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WATER GAS SHIFT REACTION CATALYZED BY IRIDIUM COMPLEXES SUPPORTED ON ZEOLITES

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Summary

Iridium compounds supported on 13-X faujasite type zeolite catalyze the water gas shift reaction. During the reaction carbonyl complexes are formed, and can be detected by IR spectroscopy. Addition of ethylene diamine enhances the catalytic activity.

Introduction

Transition metals and their complexes immobilized on solid supports (organic and inorganic polymers, inorganic oxides and related materials) have been used as heterogeneous or heterogenized catalysts in many reactions [1,2].

In particular zeolites have been used as supports for metal clusters such as $Os_3(CO)_{12}$ in catalysis of the water gas shift reaction [3]. A serious limitation to the use of this type of material is the difficulty of diffusion of bulky compounds through the comparatively small channels of the zeolite in order to enter the supercages. In order to avoid this limitation the appropriate metal complexes were synthesized within the zeolites cavities. In this method, rhodium [4] and ruthenium [5] carbonyl complexes were formed and trapped in the zeolites framework by reaction of precursor compounds (prepared exchanging Na^+ with cationic hexaminocomplexes in the zeolite) with carbon monoxide, and used as catalysts in hydroformylations. The formation of iridium carbonyl complexes by the same method has also been reported [6]. In all these cases, however, the compounds formed in the zeolite interact directly with the support to give various species with different catalytic activities and sometimes rather difficult to characterize and to identify [7]. In many cases synthetic procedures of this type have been used to prepare highly dispersed metal particles by thermal decomposition of metal complexes (or clusters) on zeolites

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[8]. The point of such formation of metal particles is related to the possibility of making preformed metal clusters of the desired nuclearity or of ensuring chain limitation in the cavities of the zeolites in processes such as Fischer–Tropsch synthesis [9].

The water gas shift reaction (WGSR):

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

is a key step in the production of hydrogen and/or synthesis gas, which are relevant to the Fischer–Tropsch synthesis. WGSR is catalyzed in the homogeneous phase by many transition metal complexes, but the activity is rather poor [10] and not competitive with that of heterogeneous systems such as ruthenium supported on zeolite or the commercial copper-based low temperature catalysts [11]. Metal carbonyl clusters are active in homogeneous phase catalysis of the WGSR [12], but the presence of a base is usually necessary to promote nucleophilic attack on the coordinated carbon monoxide [13]. Complexes of this type are also active catalysts for the shift reaction when heterogenized on polymeric supports [14]. However, there is a severe temperature limitation when organic supports are used [2]. The objective of our work is to find conditions which overcome temperature problems by using an inorganic support and to obtain a better understanding of the factors governing formation, trapping and stabilisation of metal carbonyl complexes supported on zeolite and their catalytic activity in the first step of CO hydrogenation [15].

Results and discussion

$[Ir(NH_3)_6]^{3+}$ supported on 13-X zeolite by conventional methods [4–6] was treated with CO at 1–4 atmospheres and 100–300°C with the H_2O/CO ratio kept constant at a value of 2. Under these conditions the WGSR proceeds and the results obtained at 140°C are shown in Table 1 No. 1 and Fig. 1.

The significant aspect of the Figure (which refers to CO/Ir ratio of 1700) is that three different regions can be identified (A, B and C). This behaviour could be attributed to the formation of three distinct species having different catalytic activities. The species A, B and C were isolated by keeping the supported iridium hexamino complex under the reaction conditions for suitable times and the infrared spectra of A, B and C are shown in Fig. 2. Carbonyl compounds are formed, but substantial changes in the form of the spectra occur during the reaction in which the catalyst changes from A to B to C and at the same time the catalytic activity decreases. The interesting feature is the presence of a band at 1330 cm^{-1} which can be attributed to coordinated NH_3 (this band is very intense in the IR spectrum of the procatalyst) and which is no longer present in spectra B and C. The band at 1400 cm^{-1} has been attributed to NH_4^+ bonded to zeolite framework [16] and we have confirmed this attribution by treating products A, B and C with NaCl solution: all the other bands remain unchanged, but that at 1400 cm^{-1} disappears. The species A, B and C appear to be bonded to the support by reaction with the hydroxo groups present on the surface, so that washing the zeolite-supported products with various solvents leaves the IR spectrum unchanged. The species A which we have formulated as an iridium carbonylamino compound, rather than a mixture (see later), appears to be the most active. Compound A is stabilized by the zeolite framework, probably via some chemical interactions with the reactive groups present on surface, as found, for

