

Hydrogenation Reactivity of Mono-Aromatic Compound in Polar Solvents over Ru/Al₂O₃ Catalyst

Hideyuki TAKAGI, Takaaki ISODA, Katsuki KUSAKABE
and Shigeharu MOROOKA

Department of Materials Physics and Chemistry,
Graduate School of Engineering, Kyushu University,
Fukuoka 812-8581, Japan

KEY WORDS: hydrogenation, mono-aromatic compound, polarity of solvent

INTRODUCTION

Hydrogenation of aromatic compounds is a key reaction in processes such as hydrorefining of heavy oil and production of petrochemicals. Platinum group metals have the advantage of high activity for the hydrogenation of aromatic compounds under mild reaction conditions. However, the hydrogenation activity of this metal catalyst is sometimes decreased by the presence of solvents. Thus, the solvent effects can be significant, especially for the case of noble metal catalysts, which are used for the hydrogenation of asphaltene, coal extracts and polymers under mild conditions. In a previous studies [1], we reported that oxidized Yaloum coal, which had been treated with aqueous H₂O₂ in the presence of 1-propanol at 70°C, was solubilized in ethanol at a yield of 80 wt%, based on the dry raw coal mass. The ethanol-solubilized coal was further hydrogenated over a Ru catalyst at 120°C under a hydrogen pressure of 10 MPa for 72 h [2]. As a result of this catalytic hydrogenation, the aromaticity of the coal structure was altered, and the pyrolysis reactivity was increased. However, hydrogenation reactivity of aromatic compounds in solvents other than ethanol has not yet been investigated.

In the present study, therefore, benzyl alcohol was subjected to hydrogenated using Ru/Al₂O₃ catalyst at 120°C under a hydrogenation pressure of 6 MPa. Lower alcohols, non-polar solvents and solvents containing oxygen, sulfur and nitrogen were used in these reactions, and their effect on the efficiency of the reaction was examined. Carboxylic acids were also added to the reaction system, and the effect of these compounds on the hydrogenation reactivity of aromatic compounds was also determined.

EXPERIMENTAL

Chemicals and Catalysts: Benzyl alcohol was used as substrate. Methanol (MeOH), ethanol (EtOH) and 2-propanol (2-PrOH) were used for alcoholic solvents; hexane, heptane and benzene were used for non-polar solvents; acetone, 1,4-dioxane, tetrahydrofuran (THF) and diethyl ether (DEE) were used for polar solvent containing oxygen; and dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF) and N-methyl-2-pyrrolidone (NMP) were used for polar solvents containing sulfur and nitrogen. Formic acid (HCOOH), acetic acid (CH₃COOH), butyric acid (C₃H₇COOH) and lauric acid (C₁₁H₂₃COOH) were selected for use as added carboxylic acids in the hydrogenation reaction of benzyl alcohol. An alumina supported ruthenium catalyst (Ru/Al₂O₃, Wako chemical Co., metal content=5wt%) was used as the hydrogenation catalyst.

Reaction: The hydrogenation reactions were performed in a 50 mL batch autoclave at 120°C for 0.5 h under a hydrogen pressure of 6 MPa, equipped with a magnetic stirrer, rotating at 1000 rpm. 3 g of substrate, 6 g of solvent, and 0.5 g of catalyst were mixed, and carboxylic acid, of which usage was 3g, was further added to the reaction system. After hydrogenation, the catalyst was separated by centrifugation. Products were qualitatively and quantitatively analyzed by GC-FID (Shimadzu, GC-14A) and GC-MS (Shimadzu, QP-5000), equipped with a capillary column. The hydrogenation conversion of substrate was calculated as the following equation.

$$\text{Hydrogenation conversion [\%]} = (1 - N/100) \times 100 \quad (1)$$

where N [%] was the yield of unreacted substrate. The δ value of a solvent was defined by

$$\delta = DN - AN \quad (2)$$

where DN is the donor number, and AN is the acceptor number, of the solvent [3-4]. The relative permittivity for a mixture of solvents i and j, P_{mix} , was calculated from the following equation.

$$P_{\text{mix}} = (P_i X_i + P_j X_j) / (X_i + X_j) \quad (3)$$

where P_i and P_j are the relative permittivities of solvent i and solvent j, respectively [5]. X_i and

X_i are the mass fractions of solvent i and solvent j , respectively, ($X_i + X_j = 1$).

RESULTS

Figure 1 shows the product distributions for the hydrogenation of benzyl alcohol in the presence of the solvents. The conversion of benzyl alcohol was 76% in methanol, 82% in ethanol and 81% in acetic acid. This indicates that methanol, ethanol and acetic acid had little or no effect on the hydrogenation activity over the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst. When 2-propanol was used as the solvent, the total conversion of benzyl alcohol was decreased to 35%. When hexane and heptane, which are non-polar solvents, were used as the solvent, the hydrogenation conversion of benzyl alcohol was 75% and 61%, respectively. However, the conversion of benzyl alcohol was decreased to 35% by the addition of benzene. When acetone, THF, dioxane and diethyl ether were used as the solvent, the conversion of benzyl alcohol was 31, 36, 51 and 28%, respectively. These solvents strongly retarded the hydrogenation activity over the $\text{Ru}/\text{Al}_2\text{O}_3$. The hydrogenation of benzyl alcohol was completely inhibited when DMSO, DMF and NMP were used as the solvent.

