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Supported Transition Metal Complexes

V. Liquid Phase Catalytic Hydrogenation of Hexene-1, Cyclohexene and Isoprene under Continuous Flow Conditions

K. G. ALLUM, R. D. HANCOCK, I. V. HOWELL, T. E. LESTER, S. MCKENZIE,
R. C. PITKETHLY, AND P. J. ROBINSON

The British Petroleum Company Limited, BP Research Centre, Chertsey Road,
Sunbury-on-Thames, Middlesex, England

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Three complexes of rhodium and one of iridium of the type MX(phosphine)$_n$, where X = halide and $n = 2$ or 3, have been chemically bonded to silica. The resulting materials have been shown to catalyze the hydrogenation of hexene-1, cyclohexene, and isoprene in the liquid phase under a variety of continuous flow conditions (15–50 atm H_2, 20–160°C). n-Butyl mercaptan in the feedstock reduces the activity, but increases the thermal stability of the catalysts. Continuous flow operation for 70 hr without loss of activity in the hydrogenation of hexene-1 and cyclohexene has been demonstrated for the heterogeneous complex RhBr(SIL–$CH_2CH_2PPh_2$)$_2$. (SIL–$CH_2CH_2PPh_2$ represents the phosphine ligand linked to the surface of silica.) Rhodium elution from the catalysts was extremely small, generally below the limit of detection (0.2 ppm).

INTRODUCTION

The study of supported transition metal complexes is currently attracting widespread interest (*1–3*). Results from our own and other laboratories have demonstrated that transition metal complexes may be chemically bonded to a variety of macromolecular support materials such as organic polymers and silica (*4*, *5*). In many instances, these supported complexes have been shown to possess similar catalytic activity to their homogeneous counterparts, but have the great advantage that they can readily be separated from the reaction products. Unlike those catalysts in which a transition metal complex has been deposited on a solid support (*6*) or dispersed over the support in a high boiling inert solvent (*6*, *7*), these complexes in which the transition metal is chemically bonded to the macromolecular support can be used for processing liquid feedstocks (*8*, *9*). However, despite the fact that these supported complexes function as heterogeneous catalysts, very few studies on their use in the liquid phase under continuous flow conditions have been reported.

In a previous paper (*10*), the results of batch hydrogenation tests using rhodium and iridium tertiary phosphine complexes bonded to silica have been described. Further studies on some of these catalysts have been carried out to examine their activity for liquid phase hydrogenation under continuous flow conditions. The present paper describes the results obtained in the hydrogenation of hexene-1, cyclohexene, and isoprene both in the presence and absence of n-butyl mercaptan.

Mercaptans, which are commonly found in petroleum-based feedstocks, generally exert a powerful poisoning effect on the activity of hydrogenation catalysts. *n*-Butyl mercaptan was added to many of the feedstocks used in this work to examine the effect of such compounds on the activity of the supported rhodium and iridium complex catalysts.

METHODS

The homogeneous complexes were prepared by reaction of suitable rhodium or iridium species with tertiary phosphine ligand-silanes in the desired stoichiometric ratio, and subsequently bonded to silica to produce the heterogeneous complex, by condensation of the triethoxysilyl groups with hydroxyl groups on the surface of silica. The method is illustrated for the complex $RhCl(SIL\text{–}CH_2CH_2PPh_2)_3$ in the following scheme:

$$\underset{\text{ligand-silane}}{6\,(EtO)_3SiCH_2CH_2PPh_2} + \underset{\text{complex precursor}}{[RhCl(C_8H_{12})]_2} \rightarrow \underset{\text{homogeneous complex}}{2\,[(EtO)_3SiCH_2CH_2PPh_2]_3RhCl}$$

$$\underset{\text{silica-surface}}{|\text{—}OH} + \underset{\text{homogeneous complex}}{[(EtO)_3SiCH_2CH_2PPh_2]_3RhCl} \rightarrow \underset{\text{heterogeneous complex}}{[|\text{—}O\text{—}SiCH_2CH_2PPh_2]_3RhCl}$$

(The ligand-silica may conveniently be written as $SIL\text{–}CH_2CH_2PPh_2$.)

