In Situ Conversion of Coal

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Abstract

Muetterties Catalyst (η^3-$C_3H_5Co[P(OCH)_3]_3$) is a very active hydrogenation catalyst for polycyclic aromatics, but fails to catalyze the hydrogenation of coal or asphaltenes.

A number of very active homogeneous hydrogenation catalysts have been developed.[1] These might prove useful in the hydrogenation of coal, coal derivatives, or other heavy ends. A recent paper in this journal reported the failure of several of these catalysts to bring about the hydrogenation of coal.[2] We wish to report that the Muertterties catalyst,[1b,c,d] probably the most active hydrogenation catalyst for benzene yet developed, is not capable of catalyzing the hydrogenation of coal or asphaltenes.

Experimental

All organic compounds are commercially available. Bruceton coal was kindly supplied by PERC. It was ground (ball mill) to a particle size below 300 mesh, dried in nitrogen at 110°C, and stored under dry N_2. Petroleum asphaltenes were kindly supplied by Exxon Research and the coal asphaltene was a gift from Mobil.

Since very dry, pure THF is critical to the preparation of the catalyst, we list here the steps in its preparation. After drying over anh. $MgSO_4$, it was refluxed over $LiAlH_4$ for 48 hours. After distillation into a flask containing sodium metal, it was deoxygenated with dry argon and stored in a dry box.

η^3-$C_3H_5Co[P(OCH_3)_3]_3$

Muetterties procedure[3] was used with a few modifications which are listed below. The hydrido complex, $HCo[P(OCH_3)_3]_4$, was purified using a neutral alumina column (activity IV) before recrystallization from hexane. It was eluted with hexane, and an additional 20% could be obtained by subsequent elution with 20% ether-hexane. The potassium salt $KCo[P(OCH_3)_3]_4$ was prepared in a round bottom flask equipped with a magnetic stirrer and stopcock and the cooled reaction mixture was degassed and warmed under vacuum in this flask. The catalyst η^3-$C_3H_5Co[P(OCH_3)_3]_3$, was not purified further but used in its crude form. The three steps gave the catalyst in 20% overall yield. It discolors slowly and must be stored in a dry box.

Hydrogenation Procedure

All solutions were prepared in a dry box using THF solvent. About 10%(wt) of the catalyst was added to ~2g of compound dissolved in 50 ml of THF. A Parr low pressure hydrogenator was used and reaction mixtures were prepared directly in the 250 ml heavy wall bottle. After flushing thoroughly with H_2, the reaction mixture was shaken under ca 3atm. H_2 pressure at room temperature and the pressure monitered.

Product Analysis

THF was removed on a rotary evaporator under vacuum. The reaction products were collected using preparative gc and identified by mass spectrometry. Only one product was found in each case, and the yield was determined by gas chromatography.

Methylated Asphaltene

A mixture containing 3.5g of asphaltenes (Mobil) in 30 ml of 95% ethanol was heated to boiling. The heat source was then removed. This stirred hot solution was alternatively treated with a solution of sodium hydroxide (2.5g in 2 ml of H_2O) and neat dimethylsulfate (10 ml). The heat evolved during the reaction made the solution boil. After the addition was complete, the reaction mixture was made alkaline by further addition of 0.5g of sodium hydroxide and allowed to reflux for 7 hours. The ethanol was then removed by rotary evaporator under reduced pressure. The residue was washed with 2N HCL solution and vacuum-dried.

Discussion

Muertterties catalyst causes the rapid hydrogenation of polycyclic aromatics as reported[1] (see Table 1). Also as reported, no partially hydrogenated products are formed.[1] Apparently once a molecule begins to react it goes to completion. It is known that the presence of heteroatoms does not effect the catalyst activity.[1b] However, neither coal nor asphaltenes are hydrogenated. It may be that the acidic hydrogen in these destroy the catalyst. To test this we methylated an asphaltene with base and dimethylsulfate and attempted to hydrogenate the methylated asphaltene. Again no reaction was observed. While a fascinating and very reactive catalyst, it is not promising for use with heavy ends.

During the time covered by this report Dr. Chang has spent 100% of his time and Dr. Larsen has spent 15% of his time on this project.

TABLE I. Attempted Catalytic Hydrogenation of Unsaturated Compounds Using the Muetterties' Catalyst

Compound	Solvent	Amount of Catalyst used (mg)	Temp°C	H_2 Pressure psi[a]	Rxn time h	Pressure drop, psi	Product Yield (%)[b]
Naphthalene (3.2g)	THF (50 ml)	250	21.5	45.8	96	4.6	55
Anthracene (1.9g)	THF (50 ml)	200	19	45.7	95	0.9	23
Phenanthrene (1.9g)	THF (50 ml)	400	24	44.7	98	2.0	42
Thiophene (4.9g)	THF (50 ml)	200	31	45.2	42	0	
Phenol (2.4g)	THF (50 ml)	200	21	45.2	72	0	
Pyrene (2.1g)	THF (50 ml)	350	26	45.0	46	0	
Benzofuran (2.2g)	THF (50 ml)	200	23	46.4	91	0	
Coal (Bruceton passed 300 mesh) 9.3g	THF (90 ml)	900	24	25.2	168	0	
Coal Asphaltenes (Mobil) (3.9g)	THF	600	24	44.6	48	0	
Petroleum Asphaltenes (Exxon) (2.6g)	THF (50 ml)	800	19	45.2	71	0	
Methylated Coal Asphaltenes (Mobil, 2.2g)	THF (70 ml)	350	19	45.5	50	0	

[a] The final pressures of hydrogenation were connected for temperature change. [b] The yields were determined by comparison of the amount of hydrogenation substrate in solution before and after hydrogenation using gc.

References

1. See for example (a) James, B. R., "Homogeneous Hydrogenation," Wiley, New York, N. Y., 1973; (b) Muetterties, E. L. and Hirsekorn, F. J., *J. Am. Chem. Soc.*, **96**, 4063 (1973); (c) Hirsekorn, F. J., Rakowski, M. C., and Muetterties, E. L, *ibid.*, **97**, 237 (1975); (d) Muetterties, E. L., Rakowski, M. C., Hirsekorn, F. J., Larson, W. D., Bans, V. J., and Anet, F. A. L., *ibid.*, **97** 1266 (1975);(e) Murugesan, N. and Sarkar, S., *Indian J. Chem.*, **14A**, 107 (1976).

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3. Muetterties, E. L. and Hirsekorn, F. J., *J. Am. Chem. Soc.*, **96**, 7920 (1974).