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WATER GAS SHIFT REACTION CATALYZED BY OSMIUM COMPOUNDS SUPPORTED ON ZEOLITES. EVIDENCES FOR FORMATION IN THE PRESENCE OF A BASE OF A TRAPPED HYDRIDO-CARBONYL CATALYST

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Summary

Thermal treatment of $[Os_3(CO)_{12}]$ supported on zeolite gives a new species which in the presence of base is an active catalyst for the water gas shift reaction. When NaOH is used the hydrido-carbonyl anion $[H_3Os_4(CO)_{10}]^-$ is formed, and trapped in the zeolite framework. This compound is also an active catalyst for the water gas shift reaction.

Introduction

There is much current interest in the chemistry of the water gas shift reaction (WGSR):

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

This is prompted by the recognition that this reaction is a key step in the production of hydrogen and/or syn gas required in the processes connected with carbon monoxide reduction. The WGSR has been studied in the homogeneous phase by several research groups [1], generally in basic media, using transition metal carbonyls as catalyst precursors. In basic media the cluster carbonyls of many transition metals seem to generate mixtures of carbonyl anions and/or carbonyl hydrides, which appear to be the active species in the catalytic process. The activity is in general rather poor, and not competitive with that of heterogeneous systems such as ruthenium supported on zeolites or the commercial copper-based low temperature catalyst [2]. The cluster complexes are also active catalysts for the water gas shift reaction when heterogenized on polymeric supports [3], but there is a severe temperature limitation when organic supports are used. We have used a zeolite as support in order to overcome this problem and to obtain a better understanding of the factors governing formation, trapping and stabilization of metal carbonyl complexes on zeolites and their catalytic activity in the first steps of CO hydrogenation. The osmium cluster $[Os_3(CO)_{12}]$, supported on an acid zeolite prepared from a 13X type, reacts at high temperature (180°C) with the hydroxylic groups of the support to give a species identified [5] as $[HOs_3(CO)_{10}OAl=]$ (herein after called Os-180, Fig. 1.1) by comparison with the analogous compound formed on SiO_2 [6]. Os-180 catalyzes the WGSR at 140°C under 1 atm of CO pressure in the presence of an excess of water with a maximum turnover number of 3 (moles of H_2, metal atom^{-1} day^{-1}) [5]. In continuation of our studies on zeolite-trapped species we present now results for the catalytic activity of Os-180 in basic media.

Results and discussion

A suspension of Os-180 (0.6% in osmium), obtained as previously reported [5], in diglyme or ethoxyethanol in the presence of base (aliphatic amines or NaOH) under 1 atm of CO at 130°C, and an excess of water (2% in volume) was found to catalyze the water gas shift reaction, and the results are reported in Table 1. The reactivity is usually 100 times higher than that of the same catalytic system (Os-180) used without base in a solventless medium [5], but it falls after 1 day of reaction as shown in Table 2. Non-polar solvents such as xylene gave poor results and were discarded. The reactivity of the catalytic system was tested at four different temperatures in the range 80–150°C.

Temperatures higher than 100°C seem to be necessary for a good activity of the system, but at 150°C, after a good initial activity (run 7, Table 1) there is a fast deactivation, and 130°C is the best temperature for the study. The activity of the mixture in the absence of catalyst or in the presence of Os-180, but in the absence of base, was never greater than 1% of that for Os-180 in the presence of base. The system is insensitive to the amount of added base at least in the range examined (3.5×10^{-4}–3.5×10^{-3} mol of added base), but it is rather dependent on CO

TABLE 1

WATER GAS SHIFT REACTION CATALYZED BY Os-180 IN THE PRESENCE OF ADDED BASE [a]

Run	Amount of zeolite (mg)	Content of metal (g-atom of Os × 10^7)	Temperature (°C)	Added base	TN
1	30	9.4	130	en	330
2	30	9.4	130	NaOH	616
3	30	9.4	130	n-prop	288
4	30	9.4	130	en	248 [b]
5	15	4.7	80	en	51
6	15	4.7	100	en	65
7	10	3.15	150	en	875
8	10	3.15	130	en	1125 [c]

