JOURNAL OF CATALYSIS 15, 245–249 (1969)

Catalytic Vapor Phase Hydroformylation of Propylene over Supported Rhodium Complexes

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Received February 18, 1969; revised April 15, 1969

Recently, it has been shown that transition metal compounds such as phosphine and arsine complexes of rhodium promote hydroformylation catalysis homogenously in the liquid phase. In the present investigation, these organometallic complexes were impregnated on carbon and alumina supports and employed as solid phase catalysts for the heterogeneous vapor phase hydroformylation of propylene to butyraldehyde. Both the supported phosphine and arsine complexes exhibited good activity (> 30% conversion of propylene to butyraldehyde), with the phosphine complex also displaying good long-term stability as a heterogeneous catalyst. These results demonstrate that organometallic complexes can be employed as catalysts either homogeneously or heterogeneously and may, in either case, exhibit similar catalytic properties.

INTRODUCTION

The most commonly reported (*1*, *2*) homogeneous catalysts for the liquid phase hydroformylation of olefins to aldehydes are metal carbonyl catalysts such as $Co_2(CO)_8$. These catalysts employ relatively severe reaction conditions with typical operating temperatures being 100–180°C and carbon monoxide–hydrogen pressures of 250–300 atm (high carbon monoxide pressure, > 100 atm, is necessary to prevent catalyst decomposition) (*1*, *2*). Selectivity is also a problem using these catalysts since the olefin hydroformylation is accompanied by hydrogenation reactions yielding the corresponding paraffin and alcohols.

Recently, however, a new generation of hydroformylation catalysts have been reported which are highly reactive in addition to being considerably more stable and selective. In particular, phosphine and arsine complexes of rhodium [$(\phi_3P)_2Rh(CO)Cl$, $(\phi_3As)_2Rh(CO)Cl$] are highly reactive homogeneous hydroformylation catalysts (*3*, *4*). Reaction conditions as mild as 100°C and 33 atm are quite effective for selectivity converting olefins to aldehydes ($\sim$ 99% selectivity) at a rapid rate.

The primary disadvantage of homogeneous catalysis is in the separation of the soluble catalyst and solvent from the reaction products. Hetergeneous solid-vapor catalysis, on the other hand, eliminates this problem since the catalyst remains in the solid phase while the reacting gases and products pass over it. Previous patents (*5*) have mentioned the use of both cobalt and rhodium metals on a solid support as hydroformylation catalysts with the active catalyst (believed to be the metal-carbonyl complex) being formed *in situ* when carbon monoxide is introduced. These solid supported metal–carbonyl complexes are known to decompose or volatilize and therefore, are impractical as commercial catalysts. Prior to the present studies, there has been little published information on the preparation and reactions of catalysts consisting of stable organometallic complexes dispersed on solid supports.

There is certainly reason to question whether or not a given metal complex active as a homogeneous catalyst in the liquid phase will also be active when dispersed on a solid in the absence of solvent. The present work was undertaken to examine this question, using the hydroformylation of an olefin as the model reaction system.

The olefin chosen for the investigation was propylene since it and the butyraldehyde formed would remain as gases at the reaction conditions. The results for propylene hydroformylation would, therefore, truly represent vapor phase hydroformylation over a solid catalyst. Also propylene has commercial significance because it can be ultimately converted to building block chemicals such as butyraldehyde, butanol, and 2-ethylhexanol.

EXPERIMENTAL METHOD

Apparatus. Experiments were performed in an 18-in. stainless steel tubular reactor, 0.5 in. in diameter. The high pressure reactor held a maximum catalyst charge of 50 cm^3 and was positioned vertically in a heated fluidized sand bath. Catalyst bed temperature was measured with a movable thermocouple inside of an axial thermowell. Reaction temperature was regulated with a West time-proportioning controller and essentially isothermal conditions were maintained (1.5°C gradient along a 10-in. bed at 150°C) in the reactor. The reactor was normally loaded with 30 cm^3 of catalyst, the remaining 20-cm^3 reactor volume being filled with an inert packing such as ⅛-in. Pyrex glass beads which served as a preheat section for the entering reactants.

