Hydrogenation of Olefins by Supported Transition Metal Complexes

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Summary The hydrogenation of cyclohexene with halogeno-transition metal complexes supported on phosphine-modified silica carriers has been studied; these complexes are 2 to 4 orders of magnitude more active than their homogeneous counterparts.

TRANSITION metal complexes supported on modified silica surfaces have been used as hydrogenation catalysts.[1–3] Phosphine complexes of rhodium, and to a lesser extent of iridium,[2] supported on phosphine-modified silicas have been studied in preference to other metal complexes[1,4,5]. The aim of the present work is to compare the individual hydrogenation activities of silica-supported halogenophosphine complexes of cobalt, nickel, rhodium, and palladium and to compare them with those of their homogeneous counterparts.

Table. Specific activities of homogeneous and supported phosphine-halogeno complexes in the hydrogenation of cyclohexene in THF (r_0 given in mol cyclohexene converted per g atom of metal per second).

Homogeneous catalysts	25 °C, 1 bar $10^2 \times r_0$	50 °C, 100 bar $10^2 \times r_0$	Supported catalysts	25 °C, 1 bar $10^2 \times r_0$	50 °C, 100 bar $10^2 \times r_0$
$(PPh_3)_3RhCl$	12·01	—	—	—	—
$(PPh_3)_3RhHCl_2$	0·34	—	—	—	—
$(PPh_3)_3RhH_2Cl$	9·78	—	—	—	—
$(PPh_3)_3RhCl_3$	Not detectable	—	—	—	—
$(PPh_3)_3RhCl_3$[a]	0·07	—	SIL—$RhCl_3$[a]	19·72	4568·8
$(PPh_3)_2CoCl_2$	Not detectable	0·39	SIL—$CoCl_2$	0·87[b]	200·7
$(PPh_3)_2NiCl_2$	Not detectable	0·02	SIL—$NiCl_2$	0·72	165·5
$(PPh_3)_2PdCl_2$	0·04	10·11	SIL—$PdCl_2$	4·98	1146·1[c]
$(PPh_3)_2NiBr_2$	—	0·12	SIL—$NiBr_2$	5·88[b]	1352·4

[a] Activated in H_2 at 50 °C and 100 bar. [b] Recalculated from high-pressure data. [c] Recalculated from low-pressure data.

Aerosil 360 (Degussa) was treated at 400 °C in O_2 and then $Ph_2PCH_2CH_2CH_2Si(OMe)_3$ in refluxing benzene–dioxan to yield the modified silica surface. The metal complexes were then produced by reaction with either tetrahydrofuran (THF) or methanol solutions of the corresponding metal halides. The catalysts were dried under reduced pressure before use. The rate of hydrogenation of cyclohexene was measured in THF for both types of catalyst. A cyclohexene concentration of 10 wt% was used and the reaction conditions were either 25 °C, 1 bar H_2 or 50 °C, 100 bar H_2. The reaction was first order in cyclohexene and H_2. Initial rates were determined and the catalyst activity (r_0) was expressed as mol of cyclohexene converted per g atom of metal per second.

The activity data are given in the Table, and the results can be summarized as follows. (i) The data for various homogeneous rhodium complexes are given for comparison. $(PPh_3)_3 Rh^{III}Cl_3$ is inactive at 25 °C and 1 bar H_2, but can be slightly activated by treatment in H_2 at 100 bar. The activity of homogeneous chloro-phosphine complexes of Co and Ni is not detectable at 25 °C and 1 bar, while that of the Pd complex is small. At 50 °C and 100 bar H_2 the activity ratio is 1 : 25 : 500 for homogeneous complexes of Ni, Co, and Pd, respectively.

(ii) The supported rhodium catalyst was prepared from $RhCl_3$. This trivalent rhodium complex was initially inactive, but could be activated by treatment in H_2 at 50 °C and 100 bar. Its activity at 25 °C and 1 bar H_2 was then higher than that of the homogeneous $(PPh_3)_3Rh^ICl$ complex. The valence of the metal atom and the structure of the activated supported catalyst are not yet known. A reduction to zero-valent rhodium metal, however, seems to be unlikely under the experimental conditions used. This follows from the negligible CO uptake of the activated catalyst. Moreover, the turnover numbers (calculated both per Rh atom of the immobilized complex and per surface Rh atom) are lower by 5 orders of magnitude for the activated complex compared with a silica-supported Rh metal catalyst.

(iii) The activity ratio of the supported chloro-phosphine complexes at 50 °C and 100 bar H_2 is 1 : 1·2 : 7 : 28 for the Ni^{II}, Co^{II}, Pd^{II}, and Rh^I complexes, respectively.

(iv) The supported complexes are more active than their homogeneous counterparts by factors of 10^2 to 10^4. This comparison must, however, be considered with caution, since the exact nature of the supported complexes is still unknown and their ligand spheres are certainly not identical with those of the corresponding homogeneous complexes.

(v) The bromo-phosphine complexes of Ni^{II} are more active than the chloro complexes by a factor of 6 and 8 for the homogeneous and supported complexes, respectively. The supported bromo-phosphine nickel complex shows an activity of the same order of magnitude as that of the activated chloro-phosphine rhodium and chloro-phosphine palladium complexes.

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