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CATALYTIC HYDROGENATION AND EXCHANGE REACTIONS ON GAS CHROMATOGRAPHIC COLUMNS, IN THE PRESENCE OF SUPPORTED $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$

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SUMMARY

The heterometallic cluster $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$ is decomposed under H_2 to metal particles on the inert support of a gas chromatographic column. The column is used as a catalytic reactor to hydrogenate C–C and C–O multiple bonds and to study the H-for-Cl substitution reactions on chlorinated hydrocarbons. The performance of such a column and its possible use are briefly discussed.

INTRODUCTION

Attention has recently been given to the heterometallic clusters as potential homogeneous catalysts[1–3] or as precursors of stoichiometrically defined heterogeneous catalysts[1–4]. Indeed, the presence of different metals is thought to allow a more efficient and controlled activation of small substrate molecules[5,6].

The catalytic hydrogenation reactions have extensively been studied. Some have been carried out in the presence of clusters both under homogeneous[7] and in heterogeneous conditions[8]. Moreover, the study of hydrogen–deuterium exchange processes has allowed some conclusions about the occurrence of "true cluster catalysis" under homogeneous conditions[9]. The deuteration of some intermediates or products has also permitted some hypotheses on the reaction mechanisms[10].

On the other hand, the use of on-column hydrogen–deuterium or hydrogen–tritium exchange reactions for labelling purposes and for radioactivity determination by gas chromatography (GC) of compounds containing labile tritium is well established[11–14]. These reactions show that a GC column may be used not only as a powerful separation and analysis tool, but also as a versatile "chemical reactor", offering remarkable possibilities both in catalytic hydrogenation processes and in selective exchange reactions aimed at obtaining labelled "target molecules". There are many analogies in the processes (*e.g.*, substrate–support interactions and chemisorption, hydrogen chemisorption and activation, etc.) occurring within a GC column and in an heterogeneous stationary-bed reactor.

We have already reported that the heterometallic cluster $(\eta^5\text{-}C_5H_5)NiOs_3\text{-}(\mu\text{-}H)_3(CO)_9$ (refs. 15–17) (complex 1) is active and selective in the hydrogenation

and isomerization of acetylenes and ethylenes[15] and of dienes under homogeneous conditions, where the complex behaves as a "cluster catalyst"[10]. When supported and thermally treated on γ-Al$_2$O$_3$, complex 1 is active in the hydrogenation of acetylene and benzene, and in the methanation of CO and CO$_2$ under atmospheric pressure of dihydrogen[18,19]. It also behaves as an hydrogenation catalyst for dienes when supported by GC materials, packed into a GC column and used in a GC apparatus under a stream of dihydrogen[20]; depending on the "activation" procedure and upon the "ageing" of the supported system, results typical of homogeneous or of heterogeneous catalysis are obtained.

We have extended our investigations into the behaviour of complex 1 when supported on a GC column to include the reactivity of a variety of unsaturated small molecules (acetylenes, ethylenes, aromatic hydrocarbons, organic molecules with functional groups, carbon oxides) in the presence of dihydrogen. We have also attempted on-column exchange reactions on saturated and unsaturated substrates, aimed at obtaining specific (labelled or not) "target molecules".

The results of these experiments are discussed and compared with those of the hydrogenation reactions under homogeneous conditions or on γ-Al$_2$O$_3$, in the presence of complex 1.

EXPERIMENTAL

Materials

The solvents used were carefully dehydrated over sodium. Ultrapure N$_2$ or H$_2$ (SIAD) were generally used as carrier gases; in some experiments, ultrapure acetylene, carbon monoxide and mixtures of the latter with hydrogen or helium were used (SIAD). The substrate molecules tested were commercial products (Fluka, Merck) and were checked for impurities before use both by GC and by ^{1}H NMR spectroscopy. For the deuteration and tritiation experiments, ^{2}H$_2$ and ^{3}H$_2$O (Farmitalia-Carlo Erba, and Amersham) were used, respectively.

