Cycloaddition of Carbon Dioxide to Propyne over Supported Rh_4 and Fe_2Rh_4 Carbonyl Cluster-derived Catalysts

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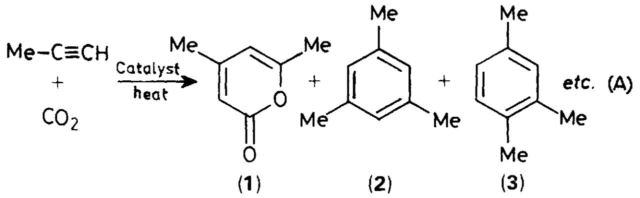
Rh_4 and Fe_2Rh_4 carbonyl cluster-derived catalysts supported on selected metal oxides such as TiO_2, Al_2O_3, and ZrO_2 exhibit catalytic activity in the formation of 4,6-dimethyl-2-pyrone by the cycloaddition of carbon dioxide to propyne under moderate conditions.

Catalytic conversion of carbon dioxide into useful organic chemicals[1] is receiving much attention from the global environmental and carbon resource utilization points of view. One example is the hydrogenation of CO_2 to methane and methanol[2] on metal catalysts. Several transition metal complexes such as $Rh(diphos)(\eta\text{-}BPh_4)$[3] [diphos = 1,2-bis(diphenylphosphino)ethane] and $Ni(COD)_2Ph_2P(CH_2)_4PPh_2$[1] (COD = cyclo-octa-1,5-diene) have been reported to catalyse cycloaddition of CO_2 to acetylenic compounds to yield pyrone derivatives in the liquid phase with low conversion and poor selectivity. Recent publications on syntheses of $(COD)\text{-}Rh_2OsH_2CO_2(PMe_2Ph)_3$[4] and $[HOs_3(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{17}][(Ph_3P)_2N]$[5] suggest that it is possible to activate the dipolar substrate CO_2 on metal carbonyl clusters. While exploring novel heterogeneous catalysts for CO_2 fixation we have used homo- and hetero-nuclear metal clusters as precursors for preparing well-characterised and highly dispersed metal particles on metal oxide supports.[6] We report here that CO_2 was incorporated into the propyne dimer to give a cycloaddition product, 4,6-dimethyl-2-pyrone, over mildly oxidised Rh_4 and Fe_2Rh_4 clusters supported on metal oxides such as SiO_2, Al_2O_3, TiO_2, and ZrO_2.



$Rh_4(CO)_{12}$, $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$ [TMBA = $NMe_3\text{-}(CH_2Ph)$], and $[TMBA]_2[Fe_3(CO)_{11}]$ were synthesized as reported in the literature.[7] Each carbonyl cluster was impregnated on the metal oxide support from hexane or tetrahydrofuran (THF) solution under N_2. After removal of the solvent the impregnated catalyst was tested for the cycloaddition reaction. This catalyst was mildly activated under flowing O_2 at 25 °C for 10 h to give the mildly oxidised catalyst. The catalyst was also treated by further oxidation at 150 °C for 2 h and subsequently reduced under H_2 with programmed heating from 25 to 400 °C for 10 h.

Oligomerization of propyne in the presence of CO_2 [equation (A)] was conducted in a stainless steel reactor under a total pressure of 60 kg cm^{-2}. The products were 4,6-dimethyl-2-pyrone (**1**), 1,3,5- (**2**), and 1,2,4-trimethyl benzene (**3**), and other oligomers which were analysed by FID GC (Shimadzu 14A) using a silicone OV-101 capillary column at 50—90 °C. Formation of 4,6-dimethyl-2-pyrone was confirmed by comparing the IR spectra of the product sample with those of an authentic sample[8] exhibiting characteristic carbonyl absorptions at 1706 and 1725 cm^{-1}, GC retention times (23.16 min compared to 23.14 min for authentic sample), and the mass spectrum (m/z 124, M^+). The pyrone (**1**) was formed only in the presence of CO_2, whereas (**2**), (**3**), and other oligomers were produced in a N_2 atmosphere under similar reaction conditions.

The activities for pyrone and propyne cyclotrimer formation on various catalysts are shown in Table 1. From Table 1 it is clear that mildly oxidised Rh_4/SiO_2 gives pyrone (**1**) as a cycloaddition product whereas the reduced form of the catalyst is inactive. To study the influence of supports,

Table 1. Oligomerization and cycloaddition of CO_2 to propyne on supported Rh_4 and Fe_2Rh_4 carbonyl cluster-derived catalysts.[a]

