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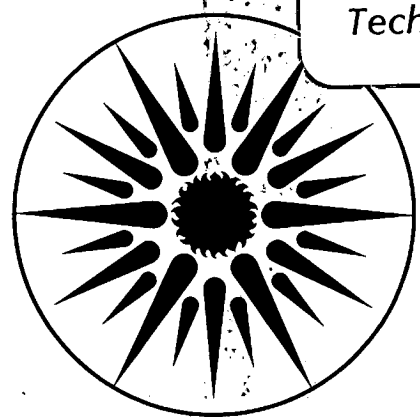
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SELECTIVE CATALYTIC HYDROGENATION OF POLYNUCLEAR
HETEROAROMATIC NITROGEN COMPOUNDS WITH
POLYMER-SUPPORTED TRANSITION-METAL COMPOUNDS

by

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ABSTRACT

The selective catalytic hydrogenation of model coal compounds such as quinoline, 5,6- and 7,8-benzoquinoline, acridine and phenanthridine were studied using transition metal catalysts supported on 2% or 20% cross-linked phosphinated divinylbenzene-polystyrene beads.

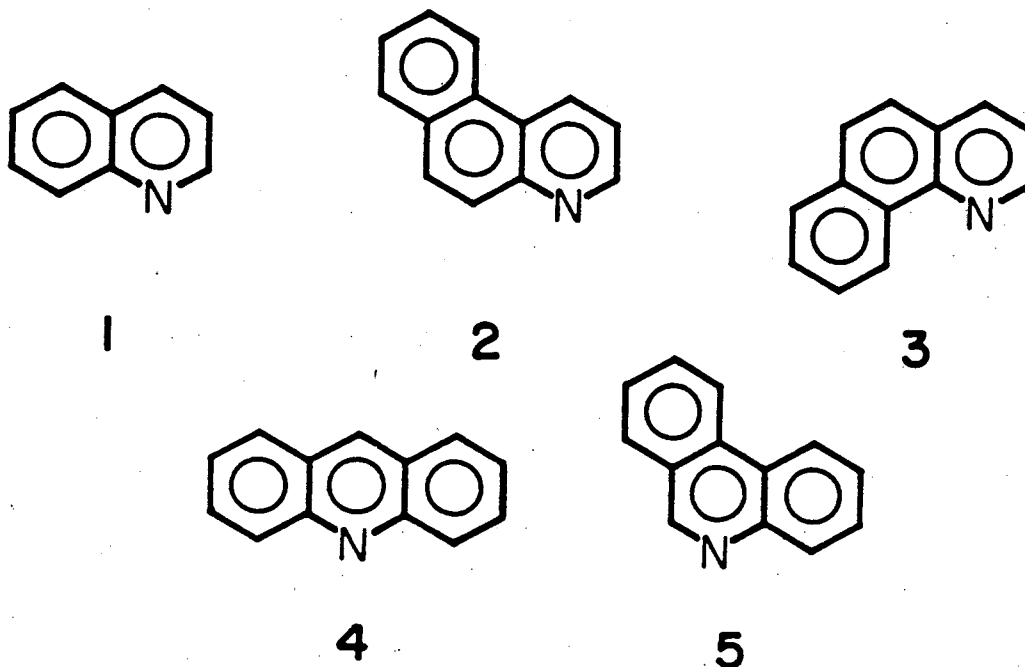
In all cases, only the nitrogen heterocyclic ring in the above-mentioned polynuclear heteroaromatic nitrogen compounds was reduced, while it was found that the 2% cross-linked beads were three times more active per metal atom than their 20% cross-linked analogues and forty times more active than its homogeneous counterpart using quinoline as the model coal compound and polymer-supported Wilkinson's catalyst $[(\phi_3P)_3RhCl]$.

A discussion of these results will be presented along with data to show; clearly, the potential of these polymer-supported catalysts in the selective reduction of polynuclear heteroaromatic nitrogen compounds in the presence of known coal liquid constituents such as pyrene, tetralin, methylnaphthalenes, cresols and 2-methylpyridine.

INTRODUCTION

Recently, we discovered that a wide variety of transition-metal compounds of Mn, Co, Fe, Rh and Ru were highly selective catalysts in the homogeneous hydrogenation of the nitrogen containing ring in polynuclear heteroaromatic nitrogen compounds (1-3). The polynuclear heteroaromatic compounds we studied (1) are known to be present in

coal and its liquid products and encompass such compounds as quinoline, 1; 5,6-benzoquinoline, 2; 7,8-benzoquinoline, 3; acridine, 4; and phenanthridine, 5. (Chart).



Chart

In order to determine whether these catalysts would have practical applications in, for example, the hydroprocessing of coal liquids at mild temperatures and low pressures of hydrogen gas (H_2), we studied several of these catalysts of Ru and Rh that were placed on polymer-supports, i.e., phosphinated divinylbenzene-polystyrene beads (PS-DVB).

These 2% or 20% cross-linked beads of PS-DVB, modified with transition-metal compounds, have many practical advantages over their homogeneous counter-parts. The utility of polymer-supported catalysts has been reviewed (4-6) and we will elaborate on some advantages that they have that can be beneficial to their ultimate use in synthetic fuel applications.