The reaction system, could be operated at a variety of conditions. The operating parameters which could be varied include temperature, pressure, gas flow rate of hydrogen and carbon monoxide, and liquid flow rate of propylene. The gases were each metered separately with an automatic flow control system, consisting of an integral orifice differential pressure transmitter used in conjunction with a Foxboro flow controller and a Cash needle control valve. Propylene was metered in as a liquid by means of a Milton Roy chromatographic pump. The hydroformylation reaction was performed at temperatures greater than the critical temperature of propylene (90°C). Consequently, upon entering the heated reactor the propylene was vaporized. The mole percentage of propylene in the feed and the extent of conversion to butyraldehyde were controlled so that butyraldehyde was also a gas under reaction conditions. After contacting the catalyst, the gaseous reaction effluent exited from the bottom of the reactor where it was cooled using a small water condenser. The gas was then subsequently chilled to approximately 5°C in a product separator to remove the condensable reaction products (*n*-butyraldehyde and isobutyraldehyde) from the gas stream. The liquid product and unreacted gas (C_3H_6, H_2, and CO) were each continuously withdrawn from the product separator. The condensed butyraldehyde product was collected in a glass flask and analyzed by gas chromatography. The remainder of the effluent gas was measured by a wet test meter; however, it was sampled for GC analysis prior to venting.

Analysis. A quantitative analysis of the reaction products was carried out on a Wilkens-Aerograph model 200 gas chromatograph using a flame detector and a 40-ft, ⅛-in. stainless steel column filled with 10% tetracyanoethylpentaerythritol (TCEPE) and 60/70 mesh Anakrom ABS (Analabs, Inc.). The liquid sample is injected into the column which is heated isothermally at 125 °C. Peak areas were obtained using an electronic integrator with digital print out (Infotronics Digital Read-out System, model CRS-10HB).

Materials. The rhodium complexes; $(\phi_3X)_2Rh(CO)Cl$, X = P, As; used in this investigation were prepared according to the method of Vallarino (*6*). The $RhCl_3 \cdot 3H_2O$, was obtained from Matthey-Bishop Co., triphenylarsine and triphenylphosphine from M & T Chemicals Inc. Other reagents were obtained from commercial sources and were the best chemical grade available (Reagent Grade or equivalent, if possible). Olefins employed were "Pure Grade" obtained from Phillips Petroleum Co. Carbon monoxide and hydrogen of CP grade were obtained from the Matheson Co.

Catalyst preparation. Three catalyst formulations were prepared in granular form for use in the fixed bed, high pressure flow reactor. These were (a) $(\phi_3P)_2Rh(CO)Cl$ on alumina, (b) $(\phi_3P)_2Rh(CO)Cl$ on activated carbon, and (c) $(\phi_3As)_2Rh(CO)Cl$ on activated carbon. The minimum volume technique was employed in all cases to disperse the organometallic complexes on the solid supports.

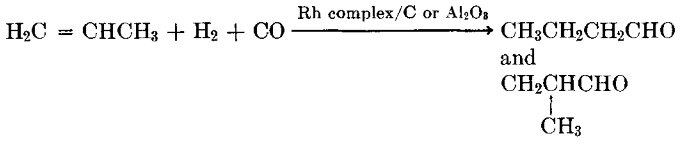
(*a*) *$(\phi_3P)_2Rh(CO)Cl$ on alumina.* A 1.10-g sample of $(\phi_3P)_2Rh(CO)Cl$ was dissolved in 20 ml of $CHCl_3$ and mixed with 50 ml (43.35 g) of 10–30 mesh, low surface area, porous alumina (SAHT993 from Carborundum Company). The mixture was stirred until the particles appeared dry and no longer adhered to the flask walls. The supported catalyst was then placed in a vacuum desiccator at "house-vacuum" overnight at room temperature to remove any residual solvent. The supported catalyst was then stored until employed in the test reaction. The total pore volume of the support was 0.383 cm^3/g.