Analysis of the reactants and products

A Carlo Erba 4200 gas chromatograph equipped with a flame ionization detector was used in order to check the purity of the compounds to be hydrogenated; these tests were also helpful for determining the retention times of both the starting materials and the products. A JEOL JNM GX 270 Fourier transform ^{1}H NMR spectrometer was also used for the above purposes. The deuterated derivatives were identified by means of a single-focusing Hitachi–Perkin-Elmer RMU 6H instrument [operated in electron impact (EI) mode at 70 eV] or by means of a Kratos MS-50 apparatus, coupled with a Carbo Erba 4200 FID gas chromatograph.

Catalytic experiments in the gas chromatograph

The apparatus consisted of two coupled gas chromatographs. A Carlo Erba Fractovap Model B was used as both injection system and "chemical reactor". It was coupled by means of a thermostatted junction to the Carlo Erba 4200 flame ionization and hot-wire detectors, acting as both flow regulator and analytical unit. The gas flowing through the system was the carrier and the reagent at the same time.

The catalytic column (1 m $\times$ 6 mm I.D.) was filled with 12 g of silanized

Chromosorb P (Johns Manville), 60–80 mesh, which had been previously wetted with
a light petroleum (b.p. 40–70°C) solution containing 35 mg of complex 1 and then
dried in a Rotavap evaporator under reduced pressure at room temperature. The
column was then heated at 155°C for 20 h in a stream of dihydrogen (25 ml/min),
while carefully controlling the possible sublimation of part of the cluster. The com-
bined effect of heat and H_2 resulted in decomposition of the cluster to metal particles
(of predictable stoichiometry, see ref. 19), so that a "pure heterogeneous" catalyst
was obtained by this procedure. The total modification of complex 1 was confirmed
by extracting the material with chloroform. No soluble compounds could be detected.

No catalytic effect was observed on pure Chromosorb P at temperatures up to
230°C, the maximum operating temperature for the catalytic system.

The retention times for the identification of the hydrogenated products were
obtained by injecting real samples of the hydrogenated substances into the catalytic
column. Retention times on the catalytic column were of the same order of magnitude
as the dead-time of the column: about 70 s.

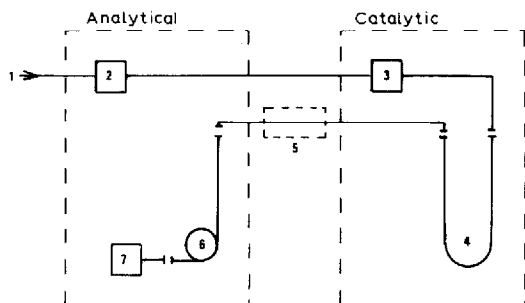A schematic diagram of the apparatus is shown in Fig. 1.

Fig. 1. Diagram of the apparatus used for catalysis experiments: 1 = carrier reactant inlet; 2 = flow
controller; 3 = injection port; 4 = catalytic column; 5 = heated connection line; 6 = analytical column;
7 = detector.

For the analysis of saturated and unsaturated hydrocarbons, the analytical
instrument was operated with a 2 m × 6 mm I.D., n-octane/Porasil C, 80–100 mesh
column; carrier gas, H_2 (25 ml/min); temperature, 10°C for 6 min, then 5°C/min up
to 155°C. In some cases, the temperature program was modified or shortened to
allow a better separation of the reaction products or simply to save time.

The detection of diphenylacetylene, phenylacetylene and their hydrogenation
products was carried out using a 2 m × 6 mm I.D., SE-30 (5% on Chromosorb W
AW, 60–80 mesh) column; carrier gas, H_2 (46 ml/min); temperature program, 60°C
for 6 min, then 10°C/min up to 240°C.

Acetonitrile, nitrobenzene, benzene, toluene and their derivatives were sepa-
rated and detected with a 2 m × 6 mm I.D., Carbowax 20M (4% on Chromosorb
W AW, 60–80 mesh) column; carrier gas, H_2 (100 ml/min); temperature program,
60°C (injection), then 2°C/min up to 190°C.

RESULTS AND DISCUSSION

Hydrogenation experiments

   Alkynes. The following alkynes have been tested: acetylene, *tert.*-butylacety-
lene, phenylacetylene, diphenylacetylene, 1- and 2-pentyne, 1- and 3-hexyne.