Figure 2 shows the product distributions for the hydrogenation of benzyl alcohol dissolved in polar solvents in the presence of carboxylic acids over the $\text{Ru}/\text{Al}_2\text{O}_3$. When ethanol was used as the solvent, the hydrogenation of benzyl alcohol was increased in the presence of acetic acid, butyric acid and lauric acid. The added carboxylic acids remained unchanged during the hydrogenation reaction under the above reaction conditions. However, formic acid strongly inhibited the hydrogenation of benzyl alcohol. When THF and acetone were used as the solvent, the addition of acetic acid increased the hydrogenation reactivity, as observed in ethanol.

Figure 3 shows the pathways for the hydrogenation of benzyl alcohol over the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst at 120°C . The hydrogenation of aromatic ring (route 1) and the hydrogenolysis of hydroxy group (route 2) proceed competitively. The 1-cyclohexylmethanol is converted to cyclohexanecarbaldehyde [6]. Toluene is produced via route 2 and methylcyclohexane is produced via hydrogenation of toluene.

DISCUSSION

Figure 4 shows the relationship between the hydrogenation conversion of benzyl alcohol and the δ values of the solvents. The donor number represents the parameter which is associated with the solvent basicity, while the acceptor number is the parameter which is associated with the solvent acidity. Thus, the effect of solvents on the hydrogenation reactivity of benzyl

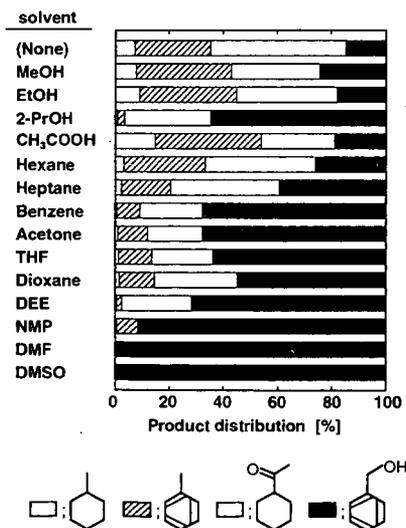


Figure 1. Product distributions for the hydrogenation of benzyl alcohol over $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst.

alcohol using the Ru catalyst is classified into four categories as follows: (1) Solvents with negative δ values are capable of accepting electrons, and methanol, ethanol, acetic acid and hexane are classified into this group. The conversion with respect to the hydrogenation of benzyl alcohol is approximately 80 % for all these solvents. Thus, the negative δ values of the solvents have no effect on the hydrogenation reactivity of benzyl alcohol over the Ru catalyst. (2) Benzene and 2-PrOH possess negative δ values and accept electrons. Since benzene was hydrogenated more preferentially than benzyl alcohol, the hydrogenation of benzyl alcohol was decreased in the presence of benzene. In the case of 2-PrOH, as shown in Figure 2, the yield of toluene is decreased in the presence of 2-PrOH to a greater extent than by methanol and ethanol. Meanwhile, the yield of cyclohexanecarbaldehyde in 2-PrOH is the same as that in methanol and ethanol. Thus, the hydrogenolysis of benzyl alcohol is suppressed by the addition of 2-PrOH. (3) Solvents with positive δ values are capable of transferring electrons, and acetone, THF, dioxane and diethyl ether can be classified into this group. In the presence of these solvents, the hydrogenation conversion decreases with increasing the δ values of the solvents. Ruthenium adsorbs oxygen-containing solvents via an interaction between the surface of the ruthenium and the pair of unshared electrons of the oxygen atom of the solvents. The active sites of the catalyst are occupied by electron donor solvents to a greater extent than electron acceptor solvents, and, as the result, the hydrogenation conversion of the substrate is decreased in the presence of members of this solvent group. (4) The activity of the Ru catalyst is inactivated in the presence of DMSO, DMF and NMP, which contain either sulfur or nitrogen.

Figure 5 shows the relationship between the hydrogenation conversion of benzyl alcohol and the relative permittivity of the solutions. The relative permittivity is related to solvent polarity. The relative permittivity is 13.1 for benzyl alcohol, 24.3 for ethanol, 20.7 for acetone and 7.4 for THF. The relative permittivity of acetic acid is 6.2, which is much smaller than that of formic acid, 58.0. Thus, the polarity of mixed solvents is decreased by the addition of acetic

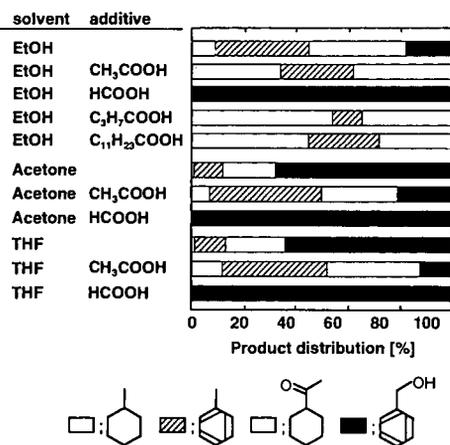


Figure 2. Product distributions for the hydrogenation of benzyl alcohol in polar solvents in the presence of carboxylic acids.