[a] All the experiments were carried out in diglyme in the presence of 3.5×10^{-4} mol of bases; p(CO) 1 atm (6.1×10^{-3} mol); $H_2O/CO = 20$; en = ethylene diamine; n-prop = n-propylamine; TN-turnover number after 24 h of reaction as: mol H_2/(g-atom Os)$^{-1}$ day^{-1}. [b] Experiment carried out in ethoxyethanol. [c] p(CO) 3 atm.

TABLE 2

TURNOVER NUMBER (TN) AFTER VARIOUS REACTION TIMES [a]

Run	Base	TN		
		1 d of reaction	2 d of reaction	3 d of reaction
1	en	330	250	200
2	NaOH	616	413	
3	n-prop	288	220	176

[a] Reaction conditions as reported in Table 1.

pressure. The catalysts after 24 h reaction were filtered off and dried in vacuum (samples A). The filtrate was evaporated to dryness (samples B). Both solids were examined by IR spectroscopy. The patterns of the spectra of samples A and B depend on the nature of the base used. The zeolite recovered from the experiments described in Run 1 of Table 1 (Type A sample) involving ethylene diamine as added base shows two broad bands in the carbonyl region at 1960 and 2040 cm^{-1} (Fig. 1.2). The solid recovered from the reaction solution (sample B) shows the same pattern, with the maximum slightly shifted to lower frequencies (2000 and 1920 cm^{-1}). We can thus conclude that the Os-180, which shows bands in the CO region at 2120w, 2080s, 2068s, 2015s, 1980sh cm^{-1}, is modified in the course of the reaction, and that about 50% of the catalyst is released into the solution. The simplicity of the band pattern and the shift to lower frequencies respect to Os-180 can be attributed to the loss of the cluster structure and possibly to formation of a mononuclear species $Os^{II}(CO)_n$ ($n = 2,3$) bonded to the surface.

A similar IR band pattern was attributed (ν(CO) 2050, 1960 cm^{-1}) in the case of ruthenium by Verdonck et al. [9] to $[Ru^{II}(CO)_2$-zeolite. Osmium carbonyl supported on various oxides gives analogous species at a temperature greater than 120°C. $[Os_3(CO)_{12}]$ reacts readily with hydroxo groups or amines [9a] and, to a minor extent, with water and alcohols. Products from primary amines or ammonia have never been isolated, but from aromatic amines and trimethylamine a few products have been identified [9b]. Under the conditions used ethylene diamine (pK_{a1} 10.7, pK_{a2} 7.5) must be present in the form en-H^+ OH^-, the solution having pH of 10.7. In such circumstances coordinated CO is susceptible to nucleophilic attack by OH^-. However we cannot ignore the presence of the residual aminic function which could react with osmium cluster to give mononuclear species.

The carbonyl $[Os^{II}(CO)_n$-zeolite] generated in the first part of the reaction in the presence of ethylene diamine (run 1, Table 1) , which is practically inactive in basic medium, we reused in the absence of base. This species catalysed the WGSR to only a minor extent (50 TN per day) but it shows a constant activity for at least 10 days. Occasional addition of CO to the system is necessary to keep the system running. The systems obtained with NaOH (run 2, Table 1) or n-propylamine as added base behave quite differently. After 24 h of reaction both the modified zeolite (sample A) and the solution (sample B) were analyzed by IR spectra. A type samples show strong bands at 2040, 2020, 2000 and 1970 cm^{-1} together with broad absorptions of medium intensity in the range 1920–1950 cm^{-1}. Samples of type B show bands at 2040s, 2020s, 2000s, 1970m, 1950m cm^{-1} (see Fig. 1.5). Samples of the type A obtained in runs 2 and 3 of Table 1 were reused as catalysts in WGSR under the same conditions of temperature (130°C) and pressure (1 atm), but without added

