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AMINATED POLYSTYRENE-BOUND Rh CLUSTER CATALYSTS FOR THE WATER GAS SHIFT REACTION

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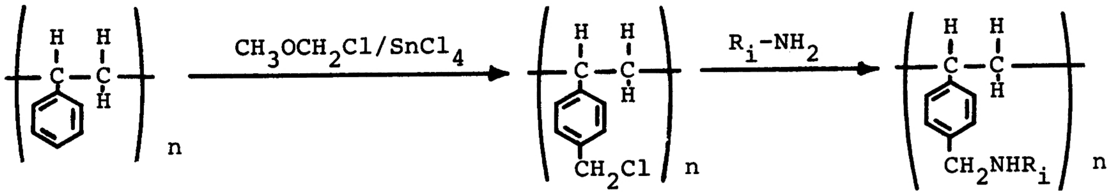
Various aminated polystyrenes are synthesized by treatment of chloromethylated polystyrene with amines. The aminated polymers are examined as an insoluble support for $Rh_6(CO)_{16}$ in the water gas shift reaction (WGSR). Diethylenetriamino polymer is the most effective support for the WGSR. This heterogenization does not lower the WGSR activity in homogeneous systems.

Recently we have studied the WGSR and its application to organic reactions using $Rh_6(CO)_{16}$-amine systems (e.g., reduction of nitro, carbonyl, and olefinic functions and carbonylation of olefins).[1)] The $Rh_6(CO)_{16}$-ethylenediamine system effectively generates hydrogen under mild WGSR conditions and the hydrogen shows different reactivity for above reactions from that in the direct used molecular hydrogen. Polymer materials are extensively used as aids in effecting chemical transformation and product isolation.[2)] We attempted to heterogenize rhodium-amine systems using aminated polymers which are synthesized from treatment of chloromethylated polystyrene with various kinds of amines. The polymer-bound Rh complexes are effective catalysts for the WGSR under atmospheric pressure of CO. A polymer containing diethylenetriamino moiety is found to be the most effective aminated polystyrene; increasing the substituents on nitrogen in ethylenediamine unit decreases the WGSR activity. The $Rh_6(CO)_{16}$-diethylenetriamino polymer system is much more active catalyst for the WGSR than the Amberlyst A-21 which has been already reported by Pittman et al.[3)]

Synthesis of aminated polystyrenes is as follows. Chloromethylated polystyrene without cross-linking was prepared in the same manner as a previous paper.[4)] Anal: C, 70.91; H, 5.98; Cl, 24.24%. Chloromethylated polystyrene was aminated by the method of Pepper et al.[5)] Diethylenetriamine is typical. To a mixture containing 2.5 g (17 mg-atom of Cl) of chloromethylated polystyrene and 30 ml of dioxane with stirring under a nitrogen atmosphere at room temperature was added 88.1 g (0.85 mol) of diethylenetriamine. After 3 days, pale yellow polymer was recovered by centrifugation, washed with KOH, methanol, and ether. The solid was dried for 24 h at 110 °C/5 mmHg to give 2.7 g of diethylenetriamino polymer. Anal: C, 70.42; H, 9.21; N, 16.64; Cl, 0%. Amberlyst A-21 and poly-4-vinylpyridines are commercially available. The apparatus for the WGSR was similar to that in the case of a previous WGSR.[1a)] The rhodium compound and aminated polymer were placed in the vessel, the reaction system (250 ml) was evacuated and flushed three times with CO and then charged to an initial CO pressure of 700 mmHg. To the vessel were successively added 2-ethoxyethanol and H_2O. The mixture was heated with stirring to 80 °C. Gas phase was analyzed periodically by gas chromatography.



	$R_iNH\text{-}$	N% (Calcd)
R_1	$NH_2\text{-}CH_2\text{-}CH_2\text{-}$	14.21(15.90)
R_2	$NH_2\text{-}\overset{CH_3}{\overset{\vert}{C}}H\text{-}CH_2\text{-}$	13.49(14.73)
R_3	$CH_3\text{-}\overset{CH_3}{\overset{\vert}{N}}\text{-}CH_2\text{-}CH_2\text{-}$	10.52(13.73)
R_4	$NH_2(CH_2)_2NH(CH_2)_2\text{-}$	16.64(19.17)
R_5	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2\text{-}$	17.35(21.27)