Precursor	Support	Pretreatment[e]	T.O.F. of Propyne ($\times 10^{-4}$) to (1)	(2)	(3)	(3)/(2) (mole/mole)
$Rh_4(CO)_{12}$	SiO_2	M.Ox	4.7 (1)	104.4 (29)	249 (70)	2.4
$Rh_4(CO)_{12}$	SiO_2	Red	—	13.9 (34)	26.8 (66)	1.9
$Rh_4(CO)_{12}$	TiO_2	M.Ox	11.4 (6)	59.3 (24)	170 (70)	2.9
$Rh_4(CO)_{12}$	ZrO_2	M.Ox	16.2 (3)	127 (27)	339 (70)	2.6
$Rh_4(CO)_{12}$	γ-Al_2O_3	M.Ox	35 (4)	251 (28)	600 (68)	2.4
$Rh_4(CO)_{12}$	MgO	M.Ox	traces	20.9 (29)	52 (71)	2.5
$Rh_4(CO)_{12}$[b]	MgO	M.Ox	4.7 (1)	173 (31)	377 (68)	2.9
$Rh_4(CO)_{12}$	SiO_2–Al_2O_3	M.Ox	—	333 (25)	979 (75)	2.9
$Rh_4(CO)_{12}$	SiO_2–MgO	M.Ox	—	152 (20)	594 (80)	2.9
$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$[c]	SiO_2	M.Ox	99.8 (8)	299 (22)	955 (70)	3.2
$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$[d]	SiO_2	Imp	19.6 (3)	219 (23)	693 (74)	3.2
$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$[d]	SiO_2	M.Ox	29.2 (5)	245 (30)	537 (65)	2.2
$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$[d]	SiO_2	Red	—	24 (31)	54.1 (69)	2.2

[a] *Conditions*: Rh loading = 2 wt%, propyne = 0.0132 mole, Rh:propyne(mole/mole) = 1:135, propyne:CO_2 = 1:8, total pressure = 60 kg cm^{-2} (27 °C), 130 °C, 10 h. The values in parentheses are mole% selectivities [*e.g.*, (**1**) × 100/(**1**) + (**2**) + (**3**)]. [b] 190 °C. [c] Total metal loading = 4 wt% (Rh = 3.15 wt%), propyne: CO_2 = 1:10, 120 °C, 16 h, Rh:propyne = 1:200. [d] Total metal loading = 2.53 wt% (Rh = 2 wt%). [e] M.Ox = mildly oxidised, Red = reduced, Imp = impregnated.

catalysts were prepared by impregnating $Rh_4(CO)_{12}$ on different metal oxides. It was found that on a neutral SiO_2 support the selectivity to pyrone is minimum while a basic support, MgO, at the same reaction temperature suppresses the conversion possibly due to the use of CO_2 in forming CO_3^{2-} on the support. When the reaction temperature is increased to 190 °C the turn over frequency (T.O.F.) of products on $Rh_4(CO)_{12}$/MgO are improved to give the same selectivity as found with the SiO_2 support. It is of interest to find that TiO_2, ZrO_2, and γ-Al_2O_3, which exhibit acid–base character, promote pyrone formation. With these supports the T.O.F.s of pyrone are in the decreasing order γ-Al_2O_3 > ZrO_2 > TiO_2. The basic surface hydroxy groups on these supports react with $Rh_4(CO)_{12}$ to give $Rh_6(CO)_{16}$[9] and $Rh^I(CO)_2$ species bound to the surface of oxides. Rh_4 impregnated on strongly acidic oxide supports such as SiO_2–Al_2O_3 and SiO_2–MgO provides cyclotrimers preferentially, implying that rhodium metal ions on acidic supports are highly active towards oligomerization but not suitable for pyrone formation.

The bimetallic carbonyl cluster $[NMe_3(PhCH_2)]_2$ $[Fe_2Rh_4(CO)_{16}]$ impregnated on SiO_2 is used to investigate the influence of the Fe ion as a promoter. Using this catalyst, after mild oxidation, the T.O.F. and selectivity to pyrone improved substantially compared to the Rh_4 cluster-derived catalyst. However, the reduced catalyst lost practically all its catalytic activity. The mildly oxidised Fe_3 cluster-derived catalyst has essentially no activity for the reaction. These results suggest that the Fe in the Fe_2Rh_4 cluster-derived catalyst promotes the stabilization of partially oxidised Rh (probably Rh^+) through a Rh–Fe–O bond as reported previously[10,11] and so enhances the trimerization and pyrone formation.

In conclusion, the supported Rh_4 and Fe_2Rh_4 carbonyl cluster-derived catalysts are active towards the cycloaddition of CO_2 to propyne to give 4,6-dimethyl-2-pyrone. We suggest that pyrone is produced on a cationic rhodium metal centre bound to a basic site (O^{2-} or OH^-) on the oxide support. The role of Fe in Rh–Fe bimetallic cluster-derived catalyst may be associated with the stabilization of cationic Rh and providing suitable basic O^{2-} sites to promote the cycloaddition of CO_2.

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