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Preliminary communication

OLEFIN HYDROGENATION BY CARBON MONOXIDE AND WATER USING A PLATINUM CHLORIDE—TIN CHLORIDE CATALYST SYSTEM

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Summary

The water gas shift catalyst system composed of K_2PtCl_4 and $SnCl_4 \cdot 5H_2O$ in $HCl/HOAc/H_2O$ under 300 Torr of CO and 180 Torr of ethylene or propylene hydrogenates the olefin when heated at 88°C. The reaction with ethylene proceeds cleanly according to the equation $C_2H_4 + CO + H_2O \rightarrow C_2H_6 + CO_2$ yielding 31 turnovers per Pt for a 24 h reaction time; the reaction with propylene is less clean, showing concurrent H_2 production from the shift reaction and isopropyl chloride formation from direct reaction of C_3H_6 with the HCl-containing medium. No evidence for significant hydroformylation is obtained. For the case of ethylene, no water gas shift catalysis is observed as long as olefin is present, and if H_2 is added to the reactant gases, it is not consumed in the course of ethane formation. Hydrogenation is thus thought to proceed via a metal hydride formed from CO oxidation, its reaction with olefin and protonation.

Homogeneous catalysis of the water gas shift reaction (eq. 1) [1—5] has rekindled interest in the use of CO + H_2O to replace hydrogen in reactions such

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (1)$$

as hydroformylation and in the reducing ability of CO + H_2O for reaction with oxidized organic substrates. Previously, we reported [2b] a highly active water gas shift catalyst system based on platinum chloride—tin chloride in strong acid media. In the present paper, we describe the reaction chemistry that occurs when ethylene and propylene are added to the system as potential substrates. No hydroformylation is observed, but hydrogenation is. An earlier study by Kitamura et al. also reports hydrogenation using CO + H_2O, but the substrates used were activated olefins, and in particular, α,β-unsaturated carbonyls and nitriles [6].

The catalyst preparation employed in this study contains 0.10 g K_2PtCl_4 (0.23 mmol) and 1.25 g $SnCl_4 \cdot 5H_2O$ (3.6 mmol) in 10 ml H_2O, 10 ml concen-

TABLE 1[a]

Olefin	P_{CO}^{init}	P_{olefin}^{init}	Δn (mmol)					Turnovers per Pt
			CO	olefin	CO_2	alkane	H_2	
ethylene	286	173	7.7	7.4	7.7	7.3	0.3	31.7
propylene	319	185	7.5	7.8	6.9	2.9	3.4	12.7

[a] Pressures in Torr were determined at 22°C. The experiments were performed at 88°C for 24 h periods using catalyst and conditions given in the text. Turnovers are based on alkane produced P_X^{init} is the initial partial pressure of X. The columns under Δn show the change in mmol of reactants and products during the course of the reaction.

trated HCl and 40 ml acetic acid. When this preparation is placed under 300 Torr of CO and 180 Torr ethylene in a 1.16 l vessel, and heated with stirring at 88° C, hydrogenation of ethylene occurs. Gas chromatographic analysis after a reaction time of 24 h (see Table 1) reveals that 31.7 turnovers of ethane per Pt are obtained, and that C_2H_6 and CO_2 are produced and CO is consumed in a 1/1/1 stoichiometry corresponding to the occurrence of eq. 2. The GC analysis is performed on a Poropak Q column with CH_4 added to the reactant gases as an internal calibrant. Deliberate omission of either tin chloride or acetic acid from the catalyst preparation results in no ethane production and the formation of a precipitate, while omission of strong acid greatly decreases the catalytic activity of the system, yielding only small amounts of ethane. No catalysis is also observed if chloride is omitted from the catalyst preparation.