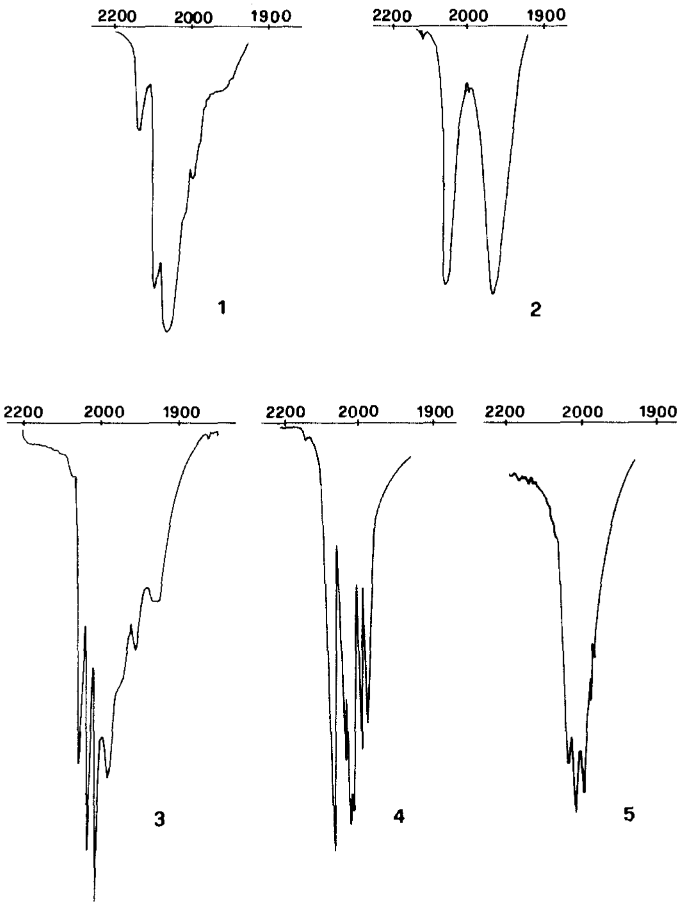

Fig. 1.1. [HOs$_3$(CO)$_{10}$OAl=] (Os-180); 2. [Os^{II}(CO)$_n$-zeolite] obtained at the end of run 1 of Table 1; 3. [H$_3$Os$_4$(CO)$_{12}$]$^-$ in KBr pellet, 4. Os$_3$(CO)$_{12}$ adsorbed on zeolite; 5. [H$_3$Os$_4$(CO)$_{12}$]$^-$ trapped in the zeolite framework.

base under these conditions the modified zeolite (herein called Os-180-H) catalyzed the WGSR with a constant activity for at least 160 h. Analysis of the solution shows that osmium is no longer released from the zeolite.

To obtain a better understanding of the nature of the compounds formed on the zeolite during the reaction we have examined the reactivity of [Os$_3$(CO)$_{12}$] as catalyst of the WGSR in homogeneous phase under the conditions used for Os-180. Some activity data were already available in the literature [1]. The cluster catalyzes the WGSR in the presence of base with an activity of few tens of turnover per day. The IR spectra of the solution at dryness (B type sample) shows patterns dependent on the base used. The spectrum of the compound obtained in the reactions with ethylene diamine as added shows 2 bands at 2000 and 1920 cm^{-1}, similar to those obtained from run 1 of Table 1 and attributed to mononuclear Os carbonyl. On the other hand with NaOH present the compound separated from the solution shows a spectrum with bands at 2040s, 2020s, 2000s, 1970m, 1950m, 1920w cm^{-1}, which is identical to the spectra of the B type sample from run 2 and similar to that of the zeolitic species separated in the same run.