   At 200°C, acetylene is quantitatively hydrogenated: ethane is the main product,
some butane and trace amounts of benzene and cyclohexane also being observed.
Blank experiments showed that the acetylene used was free from these compounds.
No cracking to methane was observed. Under the same conditions, ethylene is fully
hydrogenated to ethane and no methane is observed. In the temperture range of
40–200°C, *tert.*-butylacetylene is hydrogenated to 2,2-dimethylbutane in 100% yields.
Once more, no cracking products are observed.

   In the temperature range 60–200°C, phenylacetylene is hydrogenated to the
extent of about 90%. Ethylbenzene is the main product and, depending on the tem-
perature used, variable yields of a minor product, tentatively identified as ethylcy-
clohexane, are formed (above 150°C). By contrast, only a 4–5% yield of diphenyle-
thane is observed when diphenylacetylene is processed under the same conditions
(and also at 230°C). This is probably due to the fact that the high-boiling alkyne
(b.p. 300.2°C) is retained to some degree by the catalytic column.

   Hydrogenation of 1- and 2-pentyne and 1- and 3-hexyne to pentane or hexane,
respectively, takes place in 98–99% yield; 1–2% of cracking products is observed.
Complex 1, under homogeneous conditions[10], is efficient in the hydrogenation of the
terminal alkynes and less efficient in that of the internal alkynes; alkenes are formed,
and hence the homogeneous system shows greater selectivity.

   Aromatic hydrocarbons. At 200°C, benzene yields about 10% of cyclohexane;
no linear products are observed. Toluene, under comparable conditions, is hydro-
genated to the extent of only 1% to methylcyclohexane. Again, no linear products
are formed.

   Substrates with functional groups. In the range 100–200°C, there are indications
of the partial reduction of nitrobenzene to aniline. Indeed, when injected into the
catalytic column, the compounds can be recovered only in part, but aniline cannot
be observed. Injections of water (acting as a weak nucleophile and as a weak acid)
to free the adsorbed aniline were unsuccessful.

   Acetonitrile behaves like nitrobenzene. However, the ethylamine is retained in
the column and water injections are, once again, inadequate to free it.

   Acetone. Acetone reacts with hydrogen producing mainly propane and isopro-
panol. The latter can be hydrogenated, on the same column and under the same
conditions, to propane. The product distribution as a function of temperature, and
the mechanisms of these reactions, are under investigation.

   CO, CO_2 and CS_2. Reaction of CO with H_2 in a stream of helium. Commercial
carbon monoxide (bottles) and carbon monoxide obtained from the thermal decom-
position of $Ni(CO)_4$ were tested. At room temperature, no hydrogenation was ob-
served, whereas in the range 160–210°C low yields of methane (a few percent) were
found. Carbon dioxide was not appreciably hydrogenated under these conditions,
whereas carbon disulphide gave rise to small yields of methane.

   The absence of carbon dioxide hydrogenation under the conditions described
here may be due to the difficulty in reaching the water gas shift equilibrium during

the short contact times, in a system which is by definition not in equilibrium (see ref. 19 and the discussion below).

We have attempted to obtain water gas shift reaction (WGSR) products at 200°C by using as reactant and carrier gas carbon monoxide–helium (1:9) (50 ml/min). However, when water was injected no dihydrogen could be detected, neither the hot-wire detector nor by a flow ionization chamber (using ^3H_2O). Interestingly, and somewhat surprisingly, *methane* could be detected when water was injected in the above mixture (25 ml/min).

Thus, at least in the system here described, the formation of methane seems to be due to the reaction of carbon monoxide with water. In view of the industrial importance of this reaction, further studies are in progress.

Comparison of the hydrogenation results with those obtained in a pulse reactor

In the pulse reactor described in refs. 18 and 19, containing complex 1 supported on γ-alumina (activated generally at 250°C for 4 h in a stream of dihydrogen) and operated in the temperature range 52–240°C, acetylene is hydrogenated to ethane (about 85%) and to ethylene (about 12%); some methane is also observed (2–3%); the conversion for each cycle is 0.5–0.7 mol of substrate per mol of active metals[19]. Benzene is hydrogenated to cyclohexane (98%) and some linear hexane (0.8%) with 2.0% conversion for each cycle.

