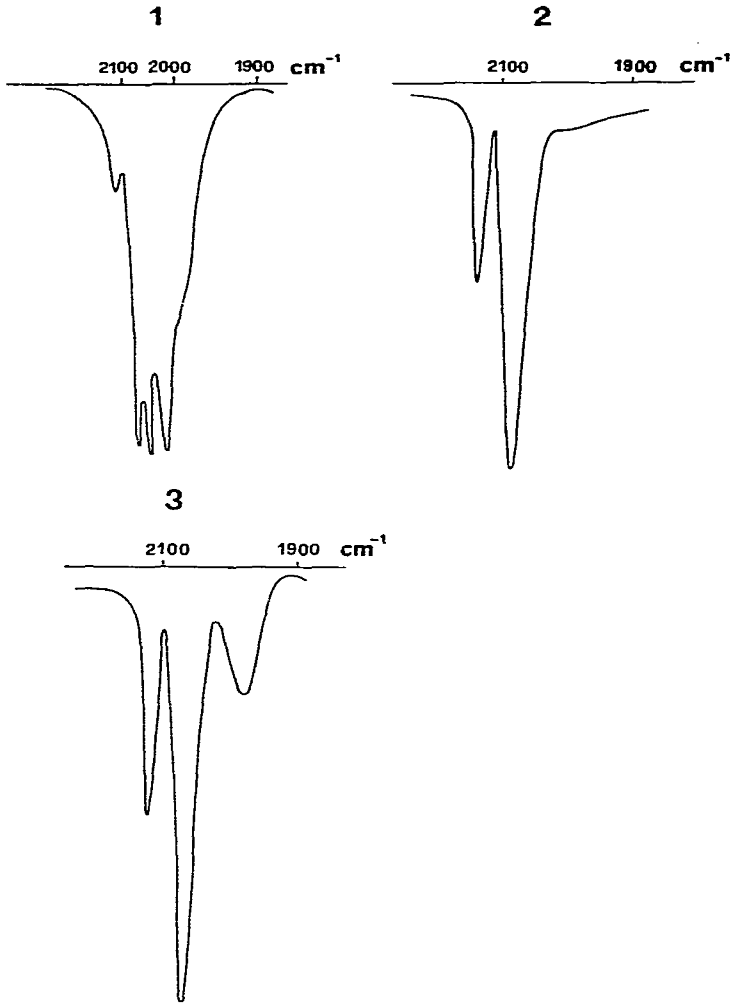

Fig. 1. Infrared spectra of catalysts Os-1 (spectrum 1), Os-2 (spectrum 2) and Os-3 (spectrum 3).

The spectrum of this species is very similar to that reported by others [8—10]. Comparison of the spectrum with that of the product from the reaction between $Os_3(CO)_{12}$ and Ph_3SiOH [8] indicated that the compound could be formulated as $[HOs_3(CO)_{10}OAl=]$ (catalyst Os-1, Table 1). This compound catalyzes the WGSR at 140°C under 1 atm of CO in the presence of excess of water, but its activity increases as the reaction proceeds. The turnover number, calculated as indicated in Table 1, increases from 0.4 calculated over the first 25 h of reaction to a value of 3 calculated over the last 20 h of reaction. The IR spectrum of the osmium-containing zeolite at the end of run 1 shows carbonyl bands at 2130m and 2050s cm^{-1} (spectrum 2, Fig. 1). This compound (Os-2, Table 1) was reused and the catalytic activity still increased with time to reach a maximum (see Table 1). At the end of run 2 the IR spectrum was checked, and the catalyst which show bands at 2120m, 2035s and 1960m cm^{-1}

TABLE 1

WATER GAS SHIFT REACTION USING $Os_3(CO)_{12}$ SUPPORTED ON ZEOLITE AS CATALYST PRECURSOR [a]

Run	Catalyst	Turnover [b]	(calculated over reaction time shown)
1	Os-1	0.4	(First 25 h)
		2	(Overall reaction; 140 h)
		3	(Last 20 h)
2	Os-2	4	(First 25 h)
		12.5	(Overall reaction; 285 h)
		12	(Last 70 h)
3	Os-3 [c]	12	(First 28 h)
		5.5	(Overall reaction; 99 h)
		0.5	(Last 20 h)
4	Os-4 [d]	2.5	(First 25 h)
		1.5	(Overall reaction; 285 h)

Reaction conditions: Temperature 140°C; p(CO) 1 atm; water added in excess. Gas analysis were performed by conventional gas chromatographic methods. [a] Adsorbed $Os_3(CO)_{12}$ on acidic zeolite prepared by conventional methods was heated up to 180°C for six days under a CO atmosphere to give Os-1. Other catalysts were obtained as described in the text. [b] Turnover number calculated as mol of CO_2 formed metal atom^{-1} day^{-1}. [c] Excess of water was added to exhausted Os-2. [d] Os-1 was thermally treated up to 240°C (ΔT(°C)/Δt(h) = 5).

(spectrum 3, Fig. 1), can by comparison with spectra reported in the literature [8], be formulated as $[(CO)_3Os(OAl{=})_2]_n$. This sample (Os-3) was tested as catalyst after addition of a large excess of water.

At the beginning of the reaction the activity was as expected, but it decreased with time and at the end of run 3 had become rather low. The IR spectrum of the catalyst at this stage showed that $Os_3(CO)_{12}$ was adsorbed on the zeolite. (The possible role of water and/or other factors in reforming the starting precursor is under investigation.) Finally Os-1 was treated under a CO atmosphere at high temperature (230—240°C) to give a product (Os-4) which presents a very similar spectrum to that of Os-3, but has a much lower activity (see Table 1).

From our results it appears that $Os_3(CO)_{12}$ supported on acidic zeolite is a precursor for catalysts having various activities for the WGSR. The active species are dependent on the activation conditions, and they are formed by reaction of osmium carbonyls with =Al—OH groups present on the zeolite.

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