The WGSR using various kinds of aminated polystyrenes and poly-4-vinylpyridines in the presence of $Rh_6(CO)_{16}$ catalyst is shown in Table 1. Use of diethylenetriamino polymer gives the highest activity for WGSR. In a series of ethylenediamino polymers, the activity decreases as following order: propylenediamino > ethylenediamino > N,N-dimethylethylenediamino polymer. The similar effect of substituents can be observed in homogeneous systems.1a) In the case of diethylenetriamino polymer, ethylenediamino moiety is situated apart from the polymer backbone. So, the diamino moiety might easily coordinate to rhodium metal to facilitate hydrogen generation, when compared to that on other ethylenediamino polymers. The low activity in the case of triethylenetetramino polymer may be caused by cross-linking of the tetramine to other chloromethyl moiety. It seems that heterogenization of ethylenediamine using polystyrene does not cause largely lowering the WGSR activity in homogeneous system (Runs 1 and 6). Use of poly-4-vinylpyridines gave moderate activity. In olefin hydrogenation using phosphinated polystyrene Ti and Rh complexes, cross-linking of polymers is preferable because of site isolation of metal active species.6) But in this WGSR, cross-linking does not lead to a good result. Pittman et al. has adopted Amberlyst A-21 as a polymer support in the WGSR and nitrobenzene reduction.3) Our prepared diethylenetriamino polymer is much more efficient for the WGSR than the Amberlyst A-21 under the present conditions.

In effect of solvent, 2-ethoxyethanol and acetonitrile are the best. Sulfolane, DMF, and nitromethane are poor solvents. $Rh_2(CO)_4Cl_2$ and $Rh_6(CO)_{16}$ complexes have the high catalytic activity; the activity of rhodium compounds decreases as following order; $Rh_2(CO)_4Cl_2$(T.N. = 6.5) > $Rh_6(CO)_{16}$(5.2) > $Rh_4(CO)_{12}$(3.5) > $RhCl(PPh_3)_3$(1.5).

In the case of $Rh_6(CO)_{16}$-diethylenetriamino polymer system, a recovered polymer by filtration was greenish black powder. The polymeric catalyst decomposed slowly on exposure to the atmosphere to pale yellow complex which lost the catalytic activity. The IR spectrum of the recovered polymer gave two strong characteristic absorption bands (1960 and 1805 cm^{-1}) as shown in Fig.1.7) The present complex appears to exist in a cluster form, but the detailed structure is not clear yet.

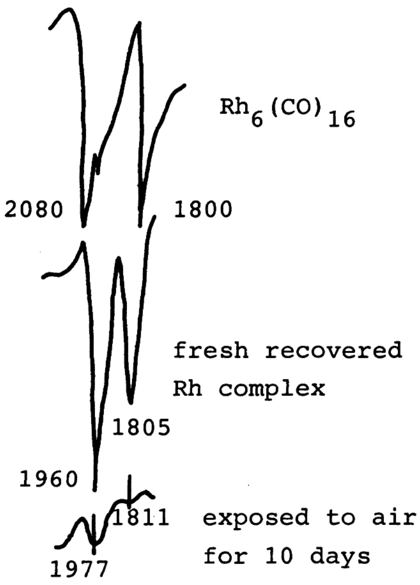
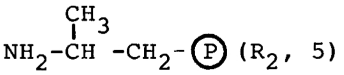
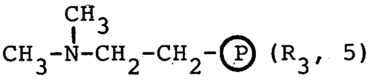


Fig. 1. IR spectra of Rh complexes.

Table 1. The WGSR Using $Rh_6(CO)_{16}$- Amine and Pyridine Polymer Systems[a)]

Run	Amine and pyridine polymer (mg-atom of N)	Turnover number (T.N.)[b)]
1	$NH_2-CH_2-CH_2-$Ⓟ (R_1, 5)	1.8
2	 $NH_2-\overset{CH_3}{CH}-CH_2-$Ⓟ ($R_2$, 5)	2.5
3	 $CH_3-\overset{CH_3}{N}-CH_2-CH_2-$Ⓟ ($R_3$, 5)	0.6
4	$NH_2(CH_2)_2NH(CH_2)_2-$Ⓟ (R_4, 5)	5.2
5	$NH_2-(CH_2)_2NH(CH_2)_2NH(CH_2)_2-$Ⓟ ($R_5$, 5)	0.8
6[c)]	$NH_2-CH_2-CH_2-NH_2$ (5)	2.3
7	Poly-4-vinylpyridine (0% cross-linked, 5)	0.7
8	Poly-4-vinylpyridine (0% cross-linked, 10)	2.7
9	Poly-4-vinylpyridine (2% cross-linked, 10)	1.4
10	Poly-4-vinylpyridine (7.8% cross-linked, 10)	1.2
11	Poly-4-vinylpyridine (0% cross-linked, 0.1)	0.5
12	Amberlyst A-21 (0.1)	0.1

a) $Rh_6(CO)_{16}$ 0.05 mmol, H_2O 0.72 ml, solvent 7 ml, P_{CO} 700 mmHg, 100 °C, 24 h.
b) T.N. = mol of H_2/g-atom of Rh, 24 h.
c) Diamine monomer was used.

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