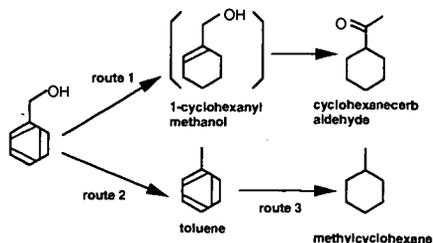


Figure 3. Pathway for the hydrogenation of benzyl alcohol over Ru/Al₂O₃ catalyst.

acid, and increased by that of formic acid. By the addition of acetic acid, the hydrogenation conversion of benzyl alcohol in ethanol, acetone and THF is increased, however, the hydrogenation reactivity is diminished by the addition of formic acid. Since formic acid is a solvent as protogenic as acetic acid, it is an electron acceptor. In addition, the relative permittivity of formic acid is much larger than that of acetic acid. Thus, the hydrogenation reactivity is affected by relative permittivity rather than the δ value for the case of formic acid.

CONCLUSIONS

1. A relationship between the hydrogenation reactivity of benzyl alcohol in polar solvent and the δ value of the solvent was found. Solvents with negative δ values did not affect the hydrogenation of benzyl alcohol over the Ru catalyst. However, solvents with positive δ values suppressed the hydrogenation of benzyl alcohol.
2. DMSO, DMF and NMP, which contained sulfur or nitrogen, deactivated the Ru catalyst.
3. The hydrogenation reactivity of benzyl alcohol in polar solvent was increased by the addition of acetic acid, butyric acid and lauric acid. The hydrogenation reactivity was related to the relative permittivity of solution. However, the hydrogenation reactivity was completely lost by the addition of formic acid with a high permittivity.

ACKNOWLEDGEMENTS

This research was supported by Japan Society for the Promotion of Science (JSPS), Organization of New Energy and Industrial Technology Development Organization (NEDO), and Center for Clean Coal Utilization, Japan (CCUJ). Support by Research for the Future Projects (Coordinator; Prof. M. Iino, Tohoku Univ.) and International Joint Research Program (Coordinator; Prof. M. Nomura, Osaka Univ.) is especially acknowledged.

REFERENCES

- [1] Isoda, T.; Tomita, H.; Kusakabe, K.; Morooka, S.; Hayashi, J.-i. *Proc. of Intern. Conference on Coal Science* **1997**, *2*, 581.
- [2] Isoda, T.; Takagi, H.; Kusakabe, K.; Morooka, S. *Energy Fuels* **1998**, *12*, 503.
- [3] Gutmann, V. *Angew. Chem. Internat. Ed.* **1970**, *9*, 843.
- [4] Marzec, A.; Juzwa, M.; Betelej, K.; Sobkowiak, M. *Fuel Proc. Tech.* **1979**, *2*, 35.
- [5] Fowler, F.W.; Katritzky, A.R.; Rutherford, R.J.D. *J. Chem. Soc. (B)* **1971**, 460.
- [6] Nishimura, S.; Hama, M.; *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2467.

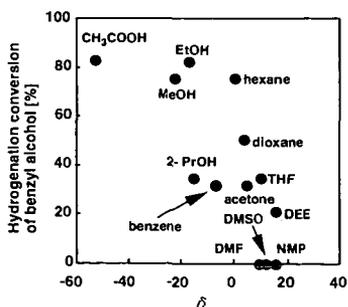


Figure 4. Relationship between hydrogenation conversion of benzyl alcohol and δ values of solvents.

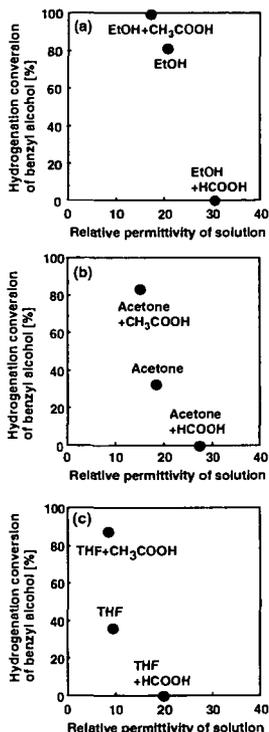


Figure 5. Relationship between hydrogenation conversion of benzyl alcohol and relative permittivity of solutions. Solvent; (a) EtOH, (b) acetone, (c) THF.