The heterogeneous complexes were generally orange or red in color and turned dark red on treatment with *n*-butyl mercaptan. Experimental details of their preparation have been reported previously (*10*). The silica used was Crosfield Sorbsil U30 grade (surface area 500 m^2/g) which was washed with dilute acid, then distilled water and dried at 180°C before use.

Hexene-1 and cyclohexene were purified by passage through a column of activated silica and then distilled from potassium under nitrogen. Isoprene (Fluka-Purum grade) was used as received, but degassed prior to use. Benzene (Analar grade) was distilled from sodium under nitrogen prior to use. Hydrogen and nitrogen (BOC white spot quality) were used without further purification.

TABLE 1

Hydrogenation of Olefins Using Heterogeneous Complex Rh/1[a]

HOS	Temp (°C)	LHSV	Yield (% mol)	
			n-Hexane	Cyclohexane
3–5	130	3.0	92	92
7–9[b]	132	3.3	93	89
14–16	132	3.0	93	79
21–23	132	3.0	91	78
28–30	160	2.2	98	96

[a] *Conditions:* catalyst: Rh/1: $RhCl(SIL\text{–}CH_2CH_2PPh_2)_3$; 0.54%wt rhodium (20 ml); feedstock: hexene-1 (15%vol), cyclohexene (20%vol), benzene (65%vol) containing 700 ppm sulfur (as *n*-BuSH); pressure: 50 atm H_2; GHSV: 600.

[b] Rhodium content of product <0.2 ppm.

The tests were carried out in a once-through continuous flow pilot plant. In all cases LHSV values refer to total feed flow rates and not just to the components to be hydrogenated. In most of the tests, *n*-butyl mercaptan was added to the feedstocks to give concentrations of 100 or 700 ppm by weight of sulfur. A catalyst bed of 20 ml was used in all cases, and the catalyst was loaded under a nitrogen atmosphere.

Product analyses were carried out by gas/liquid chromatography using columns of dimethylsulfolane (25%) and dinonylphthalate (5%) on Embacel (for hexene-1 and cyclohexene feedstocks) and ββ′-oxydipropionitrile (5%) on Embacel (for isoprene). Rhodium and iridium contents of the liquid products (concentrated 10-fold by evaporation) were determined by X-ray fluorescence techniques. The detection limit of this method was 0.2 ppm.

RESULTS

Rhodium Complexes

Initial tests were carried out using the heterogeneous complex Rh/1 {prepared from [RhCl(cycloocta-1,5-diene)]$_2$ and

TABLE 2

Hydrogenation of Isoprene Using Heterogeneous Complex Rh/1[a]

HOS	Temp (°C)	LHSV	Conversion of isoprene %mol	Yield (%mol)	
				Isopentenes	Isopentane
35–36	157	6.0	100	56	44
40–41	157	6.0	100	67	33
45–46	150	12.0	85	65	20
49–50	168	12.0	86	66	20

[a] Conditions—catalyst: Rh/1: $RhCl(SIL\text{–}CH_2CH_2PPh_2)_3$; 0.54%wt rhodium (20 ml); feedstock: isoprene (10%vol), benzene (90%vol) containing 700 ppm sulfur (as n-BuSH); pressure: 21 atm H_2; GHSV: 1000.

$(EtO)_3SiCH_2CH_2PPh_2$–rhodium to phosphorus atomic ratio of 1:3}. A feedstock of hexene-1 (15% vol) and cyclohexene (20% vol) in benzene containing 700 ppm sulfur (as n-butyl mercaptan) was used. The conditions used and the results obtained are given in Table 1. It can be seen that at 130°C and 50 atm pressure of hydrogen high conversions of both hexene-1 and cyclohexene were achieved. A slight decline in the activity was observed over the test, as shown by the yield of cyclohexane which dropped from 92% after 5 hr on stream (HOS) to 78% after 23 HOS. When the temperature was raised to 160°C at the same pressure the activity also increased with almost quantitative conversions of both hexene-1 and cyclohexene. Analysis of the product after 9 HOS failed to detect any rhodium in solution (i.e., <0.2 ppm).

