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COBALT(II) CHLORIDE AND BIS(ACETYLACETONATO)COBALT(II)-SODIUM BIS(2-METHOXYETHOXY)ALUMINUM HYDRIDE (SMAH) SYSTEMS: CONVENIENT CATALYSTS FOR HYDROGENATION

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The titled catalyst systems were found to be active and convenient for the hydrogenation of olefins and to be selective toward 1,3-COD. The catalyst was transformed to some extent during the hydrogenation of 1,3-COD: cyclooctene was formed preferentially and thereafter was hydrogenated to cyclooctane successfully.

Several years after the introduction[1-4] of sodium bis(2-methoxyethoxy)aluminum hydride (SMAH), it was widely used as a reducing agent[5] because of its stability and of its high solubility in most etheric or hydrocarbon solvents. On the other hand, in the previous publications[6-8] a number of hydrogenation catalyst systems which consist of a salt of transition metals plus reducing agent, such as Grignard reagent,[6] lithium aluminum hydride,[7] triethylaluminum,[8] etc., have been reported and discussed. We will now report novel and convenient catalyst systems which consist of $CoCl_2$ or $Co(acac)_2$ in combination with SMAH. The activity, stability, and selectivity toward diene will be described.

When SMAH solution was added to a solution of Co-salt, the solution turned to black immediately and there was an accompanying hydrogen evolution. The black-colored catalyst system appeared homogeneous when the molar ratio of SMAH to Co-salt (R/T ratio) was higher than 1.5.

The activity and stability of the catalyst system were examined by the hydrogenation of styrene, cyclohexene and ethyl acrylate. The rates of hydrogenation at definite R/T ratios are presented in Table I. It can be pointed out that the activity depends on the R/T ratio, that the activity of $Co(acac)_2$-SMAH system seems to relate more loosely to the R/T ratio and that relatively high R/T ratio seems appropriate for the hydrogenation of ethyl acrylate. No appreciable deactivation of the catalyst was observed during these hydrogenations and, then, the hydrogenation could be repeated successfully. Additionally, the stability of the catalyst was so high that it hydrogenated styrene successfully even after it was allowed to stand under argon for more than two months. It is noteworthy, however, that if $Co(acac)_3$ or $Fe(acac)_3$ was used instead of $CoCl_2$ or $Co(acac)_2$, the catalyst system deactivated nearly completely when it was allowed to stand for several hours in the absence of olefins[9] and that the deactivated catalyst could be reactivated easily by adding a small amount (0.2-0.5 moles per g.-atom of Co or Fe) of SMAH solution.

The selectivity of the catalyst system was examined by the hydrogenation of 1,3-cyclooctadiene (1,3-COD). It was found, in the preliminary experiments, that 1,3-COD uptook two moles of hydrogen in the presence of these catalysts, whereas cyclooctene absorbed no appreciable amount of hydrogen under these conditions. At first sight, these observations seemed to indicate that 1,3-COD was predominantly hydrogenated directly to cyclooctane, leaving no appreciable amount of cyclooctene. However, when the catalyst system was used for the hydrogenation of cyclooctene after the system was employed for hydrogenation of 1,3-COD, hydrogenation took place, the rate of which was higher than a half of that for 1,3-COD. It can be pointed out, therefore, that the catalyst system itself is nondiscrete in composition (nonstoichiometric) and that the hydrogenation of 1,3-COD transformed character of the catalyst to some extent, thereby raising activity for the hydrogenation of cyclooctene.

Although there are a number of investigations on hydrogenation of diene or acetylenic compounds as partly summerized by Candlin and Oldham,10) studies on change in character of the catalyst during hydrogenation utilizing relatively nondiscrete catalyst system which we observed are quite few in the literature.11) Then, the hydrogenation of 1,3-COD was studied by monitoring reaction mixture in the course of the hydrogenation. Figure 1 shows results of the hydrogenation of 1,3-COD catalyzed by Co(acac)$_2$-SMAH (R/T=3.0) system: solid lines show fractions of each components and dotted line shows amount of hydrogen uptake. Clearly, 1,3-COD was hydrogenated preferentially to cyclooctene and thereafter the cyclooctene was converted to cyclooctane. When a mixture of 1,3-COD and cyclooctene (1:3) was subjected to hydrogenation, all cyclooctene was hydrogenated successfully after 1,3-COD was consumed. It can be reasonably concluded, therefore, that transformation of the catalyst system occurred during the hydrogenation of 1,3-COD. When CoCl$_2$-SMAH catalyst system was employed, the selectivity decreased to some extent.

Nature of the catalyst system is not understood fully at this time, but there are results which indicate that cobalt hydride (or cobalt-aluminum bridged hydride) species may play an important role for the hydrogenation and that the transformation of the catalyst system during the hydrogenation may be, partly at least, due to diminution of hydrogen content of catalyst system. On the practical stand of view, the Co(acac)$_2$-SMAH catalyst system can be said to have many advantages: (a) it can be easily prepared by mixing Co(acac)$_2$ with SMAH solution, (b) activity and/or selectivity of the catalyst system can be controlled by changing R/T ratio or by pretreatment with suitable compound, and (c) even when the catalyst system deactivates during hydrogenation of a large amount of olefinic compound, it can be easily reactivated by adding a small amount of SMAH solution.

