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Authors

Fish, R.H.
Thormodsen, A.D.
Heinemann, H.

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R.H. Fish, A.D. Thormodsen, and H. Heinemann

November 1983

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A COMPARISON OF POLYMER-SUPPORTED WILKINSON'S CATALYST TO ITS HOMOGENEOUS ANALOGUE IN THE SELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS

Richard H. Fish, Arne D. Thormodsen
and Heinz Heinemann

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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This study was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Science Division, and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division, of the U.S. Department of Energy through the Pittsburgh Energy Technology Center as well as in part by the Electric Power Research Institute under Contract No. DE-AC03-76SF00098.

Abstract

The reduction of polynuclear heteroaromatic compounds of nitrogen and sulfur with 2% cross-linked phosphinated polystyrene-divinylbenzene beads modified with Wilkinson's Catalyst was compared to the homogeneous analogue. The polymer-supported catalyst had initial rates of hydrogenation that were 10 to 20 times faster than the homogeneous equivalent. The mechanism of reduction of the nitrogen heterocyclic ring was provided by substituting deuterium gas for hydrogen. The lack of aromatic hydrogen exchange in the polymer-supported Wilkinson's catalyst is evidence for steric effects being highly important. Regioselectivity for the nitrogen heterocyclic ring in the presence of other model coal liquid constituents verifies the practical nature of anchored catalysts.

A Comparison of Polymer-Supported Wilkinson's Catalyst to its Homogeneous Analogue in the Selective Reduction of Polynuclear Heteroaromatic Compounds

Richard H. Fish*, Arne D. Thormodsen and Heinz Heinemann

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Summary: A comparison between polymer-supported Wilkinson's catalyst, P -Pϕ_2Rh(ϕ_3P)$_2$Cl, and its homogeneous analogue in the selective hydrogenation of polynuclear heteroaromatic compounds provides evidence for differences in initial rates and ability to exchange aromatic hydrogens for deuterium. Cross-linking of the polymer-supported catalyst also affected hydrogenation rates, but diffusion into the polymer bead was not rate limiting. High regioselectivity for reduction of the nitrogen heterocyclic ring was found in the hydrogenation of a model coal liquid with the polymer-supported catalyst.

Recently, we found that a wide variety of transition-metal compounds catalyzed the regiospecific reduction of polynuclear heteroaromatic nitrogen and sulfur compounds.[1-3] These findings may in fact have important effects on the various synthetic fuel processes. Hydrogen gas consumption is known to be an economically limiting factor in the up-grading of synthetic fuels and in the removal of nitrogen and sulfur from these complex matrices. Hydrogen consumption by selective hydrogenation will be lower; furthermore, the reactions described here are carried out at lower temperatures and pressures than are used in conventional industrial processing.

Homogeneous catalysts have their own limitations in that recovery is often difficult or impossible. In addition, thermal stability and solubility may also present problems in practical applications. The use of polymer-supports, such as cross-linked polystyrene-divinylbenzene (PS-DVB), silica and alumina to anchor homogeneous transition-metal catalysts and overcome some of the difficulties mentioned above, has been the subject of intensive research over the last fifteen years.[4a-d]

In this paper, we wish to report on our initial results of a comparison of polymer-supported Wilkinson's catalyst, on 2% cross-linked phosphinated polystyrene-divinylbenzene (PS-DVB), with results obtained with the homogeneous analogue[2] for the selective reduction of polynuclear heteroaromatic nitrogen and sulfur compounds (Chart 1).

Initial and Relative Rates

The initial and relative rates of reduction of the substrates, 1-5, were obtained using a Parr kinetic apparatus[2] and Table 1 indicates the results of this comparison, with substrate to metal ratio, temperature, and partial pressure of hydrogen being equivalent for both forms of Wilkinson's catalyst. The polymer-supported catalysts results in Table 1 were all carried out with the same batch of 2% PS-DVB beads with excellent reproducibility upon repetition of each experiment.