(*b*) *$(\phi_3P)_2Rh(CO)Cl$ on activated carbon.* A 1.11-g sample of $(\phi_3P)_2Rh(CO)Cl$ was dissolved in 26 ml of $CHCl_3$ and added to 50 ml (8.8 g) of 10–20 mesh, high surface area, activated carbon (Nuchar C115 obtained from West Virginia Pulp and Paper Company). The total pore volume of this material was 2.971 cm^3/g. The impregnated support was prepared as described above in (a).

(*c*) *$(\phi_3As)_2Rh(CO)Cl$ on activated carbon.* A 1.24-g sample of $(\phi_3As)_2Rh(CO)Cl$ was dissolved in 27.7 ml of $CHCl_3$ and mixed with 50 ml (8.50 g) of the activated carbon described in example (b) above. The impregnated support was prepared as described above in (a).

RESULTS AND DISCUSSION

The solid supported organometallic complexes were evaluated and compared as catalysts for the propylene hydroformylation reaction, Eq. (1)



$$H_2C = CHCH_3 + H_2 + CO \xrightarrow{\text{Rh complex/C or } Al_2O_3} CH_3CH_2CH_2CHO \text{ and } CH_2\underset{\underset{CH_3}{|}}{C}HCHO \qquad (1)$$

The "base" operating conditions employed were: catalyst, rhodium complex on either carbon or alumina; catalyst charge, 30 cm^3; temperature, 148°C; total pressure, 49 atm. Feed composition of (mole %): carbon monoxide, 37.5; hydrogen, 37.5; propylene, 25. Contact time: 0.92 cm^3 of reactor void space/cm^3 of feed per min. At these operating conditions, the liquid phase hydroformylation reaction was highly selective to aldehyde products as reported previously (*4*). No significant quantities of hydrogenated products (e.g., $< 1\%$ alcohols and/or paraffins) were detected by gas chromatographic analysis for either the liquid or vapor phase reaction.

The propylene conversion and ratio of the normal to isobutyraldehyde product for each of the three solid catalysts are reported in Table 1 (greater than 95% of the propylene converted formed butyraldehyde). It is significant to note that each of the supported rhodium complexes demonstrated considerable activity for the hydroformylation of propylene to butyraldehyde ($> 30\%$ conversion).

In addition to comparing the catalyst activities, catalyst (a), $(\phi_3P)_2Rh(CO)Cl$ on alumina, was evaluated at various contact times during an extended period. Periodically, conversion was reevaluated at the base contact time (0.92 min).

No noticeable change in conversion or product isomer distribution was detected during a period of over 300 hr at reaction conditions. These results demonstrated that the supported organometallic complex catalyst had good stability properties, unlike the simple metals (or metal carbonyls) reported previously (*5*). As an added verification of the thermal stability of the organometallic complex itself, a thermal gravimetric analysis (TGA) was performed in both helium and 10% oxygen in helium atmospheres (*7*). The TGA results show that $(\phi_3P)_2Rh(CO)Cl$ complex is stable at temperatures as high as 225°C.

TABLE 1

Comparison of Hydroformylation Activity and Aldehyde Isomer Distribution[a]

Catalyst	Description	Propylene conversion (mole %)[b]	Ratio normal/ isobutyraldehyde	Comments
(a)	$(\phi_3P)_2Rh(CO)Cl$ on alumina	36.1	1.9	
(b)	$(\phi_3P)_2Rh(CO)Cl$ on carbon	46.0	1.25	Higher activity than same catalyst on alumina
(c)	$(\phi_3As)_2Rh(CO)Cl$ on carbon	32.2	Initially 4.0 Finally 1.25	Deterioration of selectivity was observed over a 5-hr period

[a] Operating conditions given in text.

[b] Selectivity of converted propylene to aldehyde product >95 mole % in all cases.

