

photoisomerization takes place at 185 nm in other cyclooctene derivatives as well.

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Received November 23, 1977

Hydrocarbon Formation from Metal Carbonyl Clusters Supported on Highly Divided Oxides

Sir:

Recent publications have described the use of transition metal cluster carbonyl complexes in the catalytic reduction of carbon monoxide to alkanes^{1,2} or alcohols³ and in the water gas shift reaction⁴ in the homogeneous phase, but the observed catalytic activities are very low under low pressures. We wish to report here our results relating to these two reactions in the heterogeneous phase, using transition metal carbonyl complexes supported on highly divided oxides. We have not only found an interesting reactivity but also quite different results when these were compared with supported metals or with metal clusters in the homogeneous phase, as far as the product distribution is concerned.

Impregnation of alumina, silica, or magnesia with various

Table I. Mass Balance between the CH₄ and CO₂ Formed and the Carbonyl Ligands When 10 mg of Cluster Supported on 200 mg of Al₂O₃ is Heated under Argon in a Sealed Glass Tube

Cluster	Temp, °C	Mol of CH ₄ /mol of cluster	Mol of CO ₂ /mol of cluster	(Mol of CH ₄ + mol of CO ₂)/mol of CO ligand
Ru ₃ (CO) ₁₂	300	0.91	10.1	0.92
Os ₃ (CO) ₁₂	400	0.30	11.8	1.00
Os ₆ (CO) ₁₈	300	1.11	18.4	1.09
Rh ₄ (CO) ₁₂	250	0.22	7.7	0.66
Rh ₆ (CO) ₁₆	250	1.26	9.2	0.65
Ir ₄ (CO) ₁₂	300	0.38	10.5	0.91

Table II. Product Distribution from the Reaction of 10 mg of Cluster Complex Supported on 200 mg of Al₂O₃ Heated under a Mixture of CO (380 Torr) and Argon (380 Torr)

Cluster	Temp, °C	Mol of CH ₄ /mol of cluster	Mol of CO ₂ /mol of cluster	(Mol of CH ₄ + mol of CO ₂)/mol of CO ligand	% convn (CO → CO ₂)
Ru ₃ (CO) ₁₂	300	5.8	42.1	4.0	55
Os ₃ (CO) ₁₂	400	10.7	97.6	6.5	52
Ir ₄ (CO) ₁₂	400	13.2	82.5	8.0	52
Rh ₆ (CO) ₁₆	400	11.9	93.8	6.6	55
Rh ₄ (CO) ₁₂	400	7.6	42.3	4.2	51
Os ₆ (CO) ₁₈	400	13.3	85.7	5.5	47

metal carbonyl clusters and subsequent heating of the supported complex under argon or CO results in the formation of CO₂, H₂, and various hydrocarbons the nature of which depends on many parameters such as the temperature, the nature of the starting cluster, the nature of the support, and, most important, its water content. There is no need for added hydrogen to carry out such reactions. We present here evidence to show that, upon heating a carbonyl cluster supported on alumina, the carbonyl ligands react with the hydroxyl groups (or adsorbed molecular water) of the support to produce H₂ and CO₂.⁵ Furthermore, part of the H₂ produced by this reaction, or water from the support, reacts with the supported cluster to produce hydrocarbons either from carbonyl or from carbide thermally produced in the cluster cages.⁶

Thus in a typical experiment 200 mg of hydrated η-Al₂O₃ (315 m²/g) was carefully mixed under argon with 10 mg of carbonyl cluster complex. This supported cluster was placed in a glass reactor evacuated at room temperature for 1 h (10⁻⁵ Torr) and then heated at increasing temperature under argon. Whereas many hydrocarbons were observed at low temperature (*T* < 200 °C), the selectivity toward methane reached 100% at 250 °C or above.

Table I indicates the mass balance between the CH₄ and CO₂ formed and the starting carbonyl ligands after all of the CO ligands have reacted (several hours at 300 °C for Ru₃(CO)₁₂, Ir₄(CO)₁₂, Rh₄(CO)₁₂, Rh₆(CO)₁₆, and Os₆(CO)₁₈, and after several hours at 400 °C for Os₃(CO)₁₂). A blank experiment carried out using 200 mg of Al₂O₃ in the absence of a cluster complex gave no hydrocarbons or hydrogen and only traces of CO₂ (presumably physisorbed on the alumina surface). In the case of Rh₆(CO)₁₆, the hydrogen source was confirmed as the water on the alumina support by carrying out the reactions with an η-Al₂O₃ partially exchanged with deuterated water. In this case CD₄ was obtained with CD₃H, CD₂H₂, CDH₃, and CH₄ as well as with H₂, HD, and D₂ (mass spectroscopic analysis). We have not carried out an exact mass balance of hydrogen evolution to check if production of excess of hydrogen would define some oxidation of the noble metal cage, as was found for supported Mo(CO)₆.⁷ However, in the case of Rh₆(CO)₁₆, the amount hydrogen (gaseous + hydrocarbon) produced was equivalent to the amount of carbon dioxide produced as expected from the stoichiometry of the water gas shift reaction.

Both thermogravimetric and infrared investigations on pure and supported cluster carbonyls⁸ have shown that, below 250 °C, the total decomposition of the molecular clusters investigated here to metals is prevented and molecular cluster aggregates (of the original or different nuclearity) are still present. Only above 250 °C does a great deal of decomposition to metal take place, in parallel as expected with selective methanation of carbon monoxide.⁹ In addition the reaction of CO with rhodium metal (prepared by H₂ reduction at 500 °C of RhCl₃·3H₂O (4% by weight) supported on η-alumina), even in the presence of added water, resulted only in traces of hydrocarbons at 250 °C.

