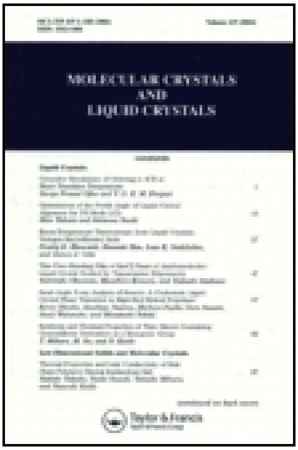

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Catalytic Hydrogenation of Solid Dihydroxybenzenes

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CATALYTIC HYDROGENATION OF SOLID DIHYDROXYBENZENES

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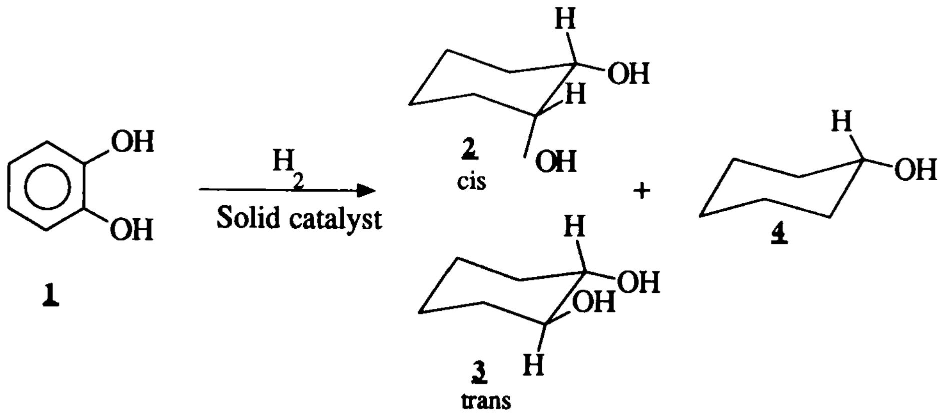
Abstract Solid dihydroxybenzenes are hydrogenated under mild conditions. Reactivity and selectivity depend on catalyst. PtO2 Adams is the best catalyst. Cis and trans-cyclohexanediols are the main products of the solid state reaction.

INTRODUCTION

Previous works in this laboratory on the catalytic hydrogenation of monophenols[1] proved that it is possible to hydrogenate organic solids to a high conversion ratio under mild conditions[2,3]. Dihydroxybenzenes (diphenols) and their hydrogenated derivatives have interesting properties. Catalytic hydrogenations of these diphenols are usually carried out in liquid or vapor phase under drastic conditions[4] (145° C and 100 bars hydrogen pressure). In this work we study the hydrogenation of 1,2-dihydroxybenzene (catechol 1)in the solid state under mild conditions and compare it with reaction in solution.

SOLID STATE REACTIONS



Experimental conditions

500 mg of 1,2-dihydroxybenzene powder (m.p 106° C) are mixed with 50 mg of catalyst. The reaction temperature is 25° C and hydrogen pressure is kept at 1 bar during reaction. Analysis of the products is performed with gas chromatography: capillary column OV-17, nitrogen gas carrier, flame ionization detector. Results are evaluated using an ENICA-10 integrator.

RESULTS

Reactivity

Different catalysts are used for the solid state catalytic hydrogenation of 1,2 dihydroxybenzene. The reactivity depends essentialy on the nature of the metal catalyst as shown in table 1.

Table 1 - Conversion ratio versus catalyst

Catalyst	(metal %)	Conversion ratio %
Pd/Al2O3	(5%)	0
Pd/CaCo3	(5%)	0
Pd/BaSO4	(5%)	0
Pd/C	(5%)	28
Rh/Al2O3	(5%)	15
Rh/C	(10%)	38
Pt/C	(5%)	41
PtO2 Adams		80

Selectivity

As expected cis and trans 1,2-cyclohexanediol(2,3) are the hydrogenation products formed. Besides the hydrogenolysis, the product cyclohexanol (4) is obtained.

Table 2 - Selectivity versus catalyst

Catalyst	(2+3) %	2/3	4 %	4/2+3
Pd/C (5%)	25	1.6	3	0.12
Rh/Al_2O_3 (5%)	14	1.6	1.2	0.08
Rh/C (5%)	35	3.1	3.5	0.10
Pt/C(5%)	28	2.7	13	0.46
PtO2	68	2.4	12	0.17

Solution state reaction

The reaction is carried out in solution under the same conditions as in the solid state and with PtO_2 as catalyst. As shown in table 3, reactivity and selectivity are modified and additional products besides those in the solid state are formed.

Table 3 - Reaction in solution

Solvent	Solubility	2 %	3 %	4 %	other compounds %
Methanol	Soluble	0	0	0	0
1,2-dichloroethane	Soluble	0	0	4	10
Cyclohexane	Slightly soluble	21	8	17	26

DISCUSSION

In the solid state dihydroxybenzenes can be hydrogenated with high conversion ratios.Products are mainly cis and trans cyclohexanediol. PtO2 Adams seems to be the best catalyst for conversion of 1,2- dihydroxybenzene in the solid state. The cis/trans ratio depends on catalyst. Whatever catalyst,cis isomer is the main hydrogenated product. This result could be compared to Siegel and Dunkel's [5,6] obtained by hydrogenation of xylenes and substituted cyclohexenes over PtO_2 Adams in acetic acid.

The aromatic ring reduction is accompained by a hydrogenolysis reaction yielding cyclohexanediol 4. Hydrogenolysis ratio varies also with catalyst. Pt/C gives the highest hydrogenolysis ratio. Hydrogenolysis reactions, considered as secondary reactions, are usually observed in the reduction of hydroxyl aromatic substrates[7].

In solution, depending on solvent, reactivity and selectivity are modified. We noticed hydrogenation does not occur in a protic polar solvent like methanol, is weak in a non-protic polar solvent like 1,2-dichloroethane. Only in a non-polar solvent, cyclohexane, the conversion ratio is similar to the solid state, but additional products are formed. In this case, the organic solid is not completely soluble. Probably, the reaction occurs between hydrogen and solid particles suspended in the cyclohexane and explains the same conversion ratio as for a solid state reaction.

CONCLUSION

It is shown that solid state catalytic hydrogenation of 1,2-dihydroxybenzene occurs under mild conditions. In these conditions high conversion ratios and good selectivity are observed. Cis and trans 1,2-cyclohexanediols are more easily obtained in the solid state than in liquid or vapor phases. Solid state reactions afford an easy and clean way to hydrogenate organic substances. This hydrogenation method can be used just as well at a laboratory scale as at an industrial scale.

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