After 30 HOS, the feedstock was changed to isoprene (10% vol) in benzene containing 700 ppm sulfur (as n-butyl mercaptan). The results are given in Table 2. Complete conversion of isoprene occurred at 157°C and 21 atm pressure of hydrogen but the activity of the catalyst declined slowly as shown by the decreasing yield of isopentane.

Heterogeneous complex Rh/2 {prepared from $[RhCl(cyclooctene)_2]_2$ and $(EtO)_3SiCH_2CH_2P(n\text{-}C_6H_{13})_2$—atomic ratio of

TABLE 3

Hydrogenation of Olefins Using Heterogeneous Complexes Rh/2 and Rh/3[a]

Catalyst	HOS	Temp (°C)	Conversion of hexene-1 (%mol)	Yield (%mol)	
				n-Hexane	Cyclohexane
Rh/2	9–12	98	100	100	100
	22–25	60	100	76	39
	33–35[b]	25	20	13	6
	77–79	80	83	54	17
Rh/3	7–8	100	100	100	100
	17–19	100	100	100	99
	27–28	60	100	96	96
	68–69	100	100	100	99

[a] Conditions: catalyst: Rh/2: $RhCl[SIL\text{–}CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$; 1.24%wt rhodium; Rh/3: $RhBr(SIL\text{–}CH_2CH_2PPh_2)_2$; 0.86%wt rhodium; catalyst vol: 20 ml; feedstock: hexene-1 (20%vol), cyclohexene (20%vol), benzene (60%vol) containing 100 ppm sulfur (as n-BuSH); LHSV: 1.5; GHSV: 1000–1250; pressure: 21 atm H_2; rhodium content of product <0.2 ppm (detection limit) in all cases.

[b] Pressure 36 atm H_2.

TABLE 4

Hydrogenation of Isoprene Using Heterogeneous Complexes Rh/2 and Rh/3[a]

Catalyst	HOS	Temp (°C)	Conversion of isoprene (%mol)	Yield (%mol)		Rhodium content of product (ppm)
				Isopentenes	Isopentane	
Rh/2	41–43	55	14	13	1	0.5
	47–50	79	82	58	24	—[b]
	55–58	100	100	43	57	—[b]
	92–93	80	23	21	2	0.3
	97–99	100	92	72	20	0.3
Rh/3	45–47	83	100	17	83	—[b]
	51–53	100	100	2	98	0.4
	58–60[c]	99	100	3	97	0.3

[a] Conditions: catalyst: Rh/2: $RhCl[SIL\text{–}CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$; 1.24%wt rhodium; Rh/3: $RhBr(SIL\text{–}CH_2CH_2PPh_2)_2$; 0.86%wt rhodium; feedstock: isoprene (20%vol), benzene (80%vol) containing 100 ppm sulfur (as *n*-BuSH); LHSV: 1.5; GHSV: 1000–1250; pressure: 36 atm H_2.

[b] Not determined.

[c] Pressure 21 atm H_2.

rhodium to phosphorus of 1:2} was tested for the hydrogenation of hexene-1 (20% vol) and cyclohexene (20% vol) in benzene containing 100 ppm sulfur as *n*-butyl mercaptan. The conditions and results are given in Table 3. The catalyst showed high activity at 98°C and 21 atm pressure of hydrogen but only low activity at 25°C and 36 atm. Furthermore, the catalyst declined appreciably in activity over the test period as can be seen by comparison of the products after 25 and 79 HOS. No rhodium elution from the catalyst was detected during the test.