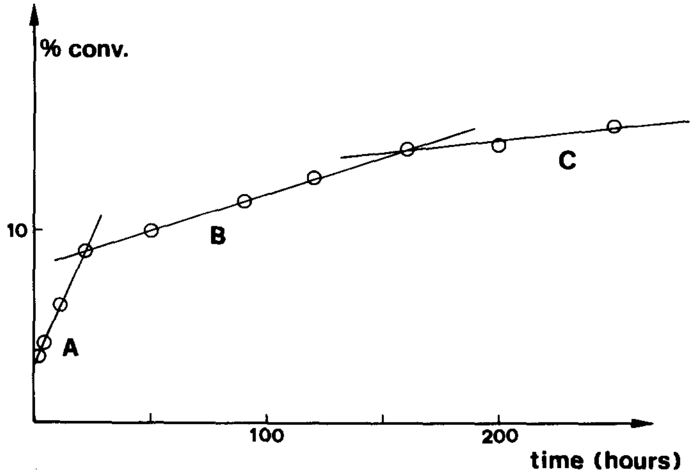

Fig. 1. Percentage conversion vs. time for the WGSR catalyzed by [Ir(NH_3)$_6$-zeolite] (see Table 1, No. 1)

example, for $Os_3(CO)_{12}$ with silica [7] or zeolite [3]. The procatalyst supported on zeolite was treated at 300°C in the presence of CO and H_2O (Table 1, No. 2). After 5 h the catalyst became completely inactive and gave iridium metal [6,17]. The IR spectrum shows no bands other than those of the support. The activity of this product was compared with that of a sample obtained by treatment at 400°C under H_2 of [Ir(NH_3)$_6$-zeolite]. The data reported in Table 1, No. 3 show the low catalytic

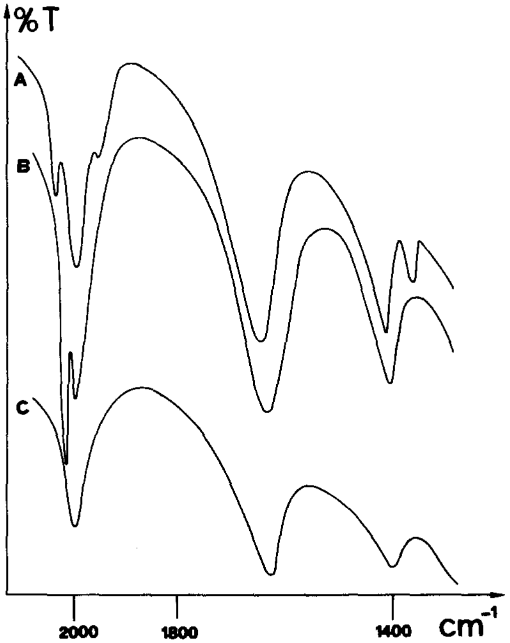

Fig. 2. Infrared spectra of the recovered [Ir(NH_3)$_6$-zeolite] after treatment with CO and H_2O under the conditions corresponding to the ranges for A, B, and C, respectively, in Fig. 1.

TABLE 1

WGSR CATALYZED BY IRIDIUM COMPOUNDS SUPPORTED ON ZEOLITE[a]

No.	Catalyst	Reaction time (h)	% Conversion	Turnover[b]	T (°C)	P(CO) (atm)	H_2O/ CO ratio	CO/Ir ratio
1	[Ir(NH$_3$)$_6$-X]	2	3.5	30	140	1	2	1700
		4	4	17				
		22	9	7				
		90	11.5	2.2				
		120	13	1.8				
		160	14	1.5				
		200	14.5	1.3				
2	[Ir(NH$_3$)$_6$-X]	2	65	820	300	1	2	1700
		3.5	70	500				
		5	71.5	260				
		10	72	170				
3	[IrMetal-X]	3	1.5	3	220	1	2	1700
		9	2.5	1.7				
		23	3	0.9				
		32	4	0.7				
4	[Ir(NH$_3$)$_6$-X]	1	7	110	220	2	2	1600
		4	12	50				
		9	19	35				
		24	42	28				
		30	51	27				
		35	55.5	26				
		50	63	25				
5	[Ir(NH$_3$)$_6$-X]	1	7.5	230	220	2	2	3100
		3	9	95				
		6	16.5	36				
		24	25	32				
6	[Ir(en)$_2$(NH$_3$)$_2$-X]	1	2	30	220	2	2	1600
		3	29	150				
		5	53	170				
		7	70	160				
		9	78	140				
7	[Ir(en)$_2$(NH$_3$)$_2$-X]	1	0.5	15	220	4	2	2500
		3	14.5	125				
		5	41.5	200				
		7	59	210				
		9	67	195				
8	[Ir(en)$_3$-X]	1	0.8	15	220	2	2	1700
		3	2.3	13				
		4	2.8	12				
		7	4.5	11				
		10	6	10				
		22	11	9				
		30	16	9				
		55	28	9				