Clearly, several important observations become apparent from the results in Table 1; namely, the initial rates of hydrogenation of nitrogen heterocyclic compounds, 1-4, with polymer-supported Wilkinson's catalyst are 10 to 20 times faster than the homogeneous equivalent. This rate enhancement is extremely relevant for practical applications

and has not been observed with many polymer-supported catalysts in reduction reactions.[4b,5]

Several reasons for the rate enhancement of the polymer-supported over the homogeneous catalyst can be formulated. One important consideration may be found in the fact that substrates 1-4 are themselves suitable ligands and a higher concentration or enrichment of substrate around the polymer-supported metal center, with a concominant loss of triphenylphosphine, may be of consequence in these rate enhancements. Other factors such as steric and electronic effects are also probably involved in these rate enhancements. The relative rate differences between 1-5 for both forms of Wilkinson's catalyst must involve steric effects as accentuated by the 5,6 and 7,8-benzoquinoline (2 and 3) rate ratio, i.e., 2/3 = 6.0 as well as 1/2 and 1/3 with rate ratios of 2 and 13 respectively. It is interesting to note that only in the case of the sulfur heterocyclic compound, 5, is the initial rate larger for the homogeneous catalyst, while overall relative rates are similar for 1-4 within each set of catalyst results.

Selectivity

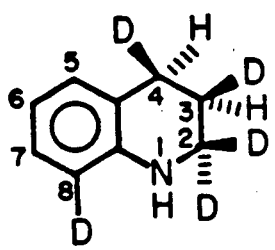
Additionally, the high regioselectivity for the heteroaromatic ring, with both forms of the catalyst, is evident (Table 1). In one case, substrate 4, the polymer-supported catalyst gave only 9,10-dihydroacridine with no 1,2,3,4-tetrahydroacridine apparent. In contrast, with the homogeneous analogue,[2] 4 gave substantial amounts of the outer ring product (~50%) and this difference may result from the more pronounced steric requirements surrounding the active metal sites on the polystyrene-divinylbenzene supported catalyst.[4a-d]

Parameters that Affect Rate

Several other parameters that were critical to study included the effect of cross-linking and diffusion rates of substrate into the PS-DVB beads. In experiments to clarify these points, the 2% cross-linked polystyrene-divinylbenzene beads with Wilkinson's catalyst were compared to the 20% cross-linked beads for reduction of 1 and the initial rate ratio for both (2%/20%) was found to be approximately 3. We also ground the 2% beads and hydrogenated substrate 1 (quinoline) using similar reaction conditions to show that diffusion of substrate into the bead was not rate limiting, i.e., both ground and whole (~30 μ) 2% cross-linked beads gave the same initial rates within experimental error.

Mechanism of Hydrogenation of 1 with Polymer-Supported Wilkinson's Catalyst

The mechanism of reduction of 1 with deuterium gas was recently elucidated with homogeneous Wilkinson's.[2] In that study, we found the following pattern of deuterium incorporation as shown, 6.



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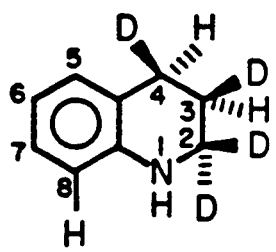

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In contrast, compound 7, shows the deuterium pattern (nmr and ms)[6] obtained with 2% cross-linked PS-DVB Wilkinson's catalyst. The pertinent difference is the lack of aromatic C-H exchange for the polymer-supported catalyst, while stereochemistry at the 3,4-double bond (cis) and reversible dehydrogenation of the reduced carbon-nitrogen bond

(positions 1 and 2) to provide 1.6D at the 2-position, via quinoline-2-d, is similar for both forms of the catalyst. Moreover, reaction of the product, 1,2,3,4-tetrahydroquinoline, with PS-DVB Wilkinson's catalyst under similar deuteration conditions, also shows by nmr and ms analysis no exchange of the aromatic hydrogen at position 8 (6.42 ppm) and is in contrast to the homogeneous catalyst result.[2] Again, steric requirements surrounding the polymer-supported catalyst active metal center may be responsible for the lack of aromatic C-H exchange.[4b]

Reduction of 1 in the Presence of Model Coal Liquid Constituents

Since the compounds shown in the Chart are prevalent in synthetic fuel products, such as coal liquids, we wanted to determine whether the selectivity for the nitrogen heterocyclic ring (with 1 as the example) would prevail in the presence of other coal liquid constituents. The model coal liquid[7], dissolved in benzene and containing (wt%) 30% pyrene, 5% tetralin, 38% methylnaphthalene, 17% m-cresol, 7.5% 1 and 2.5% 2-methylpyridine, was hydrogenated with the 2% PS-DVB Wilkinson's beads (similar conditions as shown in Table 1) to provide 1,2,3,4-tetrahydroquinoline as the only reduction product (initial rate 0.42%/min). Removal of 2-methylpyridine had no effect on the initial rate in contrast to the competitive inhibition on 1 by the pyridine derivative in the homogeneous reaction.[2] Interestingly, reduction of 1 alone, at a similar substrate to metal ratio as in the model coal liquid, provided an initial rate (0.18%/min) that was ~2.2 times slower than the rate of 1 in the presence of the model coal liquid constituents.