After the catalyst had been running for 35 HOS the feedstock was changed to isoprene (20% volume) in benzene containing 100 ppm sulfur as *n*-butyl mercaptan. The results (Table 4) showed that complete conversion of the isoprene was achieved at 100°C and 36 atm hydrogen pressure, with 57% being hydrogenated completely to give isopentane. As with the olefin hydrogenation, the activity declined

TABLE 5

Hydrogenation of Olefins with Heterogeneous Complex Ir/1[a]

Feedstock	HOS	Temp (°C)	Conversion of hexene-1 (%mol)	Yield (%mol)	
				n-Hexane	Cyclohexane
A	4–5	28	100	100	100
	8–10	28	100	100	100
B	49–50	53	27	26	3
	53–54	87	100	100	90
	67–68	84	100	100	100

[a] Conditions: catalyst: $IrCl[SIL\text{–}CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$; 2.96%wt iridium (20 ml); feedstocks: (A) hexene-1 (20%vol), cyclohexene (20%vol), benzene (60%vol); (B) feedstock A containing 100 ppm sulfur (as *n*-BuSH); LHSV: 3.5; GHSV: 1000; pressure: 15 atm H_2. Iridium content of product <0.2 ppm in all cases.

TABLE 6

Hydrogenation of Isoprene with Heterogeneous Complex Ir/1[a]

Feedstock	HOS	Temp (°C)	Conversion of isoprene (%mol)	Yield (%mol)	
				Isopentenes	Isopentane
A	18–20	22	3	0	3
	41–42	55	100	0	100
B	74–76	83	100	19	81
	99–100	81	100	29	71
	114–116	81	73	29	44

[a] Conditions: catalyst: $IrCl[SIL–CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$; 2.96%wt iridium (20 ml); feedstocks: (A) isoprene (20%vol), benzene (80%vol); (B) feedstock A containing 100 ppm sulfur (as n-BuSH); LHSV: 3.5; GHSV: 1000; pressure: 15 atm H_2. Iridium content of all products ⩽0.2 ppm.

over the test period as seen from the analyses of the products obtained after 58 and 99 HOS. In contrast to the olefin hydrogenation, detectable quantities of rhodium (0.3–0.5 ppm) were found in the product from isoprene hydrogenation.

Heterogeneous complex Rh/3 {prepared from $[RhBr(2,5\text{-dimethylhexa-1,5-diene})]_2$ and $(EtO)_3SiCH_2CH_2PPh_2$—atomic ratio of rhodium to phosphorus of 1:2}, was examined for the hydrogenation of hexene-1/cyclohexene and isoprene feedstocks under the same conditions as those used for the heterogeneous complex Rh/2. The results are given in Tables 3 and 4. It can be seen that the complex is very active, giving complete conversion of hexene-1 and cyclohexene and almost quantitative conversion of isoprene to isopentane. No decline in activity throughout the 69 hr test period was apparent. As with the heterogeneous complex Rh/2, no rhodium could be detected in the liquid products from the olefin hydrogenation, but with isoprene, rhodium concentrations of approximately 0.4 ppm were observed.

Iridium Complex

The heterogeneous complex Ir/1 {prepared by reaction of $[IrCl(cyclooctene)_2]_2$ with $(EtO)_3SiCH_2CH_2P(n\text{-}C_6H_{13})_2$—atomic ratio of iridium to phosphorus of 1:2} was tested for the hydrogenation of hexene-1 (20% vol) and cyclohexene (20% vol) in benzene and also with the same feedstock to which 100 ppm of sulfur had been added (as n-butyl mercaptan). The results are given in Table 5. In the absence of sulfur, the catalyst was extremely active and gave complete conversion to hexane and cyclohexane at 28°C and 15 atm pressure of hydrogen. The heat of reaction maintained the catalyst at this temperature even when no external heat was applied (room temperature was 18°C). In the presence of n-butyl mercaptan, the activity of the catalyst dropped appreciably and a temperature of about 85°C was required to obtain complete hydrogenation at 15 atm pressure.

The catalyst was also examined for the hydrogenation of isoprene (20% vol) in benzene and also with the same feedstock to which n-butyl mercaptan had been added to give a concentration of 100 ppm sulfur. The results are given in Table 6. In the absence of sulfur, in contrast to the results of olefin hydrogenation (Table 5), the catalyst showed very low activity for isoprene hydrogenation at 22°C and 15 atm pressure, but when the temperature was raised to 55°C at the same pressure, complete hydrogenation to isopentane occurred. In the presence of n-butyl mercaptan, the activity dropped markedly, although complete conversion of isoprene with an 81%

yield of isopentane was achieved at 83°C. Prolonged operation under these conditions led to a steady decline in activity as can be seen from the products obtained after 76, 100, and 116 HOS. Iridium contents of the liquid products never exceeded 0.2 ppm.