[a] X = 13-X faujasite type zeolite. [b] Turnover = molecules of product h^{-1} metal atom^{-1}.

activity for the WGSR of the iridium metal obtained under these conditions. The catalyst was also tried at 220°C (this temperature was chosen to be as high as possible, but to be below 250°C in order to avoid metal formation [6]). The results are similar to those found at 140°C (Table 1, No. 4) and the final spectrum has the same form as C in Fig. 2. At this temperature, however, we were not able to detect any "aminocarbonyl" intermediate. Probably the reaction follows the same path as at 140°C, but the higher temperature and the faster interaction with the support prevent the trapping of the intermediate. As mentioned before, we feel that the first species formed (A) could be an "iridiumaminocarbonyl" compound somehow trapped and stabilized in the zeolite supercages, and it probably has no homogeneous equivalent. A similar compound has been proposed as catalyst for the WGSR catalyzed by ruthenium complexes on zeolite [11]. However, to obtain better evidence in support of this hypothesis we carried out some experiments in both homogeneous and heterogeneous phases. $[Ir(NH_3)_6]^{3+}$ was used as a homogeneous catalyst in water for the shift reaction (T 150°C, p(CO) 4 atm) or in H_2O/CH_3OH mixture (T 120°C, p(CO) 4 atm), but in neither cases was any activity observed, and at the end of the run the starting material was recovered unchanged. The same compound on zeolite was also used as catalyst for the WGSR in a continuous flow reactor operating at 1 atm at 140–220°C. The catalytic activity was constant for about two hours, and then there was a fast deactivation. The last process is much faster under flow conditions, and we think that it could be attributed to easier displacement of NH_3 under such conditions, leading to a completely carbonylated iridium complex having the same spectrum as C in Fig. 1. To hinder or prevent, the easy displacement of ligand at the working temperature, the zeolite supported procatalyst was treated with an excess of ethylene diamine at two temperatures, 90 and 200°C, to give products designated as Ir-en$_1$ and Ir-en$_2$, respectively. Comparison of the IR spectra of the two products with those of authentic samples indicates that they can be formulated as $[Ir(en)_2(NH_3)_2$-zeolite$]$ and $[Ir(en)_3$-zeolite$]$, respectively, (The homogeneous analog of Ir-en$_1$ was prepared by copying as closely as possible the reaction conditions used for the heterogenized counterpart). Ir-en$_1$ and Ir-en$_2$ were used as catalysts and the results are shown in Table 1, No. 6, 7, 8.

The catalyst prepared by supporting the homogeneous analogue of Ir-en$_1$ on zeolite showed the same reactivity characteristics as Ir-en$_1$ generated on the support. The IR spectrum of the Ir-en$_1$ shows significant bands at 2060, 1480, and 1400 cm^{-1}, attributable to coordinated CO, ethylene diamine, and NH_4^+ bonded to zeolite, but no bands due to coordinated NH_3 were found. In the case of Ir-en$_2$ only bands attributable to ethylene diamine and the support were detected. Ir-en$_1$ was tested as catalyst in a flow reactor. The reaction was run for 72 h at 180 or 220°C and no loss of activity was observed during this time. The IR spectrum of the final product is the same as was found when Ir-en$_1$ was used for the WGSR in autoclave. We also found that the pressure of CO has some effect on the catalytic activity when $[Ir(en)_2(NH_3)_2$-zeolite$]$ was used (Table 1, No. 7).

The outcome of our work is clearly represented in Fig. 3. Curve A describes the behavior of the iridiumhexamino complex supported on zeolite. The activity is rather high at first, but decreases rapidly as NH_3 ligands are replaced by CO to give a fully carbonylated product, which is a less active catalyst. Curve B refers to $[Ir(en)_2(NH_3)_2$-zeolite$]$; the activity of which initially increases by replacement of the NH_3 ligands. After 5 h, the catalytic activity decreases; this is probably due to the considerable drop of the CO partial pressure, and upon restoring the original pressure the catalytic activity increases again, and remains constant until the next pressure drop is reached.

Curve C shows the behavior of a sample with almost all the ammonia molecules replaced by ethylene diamine. The activity is very low (CO cannot replace the chelating ligand), and probably due to the presence of some molecules still containing the NH_3 ligand.