The reactivity of the systems originated from the supported cluster complexes was estimated by the temperature at which a given amount of CH₄ was formed. The following order was

Table III. Hydrocarbons Formed during the Heating of Carbonyl Cluster Complexes Supported on Alumina under an Atmosphere of CO (600 Torr)

Cluster	Temp, °C	Hydrocarbons, %					
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₅ H ₁₂
Ru ₃ (CO) ₁₂	200 ^a	69	8	6	9	4	4
Rh ₄ (CO) ₁₂	250 ^b	56	18	17	5	3	1
Rh ₆ (CO) ₁₆	235 ^b	52	17	20	7	3	1
Ir ₄ (CO) ₁₂	250 ^a	93	6	1			
Os ₃ (CO) ₁₂	250	100					
Os ₆ (CO) ₁₈	250	100					

^a 100% CH₄ at 300 °C. ^b 100% CH₄ at 400 °C.

Table IV. Influence of Alumina Pretreatment on the Composition of the Fraction of Hydrocarbons Formed after Heating Rh₆(CO)₁₆ Supported on Alumina at 200 °C for 24 h under an Atmosphere of CO (600 Torr)

Temp of alumina pretreatment, °C	Hydrocarbons, %							
	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	1-C ₄ H ₈	2- <i>t</i> -C ₄ H ₈	2- <i>c</i> -C ₄ H ₈
200	4	1	55	1	7	5	19	10
300	7	1	32	1	5	7	31	18
500	6	1	40	1	2	15	20	17
900	9	1	22	1	9	8	33	19

found: Ru₃(CO)₁₂ > Os₆(CO)₁₈ > Rh₄(CO)₁₂ ≈ Rh₆(CO)₁₆ ≈ Ir₄(CO)₁₂ ≈ Os₃(CO)₁₂. With only the exception of the unexpected behavior of Os₆(CO)₁₈, this sequence is in good agreement with the order of specific activities for the methanation reaction on supported metals.¹⁰

Hydrocarbon formation was observed at temperatures as low as 150 °C and, below 250 °C, the product distribution depended markedly on the nature of the supported cluster. With Ru₃(CO)₁₂, Os₃(CO)₁₂, and Os₆(CO)₁₈ the only hydrocarbon formed was methane. With Ir₄(CO)₁₂ some ethane (9%) and propane (1%) was formed. With Rh₄(CO)₁₂, methane (93%), propane (5%), and propene (1%) were formed. With Rh₆(CO)₁₆, methane (59%), ethane (26%), propane (9%), propene (3%), and butane (1%) were formed. This would imply that hydrocarbon formation takes place on the molecular cluster units which, as above stated, are preserved in the temperature range (150–250 °C) in which C₁–C₅ hydrocarbon formation is observed. Moreover, the above product distributions do not follow the trend reported at low conversion for supported metals.¹⁰ In this latter case, the ordering according to the average molecular weight of the hydrocarbon products gives a sequence Ru >> Rh > Ir quite opposite to our sequence. On the other hand the predominant formation of C₂ and C₃ hydrocarbons follows the behavior of supported metals.

The same procedure was used to study the reaction of supported carbonyl cluster complexes under an atmosphere of carbon monoxide. The results (Table II) clearly show that the conversion of CO to CO₂ by H₂O is catalytic and that in the presence of an increased quantity of CO also the production of methane, probably catalytic, is greatly increased. In this case the reactivity for hydrocarbon formation decreases in the order Ru₃(CO)₁₂ > Ir₄(CO)₁₂ > Rh₄(CO)₁₂ ≈ Rh₆(CO)₁₆ > Os₃(CO)₁₂ > Os₆(CO)₁₈. With Ru₃(CO)₁₂, Rh₄(CO)₁₂, Rh₆(CO)₁₆, Ir₄(CO)₁₂, other low molecular weight hydrocarbons are also formed as shown in Table III.

Results of preliminary studies on the influence of the support used in these reactions show that high surface area silica or magnesia may be also used as the support and as the hydrogen source. More interesting is the observation that the product distribution is highly dependent on the temperature of pretreatment of the support (in this case the cluster is solubilized in CHCl₃, the solution is contacted with the dehydrated support, and the solvent is removed under vacuum). With Rh₆(CO)₁₆ on alumina a selectivity in the hydrocarbon fraction of 95% in favor of low molecular weight olefinic hydro-

carbons (mainly ethylene and butenes) can be reached when the support is previously dehydrated at 200 °C or above (Table IV). In the absence of cluster (i.e., Al₂O₃ + CHCl₃), only a trace of methane was formed after 24 h at 200 °C. The high selectivity to ethylene and butenes is remarkable when compared with supported rhodium.¹⁰

This is the first reported case of such a clear formation of light C₂–C₅ hydrocarbons other than methane from transition metal carbonyl clusters, since their formation in homogeneous phase with similar cluster compounds is not so remarkable;^{1,2} moreover, our results indicate that supported cluster carbonyl complexes can be potential catalysts for hydrocarbon synthesis in which the product distribution is determined by the nature of the cluster, the mode of impregnation, the nature of the support, and its water content, as well as the nature of the hydrogen source. In fact we have made preliminary observations that similar but not identical results can be achieved using H₂ as the hydrogen source.

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Received August 17, 1977