Contact time was varied from 0.44 to 0.92 min by adjusting total flow rate at the base feed composition. The definition of contact time is "void-free catalyst volume divided by actual gas volumetric flow rate" or

$$\tau = \frac{V_c \epsilon}{Q}$$

where V_c = catalyst bed volume (cm^3); ϵ = void fraction catalyst bed; Q = volumetric flow rate of reactor fed at operating conditions (cm^3/min); and τ = contact time (min).

The effect of contact time on conversion is shown in Fig. 1 for catalyst (a). As one would expect, the conversion increases with contact time. Liquid product distribution was relatively insensitive to contact time over the range investigated and a typical analysis of the liquid product is given in Table 2.

TABLE 2

Liquid Product Distribution

Component	Wt %
Propylene	4.84
Isobutyraldehyde	32.50
n-Butyraldehyde	60.00
1-Butanol	0.46
High boiling by-products	2.20

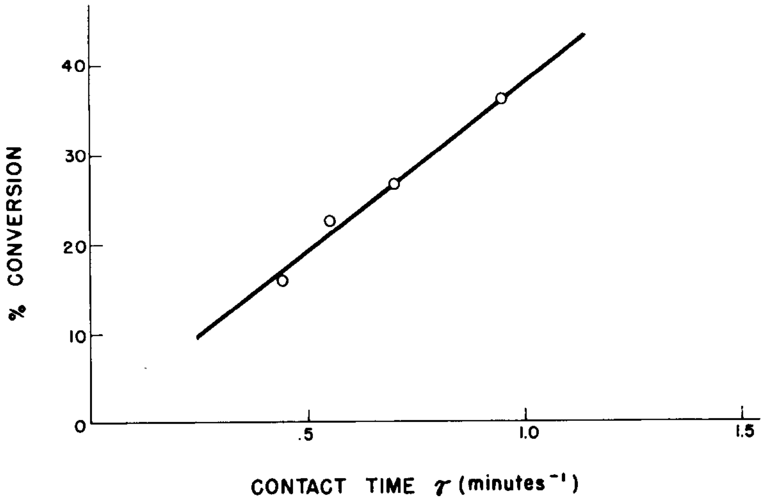


Fig. 1. Propylene conversion versus contact time: temperature 148°C; total pressure 49 atm; and, feed composition (mole %): carbon monoxide, 37.5; hydrogen, 37.5; propylene, 25.

Since this study was exploratory in nature, no attempt was made to study further the effects of other operating parameters such as temperature, pressure, and hydrogen/carbon monoxide ratio.

Certain parallelisms can be drawn between the catalytic performance of the complexes in liquid solvent and on solid supports. Catalyst (c) (arsine complex of rhodium on carbon) when employed in a homogeneous liquid phase hydroformylation reaction was unstable and decomposed quite rapidly. This result also occurred in the vapor phase using the solid form of the catalyst. The product selectively decreasing from a normal/isobutyraldehyde ratio of 4:1 initially, to a final ratio of 1.25:1 after 5 hr running time.

Similarly, catalyst (a) (triphenylphosphine complex of rhodium on alumina) which was quite stable in liquid phase hydroformylation reactions (*4*), exhibited excellent stability as a heterogeneous catalyst with no significant change in activity or selectivity over 300-hr period. In addition, the normal/isobutyraldehyde ratio (~2:1) was essentially the same as had been obtained at 150°C for liquid phase propylene hydroformylation using this organometallic complex catalyst system.

It is quite likely that in addition to propylene, olefins such as ethylene and butene might also be hydroformylated in the vapor phase over a solid catalyst. These olefins all have moderate critical temperatures (10–147°C) thereby insuring that a vapor phase reaction could take place at temperatures not extreme enough to cause decomposition of the hydroformylation catalyst. It is also possible that in the future coordination complexes of higher thermal stability might be prepared to effect the vapor phase hydroformylation of higher molecular weight olefins.

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