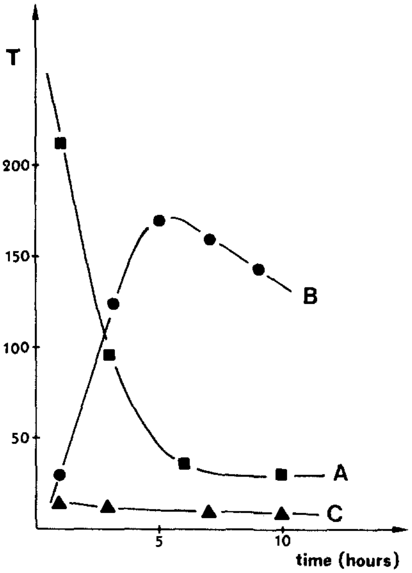

Fig. 3. Turnover (molecules of products h^{-1} metal $atom^{-1}$) vs. time. A = $[Ir(NH_3)_6$-zeolite]; B = $[Ir(en)_2(NH_3)_2$-zeolite]; C = $[Ir(en)_3$-zeolite]; en = ethylene diamine.

In conclusion, the active species seems to be an iridium-ethylene diamine-carbonyl compound which requires higher temperatures and longer times for its formation than the corresponding amino complex and is less reactive. But this catalyst lasts longer than the amino analog under the reaction conditions, because the ethylene diamine is not displaced by CO at these temperatures and pressures, so that the inactive, totally substituted iridium carbonyl cannot be formed.

Experimental

$[Ir(NH_3)_6]Cl_3$ was prepared according by the literature method [18]. The zeolite was a pelletized 13-X faujasite type used without any chemical treatment, but ground to give a 60–100 mesh fraction. The iridium content of the zeolite was 1.6% by weight and was determined by A. Bernhandt Mikroanalytisches Laboratorium, Elbach über Engels Kirchen, W.G.

Gases, from SIO, had purities of more than 99.9%.

IR spectra, in KBr pellets, were recorded on Perkin–Elmer 683 and 180 instruments.

The reaction products were determined by GC using a Perkin–Elmer 3920 instrument equipped with a TC detector.

Static experiments were performed using a stainless steel "Berghof" autoclave equipped with a gas sampling device.

Flow experiments were performed using a continuous flow reactor operating at total pressure of 1 atm with $H_2O/CO = 2$.

Acknowledgements

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References

1 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem., 15 (1977) 189.
2 G. Strukul, M. Bonivento, M. Graziani, E. Cernia and N. Palladino, Inorg. Chimic. Acta, 12 (1975) 15.
3 R. Ganzerla, M. Lenarda, F. Pinna and M. Graziani, J. Organometal. Chem., 208 (1981) C43.
4 E. Mantovani, N. Palladino and A. Zenobi, J. Mol. Catal., 3 (1977) 285.
5 P. Jackson, B.F.G. Johnson, J. Lewis, R. Ganzerla, M. Lenarda and M. Graziani, J. Organometal. Chem., 180 (1980) Cl.
6 P. Gelin, G. Coudurier, Y. Ben Taarit and C. Naccache, J. Catal., 70 (1981) 32.
7 R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, J. Organometal. Chem., 213 (1981) 215.
8 M. Niwa, T. Iizuka and J.H. Lunsford, J. Chem. Soc. Chem. Commun., (1979) 684.
9 H.H. Nijs, P. Jacobs and J.B. Uytterhoeven, J. Chem. Soc. Chem. Commun., (1979) 180.
10 P.C. Ford, Accounts Chem. Res., 14 (1981) 31.
11 H.H. Nijs, P. Jacobs and J.B. Uytterhoeven, J. Chem. Soc. Chem. Commun., (1979) 181.
12 P.C. Ford, P. Yarrow and H. Cohen in P.C. Ford (Ed.), Catalytic Activation of Carbon Monoxide, p. 95, A.C.S. Symposium Series 152, 1981.
13 J. Kaspar, R. Spogliarich, G. Mestroni and M. Graziani, J. Organometal. Chem., 208 (1981) C15.
14 R.C. Ryan, G.M. Wiemon, M.P. Dalsanto and C.U. Pittman, J. Mol. Catal., 5 (1979) 319.
15 G. Henrici-Olivé and S. Olivé, J. Mol. Catal., 16 (1982) 187.
16 J.W. Ward in E.M. Flaningen and L.B. Sand (Eds.), Molecular Sieves-Zeolites, II Am. Chem. Soc., 102 (1977) 456.
17 P. Gelin, Y. Ben Taarit and C. Naccache, XVII Int. Congress on Catalysis, Paper B15, Tokyo 1980.
18 G. Watt, J. Inorg. Nucl. Chem., 24 (1962) 1067.