This impressive result emphasizes the highly selective reaction taking place in the presence of other functionalities i.e., regiospecific reduction of the nitrogen heterocyclic ring as well as the rate enhancement phenomena, and provides dramatic evidence for the potential usefulness of polymer-supported catalysts in synthetic fuel (hydroprocessing) applications.[8]

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(5) Pittman, C.U. Jr., Smith, R.J. and Hanes, R.M. J. Am. Chem. Soc. 1975, 97, 1742.

(6) The ^{1}H 250 MHz nmr spectrum (benzene-d_6) for 1,2,3,4-tetrahydroquinoline-d_3 had signals at 1.90 (H-3); 2.73 (H-4); 3.24 (H-2); 6.42 (H-8); 6.55 (H-5) and 6.93 (H-1 and H-7) ppm with areas of 1:1:0.4:1:1:2 respectively, and EIMS data provided the m/e 136 ion.

(7) This model coal liquid was suggested by Linda Atherton of the Electric Power Research Institute.

(8) These results were presented at the N.Y. Academy of Sciences Conference on Catalytic Transition Metal Hydrides, New York, NY, November 15-17, 1983; at The 1983 International Conference on Coal Science, Pittsburgh, PA, August 15-19, 1983; at the Eighth Annual EPRI Contractors on Coal Liquefaction, Palo Alto, CA, May 11-13,

1983, and in a poster session at the Fourth International Symposium on the Relations between Homogeneous and Heterogeneous Catalysis, Asilomar, CA, October 2-5, 1983.

Table 1

Comparison of Initial and Relative Rates of Hydrogenation of Substates 1-5 Using Both Polymer-Supported and Homogeneous Wilkinson's Catalysis[a]

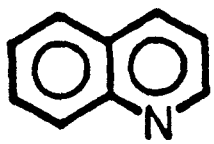
Substrate	Product[b]	Polymer-Supported Rates[c] Initial (%/min)	Relative	Homogeneous Rates Initial (%/min)	Relative	PS/H Rate Ratio
1, Quinoline	1,2,3,4 Tetrahydro-	.29	1	.013	1	22
2,5,6 Benzoquinoline	1,2,3,4 Tetrahydro-	.14	.48	.0065	.5	22
3,7,8 Benzoquinoline	1,2,3,4 Tetrahydro-	.024	.08	.0012	.09	20
4, Acridine	9,10 dihydro-	~.4	~1.4	~.04	~3	10
4, Acridine	1,2,3,4 Tetrahydro-	0	0	.047	3.6	0
5, Benzothiophene	2,3 Dihydro	~.03	~.1	.044	3.4	.7

a) Reaction conditions were as follows: P_{H2}=310 psi, T=85°C, sub./Cat.=91/1, Benzene (20 ml), 1 mmole substrate in each case, with either 10.2 mg of homogeneous $RhCl(PPh_3)_3$ or 52 mg of polymer-supported Wilkinson's catalyst [2% cross-linked, 2.19% Rh, initial P/Rh=2.9 (Strem Chemical Co.), P/Rh after reaction with substrate 1-5 ~3.3] contained in a wire basket attached to the end of the dip-tube of the kinetic apparatus.

b) Analysis by gas chromatography.

c) Plots of % conversion vs. time provided initial (pseudo zero order) rates. Rates are relative to quinoline (1.0). Substrates, 1-5, were reacted with the same beads for all initial rates reported.

Chart 1



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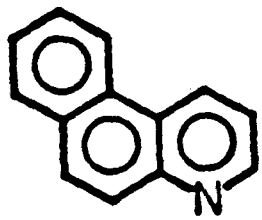

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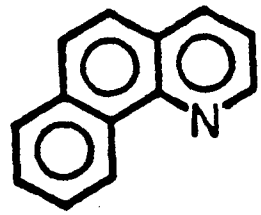

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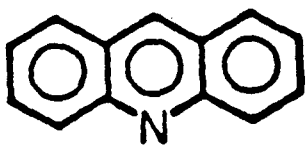

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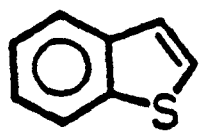

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