The polymer-supported catalysts can be easily recovered by simple filtration, thus, this trait provides a means of reusing them at substantial economic savings. The inert supports can be easily functionalized and this allows a great variety of metal compounds to be used to modify the surfaces of these supports. The important aspect of selectivity can also be maintained as compared to their homogeneous analogues and is significant to the goals we strived to attain in the present study.

Finally, it should be emphasized that few synthetic fuel applications have been published (7) concerning these polymer-supported catalysts and the results we present in this paper shows definitively the potential they have in many industrial processes concerned with hydroprocessing.

RESULTS AND DISCUSSION

The initial studies with the polymer-supported catalysts were carried out with 20% cross-linked PS-DVB beads modified with Wilkinson's catalyst, $\boxed{P}-\phi_2P-Rh(P\phi_3)_2Cl$, 2.2% Rh loading at 80°C, 350 psi H₂, substrate/cat ratio ~95:1 for 25 hrs in benzene.

The results obtained under the above-mentioned conditions for the model coal compounds, 1-5, were as follows: compound 1 (100%, 1,2,3,4-tetrahydroquinoline); 2 (66%, 1,2,3,4-tetrahydro-5,6-benzoquinoline); 3 (12%, 1,2,3,4-tetrahydro-7,8-benzoquinoline); 4 (97%, 9,10-dihydroacridine) and 5 (100%, 9,10-dihydrophenanthridine). We also studied a polymer-supported ruthenium catalyst on PS-DVB i.e., $\boxed{P}-\phi_2P-Ru_4H_4(CO)_{11}$. This proved to be less active than Wilkinson's catalyst; however, using the 20% cross-linked beads with ~0.8% Ru loading at 150°C, 350 psi H₂ and a substrate/catalyst ratio of ~200:1 a 85% conversion of 1 to 1,2,3,4-tetrahydroquinoline was obtained.

Several important parameters including bead and pore size, concentration of metal compound, degree of cross-linking, and swelling properties all contribute to the diffusion rate of the substrate to the metal center. In this regard, we studied several of these parameters to define more clearly which would affect the reactivity

of the polymer-bonded Wilkinson's catalyst with compounds 1-5.

The 2% cross-linked DS-DVB beads modified with Wilkinson's catalyst were tested on 1 and found to be approximately three times more active than the corresponding 20% cross-linked beads with similar loading of the rhodium complex. More importantly, we also discovered that the 2% cross-linked beads with Wilkinson's catalyst were forty times more active per metal atom than the homogeneous counterpart. These latter results were extremely rewarding and enhance the potential practical application of these polymer-supported catalysts.

In continuing our studies, we decided to determine the relative rates of conversion of 1-5 with the 2% cross-linked polymer-supported Wilkinson's catalyst. Table 1 contains the data we obtained and shows for compounds, 1-4, a relative rate sequence of 4 > 1 > 2 >> 3. The reduction product of 5, 9,10-dihydrophenanthridine, tends to dehydrogenate in the injection port of a gas chromatograph to some extent making any relative rate for 5 difficult to obtain, but it is faster than compound 1 and possibly equal or better in rate to 4.

Table 1

RELATIVE RATES OF HYDROGENATION USING 2% CROSS-LINKED
PS-DVB BEADS MODIFIED WITH WILKINSON'S CATALYST^a

<u>Substrate</u>	<u>Relative Rate</u>	<u>(%/min)</u>
<u>1</u>	1	0.28
<u>2</u>	0.7	0.19
<u>3</u>	0.09	0.024
<u>4</u>	1.4	0.40

- a. 0.52 g of 2% cross-linked beads (2.19% Rh) in a wire basket attached to the dip-tube in a Parr kinetic apparatus at 85°C for 24 hrs with 350 psi H₂ gas. The substrate to catalyst ratio is approximately 100:1.

The hydroprocessing of coal liquids can be more economically viable if the amount of hydrogen gas is reduced and the temperature for reaction was lowered. In order to

test the applicability of our polymer supported 2% cross-linked Wilkinson's catalyst, we studied its reactivity and selectivity with a model coal liquid.

The model coal liquid containing 30% pyrene, 6, 5% tetralin, 7, 38% methylnaphthalene, 8, 17% m-cresol, 9, 7.5% quinoline, 1, and 2.5% 2-methylpyridine, 10, was hydrogenated with the 2% cross-linked beads modified with Wilkinson's catalysts (3% Rh) at 100°C for 5 hr. with 500 psi H₂ to give a 45% conversion of 1 to 1,2,3,4-tetrahydroquinoline. In addition, removal of 10, 2-methylpyridine, increased the yield of 1,2,3,4-tetrahydroquinoline to 67%. Importantly, no other compound in the model coal liquid was hydrogenated.

CONCLUSIONS

We have demonstrated that polymer-supported transition-metal compounds can selectively reduce the nitrogen heterocyclic ring in model coal compounds under mild hydrogenation conditions in the presence of other coal liquid constituents. Since hydrogen gas is the critical component in any economically viable hydroprocessing reaction, the results with these polymer-supported catalysts may lead to future substantial reduction in hydrogen consumption as well as lower overall operating costs. We hope to further our studies into those model coal liquid constituents that inhibit the rate of hydrogenation of polynuclear heteroaromatic nitrogen compounds as well as those that can increase their rates. Finally, these studies, may in fact, initiate ideas concerning the facile removal of nitrogen from the saturated nitrogen ring in these coal liquid constituents under relatively mild reaction conditions.

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