Finally carbon monoxide and dioxide are hydrogenated (0.2–0.3% conversion) to 100% methane and (0.09–0.3% conversion) to 90% methane and 10% carbon monoxide, respectively[19]. Thus, complex 1 on γ-alumina is apparently more efficient than when supported on Chromosorb. However, in the present system, neither cracking nor linear products are observed from the hydrogenation of acetylene and of the aromatic hydrocarbons.

There is strong evidence that the (very efficient) methanation of carbon dioxide on the complex $1/γ-Al_2O_3$ catalyst occurs in two steps, *i.e.*, the reaction at high temperatures of CO_2 with H_2 to give CO and H_2O (WGSR)[9], followed by the hydrogenation of CO to methane. However, on the catalytic column described here methane is obtained upon reaction of CO with *water*, and this fact is not contrary to the findings on the system complex $1/γ-Al_2O_3$.

On-column exchange reactions

Hydrogen–chlorine exchange. These reactions occur for some saturated substrates, with varying degrees of difficulty, depending probably upon the nature (and reactivity) of the molecules. Thus, methane is obtained from dichloromethane (30%), chloroform (12%), carbon tetrachloride (4%) and methyl chloride (0.8%), at 230°C in a stream of dihydrogen. No silane, but only hydrogen chloride was observed in the hydrogenation of tetrachlorosilane, probably because, as in the case of amines, the support material in the catalytic column is not inert enough for such reactive molecules.

The hydrogenation of $C_2{}^2H_4$ and the possible hydrogen–deuterium exchange on this substrate have also been studied. At 200°C, the reaction with H_2 is complete, but only 28% of the hydrogenation products consists of $C_2{}^2H_4H_2$; besides, a H-for-^{2}H exchange reaction occurs, and the derivatives $C_2{}^2H_3H_3$ (26%) and $C_2{}^2HH_5$ (46%) are formed (GC–mass spectrometric analyses), thus indicating that, at least

at relatively high temperatures, exchange processes also take place with considerable efficiency.

The catalytic system described here, based on a GC column used as chemical reactor, shows some advantage when compared with the "classical" homogeneous and heterogeneous systems: (i) simple construction and relatively "mild" operating conditions (low H_2 pressures and reaction temperatures generally lower than those used in the heterogeneous pulse reactions[19], with yields relatively high when considering the short contact times on the column), and (ii) good versatility coupled with the possibility of selectively collecting the (known) hydrogenation products.

The use of two gas chromatographs is obviously not necessary. Any thermostatic system coupled with a reliable injection device may be substituted for the first instrument. Coupling of both catalytic and analytical columns in the same instrument is not recommended, because the temperature requirements for the two columns may be different. Moreover, previous experiments had shown that, at least when complex 1 is not completely decomposed, partial sublimation into the analytical column occurs, with loss of efficiency[20].

The versatility of the system is evidenced by the great variety of operating conditions and of substrates one can work with in a limited period of time. However, there are some technical difficulties with high-boiling compounds and/or with molecules having functional groups. Some of these are probably due to the lack of complete inertness of the support. They could be overcome by choosing a material different from silanized Chromosorb P and/or by shortening the contact time through the use of a shorter catalytic column. A large increase in the flow-rate of H_2 might be useful in principle, but would cause detection and identification problems.

The method proposed is comparable (with regard to its efficiency) to the homogeneous[10] and heterogeneous[19] systems described elsewhere and based on complex 1, at least if we consider the hydrogenation of acetylenes, dienes and benzene. However, as expected for a heterogeneous catalysis, low selectivity is observed.

Lower efficiency in the methanation of carbon monoxide and dioxide than is observed with complex $1/\gamma$-Al_2O_3 in a pulse reactor is observed. This fact is probably due to the short contact times allowed by the flow-rate of the carrier and reactant gas required for a good separation of the products.

A final advantage of the chromatographic system is the possibility of coupling the catalytic column with a preparative gas chromatograph: this would permit one to collect selectively the "labelled" molecules and to separate them from other products. This would be of particular relevance for labelled molecules of pharmacological or of biological interest.

The potential applications of a method allowing the catalytic hydrogenation, identification and selective collection of the products in the same apparatus are obvious and are the subject of active research in our laboratories.

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