DISCUSSION

Batch tests with the heterogeneous complex Rh/1 had shown that it catalyzed the hydrogenation of olefins and isoprene under sulfur free conditions. When the complex was treated with *n*-butyl mercaptan, the hydrogenation activity was reduced, although the catalyst still possessed considerable activity even when concentrations as high as 1000 ppm of sulfur (as *n*-butyl mercaptan) were present in the feedstocks. The mercaptan-treated complex was thermally much more stable than the parent species and showed no evidence of decomposition to metallic rhodium under hydrogen pressure even at temperatures approaching 200°C. [The nature of mercaptan-treated species has been discussed elsewhere (*10, 11*)]. The pilot plant tests with heterogeneous complex Rh/1 were designed to examine the activity and stability of the catalyst under continuous flow conditions. The results show that the catalyst does possess good activity even in the presence of 700 ppm of sulfur, but that a slow decline in the catalytic activity does occur.

In an attempt to prepare supported complexes with higher activity and stability than Rh/1, a series of batch tests were carried out using species of the type MXP_2 (where M = Rh or Ir; X = Cl, Br or I; P = tertiary phosphine ligand-silica containing alkyl, cycloalkyl or aryl substituents on the phosphorus). The ratio of M:P of 1:2 was chosen since it had been shown that, in homogeneous systems (under sulfur-free conditions), MXP_2 species were more active hydrogenation catalysts than those of the type MXP_3 (*12*). The results of these batch tests indicated that variations in the substituents on the tertiary phosphine ligand had only a small effect on the activity and that bromide complexes were significantly more active than chloride ones. On the basis of these tests, three heterogeneous complexes were chosen for examination under continuous flow conditions in the liquid phase to determine their activity and stability during hydrogenation of hexene-1, cyclohexene and isoprene (generally containing added *n*-butyl mercaptan) and to see whether any loss of rhodium or iridium from the catalyst could be detected. The heterogeneous complexes chosen were:

$RhCl[SIL\text{-}CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$ (Rh/2),
$RhBr(SIL\text{-}CH_2CH_2PPh_2)_2$(Rh/3), and
$IrCl[SIL\text{-}CH_2CH_2P(n\text{-}C_6H_{13})_2]_2$(Ir/1).

The rhodium complexes were examined under identical conditions. It can be seen from the results (Tables 3 and 4) that complex Rh/3 is not only considerably more active than complex Rh/2 (compare conversions at 60°C after approximately 25 HOS for olefin hydrogenation) but also considerably more stable over the duration of the test. Indeed, no decline in the activity of Rh/3 was apparent over 70 HOS. Whether the loss in activity of the complexes with the alkyl substituted phosphines is due to lower thermal stability compared with those with aryl substituted phosphines and/or to their greater sensitivity to minute traces of oxygen in the feedstocks is not clear. However, the results of these tests clearly demonstrate that for liquid phase hydrogenation under continuous flow conditions the nature of the substituents does have a marked effect on both the activity and stability of the supported complex catalysts.

Elution of rhodium from the catalyst was monitored in both cases. During the olefin hydrogenation, no rhodium could be detected but, when an isoprene feedstock was used, trace amounts of rhodium were detected in the products. When the feedstock was changed back to hexene-1/cyclohexene, rhodium elution ceased, but on returning to the isoprene feedstock rhodium could again be detected in the liquid product. This occurred for both catalysts. The cause of this elution is not clear. It may be a trace impurity in the isoprene or the stabilizer (4-*t*-butyl catechol, present to prevent polymerization of the isoprene) which reacts with the complex and results in cleavage of the rhodium phosphorus bonds which link the metal center to the surface of the silica. Alternatively, isoprene itself may compete with the phosphine for the coordination sites on the rhodium and lead to a show displacement of phosphine from the complex. Displacement of the phosphine might be reduced by the use of a more strongly chelating phosphine of the type SIL–$CH(CH_2PPh_2)_2$. Further studies are necessary to establish the reasons for loss of rhodium in the hydrogenation of isoprene feedstocks and to examine possible methods of preventing the loss.