$$C_2H_4 + CO + H_2O \rightarrow C_2H_6 + CO_2 \qquad (2)$$

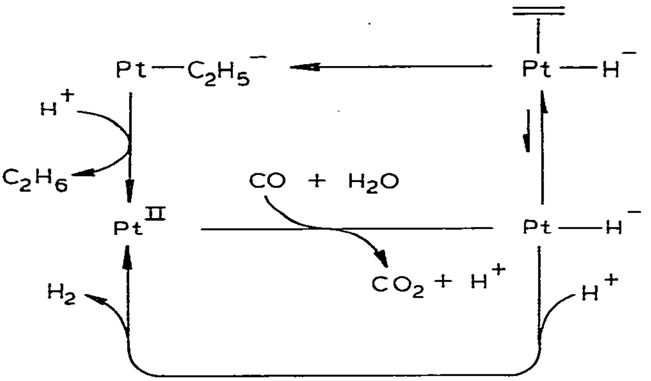
When hydrogen is added to the reactant gas mixture of CO + ethylene, olefin hydrogenation occurs with no decrease of H_2 present, as determined by GC analysis, and at the same rate as in the absence of H_2. While the catalyst system is an efficient water gas shift catalysis under CO alone [2b], when ethylene is present, only ethylene hydrogenation is observed as determined by CO and C_2H_4 consumption, CO_2 and C_2H_6 production, and the absence of any product H_2. After all ethylene is consumed, however, the system reverts to water gas shift catalysis. These observations strongly suggest that in this system hydrogenation does not proceed from H_2 formed separately by the shift reaction 1, and that hydrogenation is a very efficient competitive reaction to catalysis of reaction 1. The present system differs from the Pt—Sn catalyst system reported previously by Cramer [7] which becomes inactive for ethylene hydrogenation when CO is present with the reactant gases.

The hydrogenation of propylene to propane is also promoted by the present catalyst system under the conditions given above, but an analysis of reactants (see Table 1) shows that the system is less selective than when ethylene is the substrate. Both propane and H_2 are formed, presumably by reactions 3 and 1, and their combined total is nearly equal to the amount of CO_2 produced in the 24 h reaction period corresponding to 20 turnovers per Pt. Thus there is an approximate balance between reduced and oxidized products. The fact that sig-

$$C_3H_6 + CO + H_2O \rightarrow C_3H_8 + CO_2 \qquad (3)$$

nificantly less propane was produced than propylene consumed led us to analyze the reaction solution by GLC methods. We find evidence for isopropyl chloride formation*. While a mass balance for propylene and its products has not been achieved in this system, we believe that the major competing reaction for propylene in addition to catalyzed hydrogenation is simply electrophilic addition to the olefin of HCl which is part of the catalyst medium. Studies to minimize this reaction pathway are in progress, as are extensions to other substrates.

The results obtained with ethylene as substrate offer insight into the mechanism of hydrogenation catalysis. Since reaction 2 does not occur via the consumption of prior formed H_2 or added H_2, the hydrogenation probably occurs via the reaction of ethylene with a platinum hydride species formed in the water gas shift cycle followed by protonation. The fact that the rates of catalysis of reactions 2 and 1 in the presence and absence of C_2H_4, respectively, are comparable, but that ethylene inhibits water gas shift catalysis, suggests that the Pt—H species which promotes formation of H_2 in reaction 1 reacts preferentially with ethylene to enter the hydrogenation cycle, as shown in eq. 4. Because of the similarity of the rates for 1 and 2 at 88° C, the rate determining steps for the two catalytic processes must have similar kinetic barriers. That the catalyst solution is light yellow when olefin is present and orange when it is absent indicates that different species predominate in solution for the catalysis of reactions 1 and 2, and this suggests that the RDS is in the reduction part of the catalysis, and not in the common oxidation of CO to CO_2.



(4)

In summary, the Pt—Sn catalyst preparation described here has been shown to use CO + H_2O to hydrogenate the simplest olefins; the effectiveness of this system to use CO + H_2O to reduce other organic substrates is being examined, as is the mechanism of the catalysis.

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*The volatile components of the solution were separated from the non-volatiles by a bulb-to-bulb vacuum transfer. A $AgNO_3$/ethylene glycol column was used to detect isopropyl chloride.

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