EXPERIMENTAL: SMAH was used as a 0.5 mol./l solution in THF-benzene. Solvent, THF, was distilled from lithium aluminum hydride shortly before use. The preparation of catalyst systems and hydrogenation of olefins were carried out in a magnetically stirred flask at 0°C and under an atmospheric pressure of hydrogen. In most experiments, about 2 millimoles of Co-salt, 60-80 ml. of THF and 1 ml. of olefin were

Table I. Hydrogenations catalyzed by Co(acac)$_2$ and CoCl$_2$-SMAH systems.*

Co(acac)$_2$-SMAH				CoCl$_2$-SMAH			
R/T	ST	EA	CH	R/T	ST	EA	CH
2.44	40	-	2	1.51	53	-	17
2.84	40	33	30	1.98	85	-	24
4.98	53	48	1	5.02	0	33	0
12.93	53	57	7				

* Rates of hydrogenation are represented by ml. H$_2$/min. ST=styrene, EA=ethyl acrylate, CH=cyclohexene.

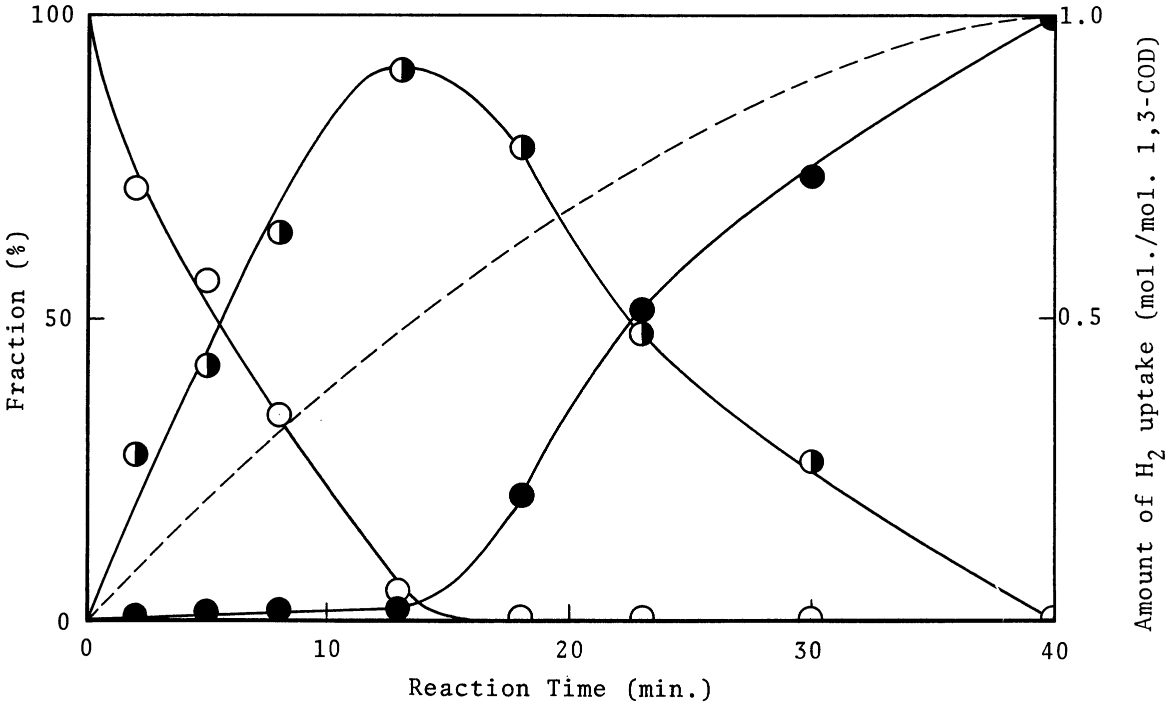

Fig. 1 Time-fraction plots of the hydrogenation of 1,3-COD.

—●—:cyclooctane.
—◐—:cyclooctene.
—○—:1,3-COD.
----:hydrogen uptake.

Co(acac)$_2$: 0.004 mol.
1,3-COD: 5 ml.
THF: 100 ml.

used. The monitored hydrogenation of 1,3-COD was carried out by withdrawing an aliquot (3 ml.) of reaction mixture, which was immediately quenched with dilute hydrochloric acid, extracted with ether and gas chromatographed.

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REFERENCES AND NOTES

1) Ceskoslavenska Akademie Ved., Fr. Pat. 1,546,482; Brit. Pat. 1,189,512.

2) B. Casensky, J. Machacek, and J. Vit, Czech. Pat. 134,720.

3) K. Ichiriki, Yuki Gosei Kagaku Kyokai Shi, 27, 1246 (1969).

4) J. Vit, Org. Chem. Bull., 42, 1 (1970).

5) J. Malek and M. Cerny, Synthesis, 1972, 217. and references cited therein.

6) Y. Takegami, T. Ueno, and K. Kawajiri, Kogyo Kagaku Zasshi, 64, 1068 (1963), Bull. Chem. Soc. Japan, 39, 1 (1966).

7) Y. Takegami and T. Ueno, Kogyo Kagaku Zasshi, 67, 246 (1964); Y. Takegami, T. Ueno, and T. Fujii, Bull. Chem. Soc. Japan, 38, 1279 (1965), Kogyo Kagaku Zasshi, 67, 1009 (1964), ibid., 69, 1467 (1966).

8) Y. Takegami, T. Ueno, and T. Fujii, Bull. Chem. Soc. Japan, 42, 1663 (1969).

9) No such deactivation was observed in the presence of olefin; for example, an $Fe(acac)_3$-SMAH catalyst prepared from 0.002 moles of $Fe(acac)_3$ hydrogenated more than 0.2 moles of styrene over a period of 3.5 hours without any apparent deactivation.

10) J. P. Candlin and A. R. Oldham, Discuss. Faraday Soc., 46, 60 (1968).

11) T. Ueno, Shokubai, 12, 115 (1970).

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