

Different Reaction Pathways for the Hydrogenation of *o*-cresol on Ruthenium, Rhodium, Palladium and Platinum Nanoparticles Supported on Carbon

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Introduction

Alkyl substituted cyclohexanols are intermediates for the fragrance and pharmaceutical industry. Alkylcyclohexanols are generally prepared by the hydrogenation of alkylphenols, and alkylcyclohexanones and alkylcyclohexanes are also formed in this process. Alkylcyclohexanones are sometimes preferable product. Compared with the oxidation of alkylcyclohexane and a two-step process via alkylcyclohexanone, the single-step hydrogenation of alkylphenols to alkylcyclohexanones over supported metal catalysts has a commercial advantage, particularly in terms of capital costs and energy savings [1]. For the hydrogenation of alkylphenol, the predominant product may be alkylcyclohexanol, alkylcyclohexane or alkylcyclohexanone, which depend on the catalyst employed and the reaction. Some studies [2-6] also indicated that the support used played a primary role in the hydrogenation of phenol. The mechanism of this reaction has been the focus of a number of publications. Two kinds of reaction pathways are proposed. In the direct route, alkylphenols are directly reduction to alkylcyclohexanols. In the indirect route, alkylphenols are reduction to alkylcyclohexanones and then further to the corresponding alkylcyclohexanols. There is no general consensus, but some different proposals with respect to the mechanism of hydrogenation alkylphenols to alkylcyclohexanols on different metal catalysts. In this paper, we discussed the relations between reaction route and active metal nanoparticles that are supported on active carbon by the same method to avoid the effect of preparation method and support.

Materials and Methods

The Ru/C, Rh/C, Pd/C, and Pt/C [7-12] catalysts were obtained by colloid method. The Brij-35 and Tween-20 stabilized metal colloidal particles solution were firstly prepared. Then active carbon was used to adsorb metal colloidal particles. The hydrogenation of *o*-cresol was carried out in a 70 ml stainless steel autoclave. The products were analyzed by gas chromatography (Agilent 6890N) and GC-MS (GCT CA156).

Results and Discussion

To establish the reaction pathways for the hydrogenation of *o*-cresol on Ru/C, Rh/C, Pd/C, and Pt/C catalysts, we first carried out hydrogenation experiments in a batch reactor by feeding *o*-cresol and following the reaction with time. The results of products distribution in the hydrogenation of *o*-cresol indicated the yield of *o*-methylcyclohexanone over different catalytic systems increased in the order Pt/C<Ru/C<Rh/C<Pd/C, which is a direct consequence of the different catalytic properties of four kinds active metal. On Pd/C catalytic systems, *o*-methylcyclohexanol observed during the reaction process was only in small amounts and *o*-methylcyclohexanone was mainly product before *o*-cresol disappeared. During the course of the reaction, *o*-methylcyclohexanone can be isolated, and the role of this compound as an "intermediate" in *o*-cresol hydrogenation can be proved. However, the order of the catalytic activity for *o*-methylcyclohexanol is Pd/C<Pt/C<Rh/C<Ru/C. The ring hydrogenation requires

typically high pressure and high temperature. However, Ru/C catalytic systems catalyzed *o*-cresol to *o*-methylcyclohexanol in mild conditions (50 °C, 0.8-1MPa). In addition, some cleavage occurs in the hydrogenation process, the amount of *o*-methylcyclohexane depending on reactive metal. The yield of *o*-methylcyclohexane over four kinds catalytic systems increased in the order Ru/C<Pd/C<Rh/C<Pt/C.

Now that *o*-methylcyclohexanone may be an intermediate in the hydrogenation of *o*-cresol, we also fed *o*-methylcyclohexanone as a reactant. The hydrogenation of *o*-methylcyclohexanone to *o*-methylcyclohexanol was examined in order to probe the overall reaction network. The results showed that the catalytic activity increased in the order Rh/C<Pd/C<Ru/C<Pt/C. Moreover *o*-methylcyclohexane wasn't detected in the hydrogenation of *o*-methylcyclohexanone process over four kinds of catalysts. So the route of the hydrogenation *o*-methylcyclohexanone to *o*-methylcyclohexane can't occur. On the basis of kinetic curves presented herein, the hydrogenation of *o*-cresol to *o*-methylcyclohexanol on Rh/C catalyst is much faster than the hydrogenation of *o*-methylcyclohexanone to *o*-methylcyclohexanol. We can conclude that in the hydrogenation of *o*-cresol, formation of *o*-methylcyclohexanol from *o*-cresol does not require ketone intermediates, and reaction through both the direct route and the indirect route when the Rh/C catalyst is used. However, Pd/C reached a completely different conclusion. The kinetic curves indicate a sequential transformation: *o*-cresol to *o*-methylcyclohexanone to *o*-methylcyclohexanol, which is the indirect route. In the case of Pt/C and Ru/C, it was possible to conclude that the alkylphenols were formed on such catalysts through both the direct route and the indirect route. However, another possibility involves that the reduction of *o*-cresol to *o*-methylcyclohexanone is slow and the direct route can be negligible.

When Pd/C was used as catalyst, the overall hydrogenation of *o*-cresol to *o*-methylcyclohexanol has been viewed as occurring in a stepwise fashion with *o*-methylcyclohexanone as a reactive intermediate. The accumulation of *o*-methylcyclohexanone led to the high selectivity of *o*-methylcyclohexanone. Moreover, Ru/C was preferred for the hydrogenation of alkylphenols to alkylcyclohexanols, and Pt/C was suitable for the hydrogenation of carbonyl.

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Significance

Help industrial production of alkylcyclohexanols and alkylcyclohexanones by analyzing dynamics and mechanisms of the hydrogenation of alkylphenols.

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