The complex $Os_3(CO)_{12}$ is known to react in iso-butanol in the presence of KOH [10] to give initially $[H(O\text{-}But)Os_3(CO)_{10}]$ as the main product, but after prolonged reaction times (36 h) $[H_3Os_4(CO)_{12}]^-$ is the major product; the spectra of these species show bands at 2048s, 2022s, 2000s, 1976m [11] which is identical to that of the compound we obtained from the reaction of $Os_3(CO)_{12}$ in homogeneous phase. Thus it is probable that the active species in the homogeneous reaction and the species lost from the zeolite in runs 2 and 3 reported in Table 1 is the anion $[H_3Os_4(CO)_{12}]^-$. Knözinger and coworkers prepared [12a] an unidentified species supported on γ-Al_2O_3 by reaction of $[H_4Os_4(CO)_{12}]$ having IR bands at 2123w, 2091w, 2058s, 2027s, 2012s cm^{-1}. Recently Gates et al. [12b] prepared the anion $[H_3RuOs_3(CO)_{12}]^-$ supported on γ-Al_2O_3, and this has an IR spectrum very close to that of Os-180-H we formed on zeolite. For a better characterisation of their anion Gates et al. extracted it into CH_2Cl_2 as the Ph_4As^+ salt. We have tried the same procedure with our compound using NEt_4Cl, but observed no extraction of the anion, which is probably trapped in the cage of the zeolite. We prepared $[Os_3(CO)_{12}]$ supported on γ-alumina as described in literature, to obtain the alumina analogue of Os-180. This species was subjected to the reaction conditions reported for run 2 of Table 1. The hydrido carbonyl anion $[H_3Os_4(CO)_{12}]^-$ is formed but nothing remains on the support and the compound is found only in solution. This proves that the anion can be prepared from the supported species but remains on the support under the reaction conditions only if a zeolite is used. When a cluster is supported by reaction with the zeolite or a carbonyl ion is exchanged with cations, some molecules will be situated on the external surface and some inside the zeolitic cages, and migration from the cages to the surface during thermal treatment cannot be excluded [13].

It seems that under our conditions a carbonyl hydrido anion is formed during the reaction and some of this, presumably situated on the external surface, is lost in solution and some is trapped in the cages. The latter, stable in absence of base, catalyzes the WGSR for a long period of time at constant activity. To have a better proof of this assumption we used Os-180-H as hydrogenation catalyst at 3 atm of pressure of H_2 at 70°C; it readily catalyzed the hydrogenation of propene, but not that of the bulkier norbornadiene, following a typical zeolite shape selectivity pattern.

We conclude that by reaction of suitable reagents with complexes supported on zeolites it is possible to prepare catalysts for various reactions (for example WGSR and olefin hydrogenation) which are stable in the reaction conditions and exhibit shape selectivity due to the special structure of the zeolite. Catalysts of such a nature, suspended in suitable solvent from which they can be easily separated, maintain their identity and selectivity in the above reactions. Furthermore, we have always observed enhanced reactivity in the supported catalyst, compared with the homogeneous counterpart, and this can be tentatively attributed to possible activating interaction of the coordinated carbonyls with the Lewis acid centers of the zeolite structure.

Experimental

$Os_3(CO)_{12}$ was purchased from Strem Chemical Company. The sodium form of 13X zeolite was obtained from Linde and used without any chemical treatment but ground to 60–100 mesh. Gases, from SIAD, had purities > 99%.

Static experiments were performed using glass batch reactors or a stainless steel "Berghof" autoclave equipped with a gas sampling device. IR spectra, in KBr pellets, were recorded with a Perkin–Elmer 683 instrument.

Reaction products were analysed by GLC using a Perkin–Elmer 3920 instrument equipped with a thermal conductivity detector, with N_2 as the carrier gas. For analyses of H_2 we used a calibration curve, since the response of this gas is not proportional to that of the products of the WGSR.

The conditions of a typical reaction were: T 130°C; 20 ml of solvent; 3.3×10^{-4} mol of base; $P(CO)$ 1 atm.; 30 mg of catalyst. (0.6% of osmium) solvent/$H_2O = 10$; $H_2O/CO = 20$; $CO/Os = 5000$; base/Os = 30.

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