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HYDROGENATION WITH IONICALLY HETEROGENEIZED PENTACYANO COBALTATE

A. M. Rosan,* R. K. Crissey and I. L. Mador

Allied Corporation
Corporate Research and Development
Morristown, New Jersey 07960

Abstract: Hydridopentacyano cobaltate ionically anchored to an anionic ion exchange resin provides a convenient and stable hydrogenation catalyst.

A significant advance in homogeneous catalysis comprises the anchoring of soluble complexes to polymer ligands, affording ease in product separation, catalyst recovery and recycle.[1] Despite the utility of numerous ionic catalysts and the development of ion exchange technology, limited attention has been accorded the use of such hybrid catalysts.[2]

We report that binding of hydridopentacyano cobaltate $HCo(CN)_5^{3-}$ to various anion exchange resins provides a stable supported catalyst useful in three-phase hydrogenation reactions.

Preformed hydridopentacyano cobaltate (0.2 M) is readily exchanged onto 20-50 mesh cationic strong base resins of the quarternary amine type (e.g., BIO-RAD AG-1 x8 (PS)-$PhCH_2NMe_3^{\oplus}$ $X^{\ominus}$ or BIOREX-9 (PS)-$MePyrMe^{\oplus}$ $X^{\ominus}$ where $X^{\ominus}$ = $Cl^{\ominus}$, $OH^{\ominus}$)[3] or conveniently prepared in situ via cyanation of 1/5 molar equivalent cobaltous chloride with AMBERLYST A-$26^{\oplus}$ $CN^{\ominus}$ [4] or AG-$1^{\oplus}$ $CN^{\ominus}$ [5] under hydrogen. The bound complex displays characteristic IR absorptions assigned to ν_{CN} at 2086 cm^{-1} and ν_{Co-H} at 1850 cm^{-1}.[6] SEM micrographs reveal excellent penetration and uniform distribution of cobalt within the beads.

These polymers efficiently catalyze the partial hydrogenation of dienes with typical results shown in Table 1. Thus hydrogenation of butadiene proceeds readily at room temperature with rates comparable to soluble, aqueous $HCo(CN)_5^{3\ominus}$.[7] We note parenthetically that the insoluble air stable alkaline earth dimer, $Ba_3[Co(CN)_5]_2$,[8] is a convenient precursor of an active soluble hydrido complex. As demonstrated for catalysts 1, 3, and 4, high activity is maintained on recycle. Furthermore, minimal cobalt loss was experienced and control experiments confirmed the complete inactivity of any soluble component. In the range of 5-30 wt % catalyst suspended in water, the hydrogenation rate was proportional to the catalyst charge demonstrating the absence of diffusional constraints. The utility of these materials was further shown by the long term activity of catalyst 1 in a continuous atmospheric pressure flow system (H_2/C_4H_6 = 3, 12 cc/min, contact time 1 min, 25°C). In the presence of co-feed water steady state conversions > 5% were realized over many hours with trans/cis/1-butene (t/c/1) = 30.5:1.8:1. Under these conditions water is a necessary ingredient as observed in other systems.[9,10] The relative hydrogenation rates in a batch reactor with catalyst 2 are 1:0.8:0.17:0.10:0 in H_2O, 80% aq THF, 50% aq MeOH, MeOH and THF respectively, demonstrating the limited tolerance for co-solvents.

Interestingly, the selectivity displayed by catalysts 1-4 increases with conversion. In the best cases examined, catalysts 1 and 4, at 99-100% conversion the product distribution (t/c/1) was 88:4.5:7 and 91:3:6, respectively. Thus these catalysts show a greater selectivity for internal olefin formation producing less terminal product than aqueous $HCo(CN)_5^{3-}$. In contrast to the latter, there is no dependence of selectivity on solvent or CN/Co ratio although activity declines at CN/Co > 5.

These observations are consistent with a catalyst structure in which the stoichiometric requirement for three cationic binding sites per cobalt strongly influences the relative stabilities of σ and π intermediates.

The high cobalt/sodium ratios characteristic of the hybrid catalysts 1 and 2 indicate that the anionic cobaltate is strongly bound to the polymer. In this case, an additional advantage accrues from the nearly complete anion exchange in that aqueous suspensions of, for example, catalyst 2 are practically neutral. This allows for hydrogenation of base sensitive substrates permitting selective conversion of acrolein to propionaldehyde.

TABLE 1

BUTADIENE HYDROGENATION WITH BOUND PENTACYANO COBALTATE

Catalyst	% Co	Hydrogenation Rate[a]	Solvent	C[b]	Products			Ref.
					t	c	l	
1. BIOREX-9 $HCo(CN)_5$[d,e,g]	6.7	19	H_2O	100	88	4.5	7	This work
		14[f,h]	H_2O	66	90	3	7	This work
2. BIO-RAD AG-1(x8) $HCo(CN)_5$[d]	3.7-4.8	20	H_2O	25	90	5	5	This work
		16, 8[f]	80% aq THF	100	91	3.5	5	This work
		3.4	50% aq MeOH	50	94	2	4	This work
3. BIO-RAD AG-1(x8) CN+1/5 $CoCl_2$[c,e]	2.2	19, 13[f]	H_2O	91	77	12	11	This work
4. AMBERLYST A-26 CN+1/5 $CoCl_2$[c]	2.2-3.2	22, 23[f]	H_2O	100	91	3	6	This work
5. $Ba_3[Co(CN)_5]_2$		15	H_2O	25	83	3.5	13	This work
6. $HCo(CN)_5{}^{3-}$		6[i]	H_2O	N.D.	4	1	95	10
		22	H_2O	100	78	2	20	11
		N.D.[j]	H_2O	N.D.	86	1	13	12
		N.D.	H_2O	100	85	2.5	12.5	13
		N.D.	H_2O	N.D.	14	2	84	14
		N.D.	glycerin-MeOH	N.D.	84	6	10	15
		17[k]	H_2O	N.D.		N.D.		16

[a] $H_2/C_4H_6 = 3$, 70-75 psig, 25°C, 800 rpm, rate expressed as moles consumed/mole Co-min x 10^{-3}.

[b] Conversion

[c] Catalyst prepared in situ.

[d] Via exchange of OH^- form.

[e] The homogeneous component containing < 5% leached cobalt was inactive.

[f] Recycle activity

[g] 0.19% Na

[h] recovered catalyst contained 6.2% Co, 0.14% Na.

[i] CN/Co = 6

[j] CN/Co = 4.5

[k] Substrate is 1,3-cyclohexadiene

N.D. = Not determined

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