The heterogeneous iridium complex Ir/1 was initially examined using sulfur-free feedstocks. With hexene-1/cyclohexene total conversion occurred at ambient temperature, but very little conversion of isoprene occurred at 22°C, although the hydrogenated product obtained was exclusively isopentane. At 55°C, however, total conversion of isoprene to isopentane occurred and it seems likely that at the lower temperature a stable complex between isoprene and the iridium is formed. However, even though isoprene appears to bond strongly to iridium under these conditions, there does not appear to be any displacement of the phosphine groups from the iridium, as no iridium could be detected in the liquid products from isoprene hydrogenation at 55°C.

When feedstocks containing *n*-butyl mercaptan were used, higher temperatures were needed to obtain high conversions of both hexene-1/cyclohexene and isoprene feedstocks. However, the complex Ir/1 is much more active than the analogous rhodium complex with the same ligands (Rh/2), even though the iridium complex was tested under milder conditions (lower pressure and higher LHSV). This can be seen by comparison of the products of hexene-1/cyclohexene hydrogenation after 79 HOS for Rh/2 (Table 3) and after 68 HOS for Ir/1 (Table 5) and by comparison of the products of isoprene conversion after 93 HOS for Rh/2 (Table 4) and after 100 HOS for Ir/1 (Table 6). (Even with the more active supported iridium complex, there was no evidence of any hydrogenation of the benzene in the feedstocks.) As in the case of the rhodium complex Rh/2, the iridium complex Ir/1 showed a slow but steady decline in activity over the duration of the test.

However, in view of the much greater activity and stability of the complex Rh/3 over Rh/2, it seems likely that a heterogeneous complex IrBr(SIL–$CH_2CH_2PPh_2)_2$ would show even greater activity than the complex Ir/1 and would also be much more stable under continuous operation.

CONCLUSIONS

The results of these studies demonstrate that rhodium and iridium complexes chemically bonded to silica through tertiary phosphine ligand-silanes are truly heterogeneous catalysts for the liquid phase hydrogenation of olefins and dienes, but that they retain some features normally associated with homogeneous catalysts, e.g., control of catalytic properties by variations in the ligands. Unlike many heterogeneous hydrogenation catalysts, these heterogeneous complex catalysts still retain substantial hydrogenation activity in the presence of *n*-butyl mercaptan. Considerable differences in both activity and stability of rhodium complexes with different halide and phosphine ligands are apparent when the catalysts are operated under continuous flow conditions, although these differences were much less marked in batch tests. The complex RhBr(SIL–$CH_2CH_2PPh_2)_2$ has been shown to have the best combination of high activity and stability under the conditions used, and to operate for 70 hr at temperatures up to 100°C without loss in activity.

The heterogeneous iridium complex $IrCl[SIL-CH_2CH_2P(n-C_6H_{13})_2]_2$ has been shown to be much more active than its rhodium analogue, although a slow decline in activity was apparent over the 116 hr test. By analogy with the rhodium species, complexes of the type $IrBr(SIL-CH_2CH_2-PPh_2)_2$ should show higher activity and stability and deserve further investigation.

No loss of metal from the catalysts was detected in the hydrogenation of hexene-1/cyclohexene feedstocks, but very low rhodium elution was detected in the hydrogenation of isoprene. Additional work is required to establish the cause of rhodium elution and to devise methods of preventing it, since even loss of traces of metal will ultimately lead to a decline in the activity of the catalyst and limit the usefulness of these catalysts for the hydrogenation of isoprene. Elution of iridium, on the other hand, appears to be much lower, and iridium catalysts may prove more satisfactory for the hydrogenation of dienes under continuous flow conditions.

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