

RHODIUM COMPLEXES IMMOBILIZED ON NANOPOROUS SILICA FOR OCTENE HYDROFORMYLATION

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Abstract. Rhodium was immobilized on the aminated SBA-15 in order to evaluate it as a heterogeneous catalyst for 1-octene hydroformylation. The triphenylphosphine ligand remarkably improved the activity. Hydroformylation activity of 1-octene was higher than that of branched and/or inner octenes. At a reaction temperature of 120 °C, hydroformylation of 1-octene was more prevailing than isomerization, and thus the nonyl aldehyde yield reached a maximum.

1. INTRODUCTION

Micelle-templated nanoporous silica contains ordered mesoporosity and has a large surface area, thus being able to fix a large amount of metal complexes and to enable to form an ordered active site. Another advantage is inducing a shape selective reaction for manufacturing a chemical with large molecules since its pore size is bigger than that of a microporous support. These materials have a potential for active heterogeneous catalysts [1].

Higher aldehyde is a high value added chemical that holds a very important role in the chemical industry [2-3]. Hydroformylation is widely known to produce aldehyde by reacting higher olefin with hydrogen and carbon monoxide in the presence of an appropriate catalyst. Since linear aldehyde has more commercial value than branched aldehyde, there have been studies on catalysts to increase the ratio of linear aldehyde/branched aldehyde (L/B).

Homogeneous catalysts, comprised of rhodium and ligand, have been used in the hydroformylation reaction process of olefin. A ligand actually causes significant differences in the activity and selectivity

of hydroformylation. Such a homogeneous catalyst has a couple of disadvantages such as the complicate process of catalyst recycle and high cost. One of the solutions is to heterogenize the catalyst, for which researches have been conducted on the rhodium catalysts fixed onto inorganic support such as SiO₂, Al₂O₃, clay, and zeolite [4-7].

In this paper, SBA-15 was selected as an ordered mesoporous silica, then the organo-silane functionalization was performed by post synthesis methods [8]. In addition, rhodium complexes were immobilized on amine-functionalized SBA-15. The synthesized catalyst, SBA-15/AEAPMDMS/Rh, was used for hydroformylation of 1-octene. This study investigated the effects of the kinds of ligand and reaction temperature on catalyst activity and product selectivity.

2. EXPERIMENTAL DETAILS

SBA-15 was prepared according to the past reference [9]. A detailed experimental description for amine-functionalized SBA-15 with AEAPMDMS is as follows, 0.5 g of as-synthesized mesoporous

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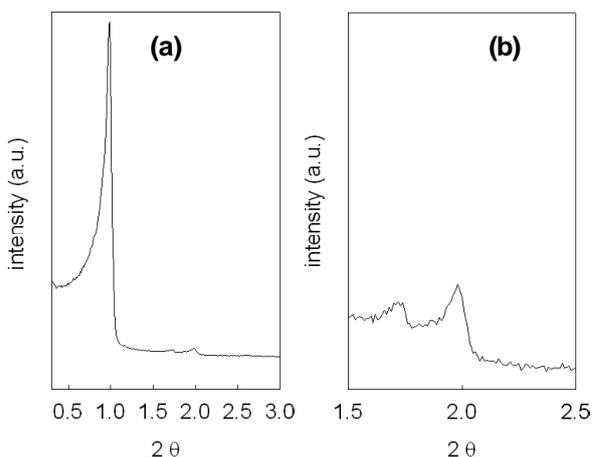


Fig. 1. XRD patterns of the SBA-15/AEAPMDMS/Rh.

materials were dispersed in 75 ml of toluene for 0.5 h at 50 °C with stirring. After then 3.5 mg of p-toluenesulfonic acid and 1.0 mmol of AEAPMDMS were added. The mixture was heated up to 120 °C and kept stirring for 2 h. After 2 h refluxing the solid product was filtered, washed with ethanol several times. The resulting solid was dried at 100 °C for 12 h.

Rhodium-derived catalyst was prepared as previous research [10]. 5 g of amine functionalized SBA-15 was added to a solution of 0.185 g $\text{Rh}_4(\text{CO})_{12}$ in n-hexane under N_2 . The mixture was stirred at room temperature under N_2 condition for 5 h. The solid powder became brown during the stirring and the solution was changed colorlessness. After 5 h the colorless solution was drawn off through a syringe under N_2 and the resulting solid was washed three times with n-hexane. Finally the resulting solid was dried under vacuum.

Table 1. Nonylaldehyde yield in hydroformylation.

Feed	Nonylaldehyde yield (%)
1-octene	69.1
trans-2-octene	-
trans-3-octene	-
trans-4-octene	-
2-methyl-1-heptene	29.6
2-methyl-2-heptene	-
2.4.4-trimethyl-2-pentene	-

Catalyst: SBA-15/AEAPMDMS/Rh
 Reaction condition: 300 psi, 120 °C,
 Reaction time: 30 min

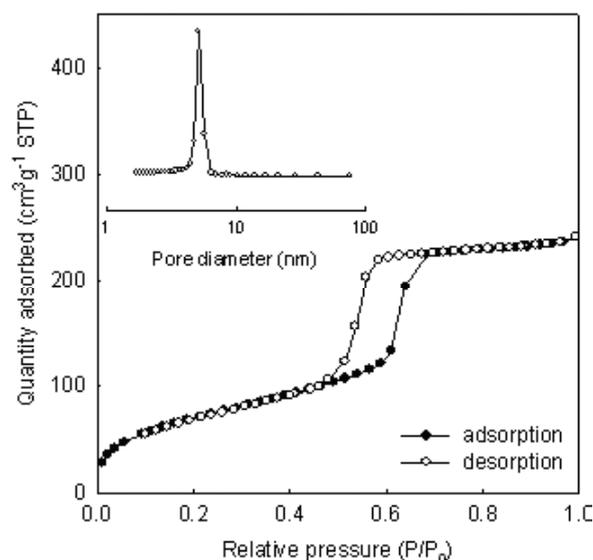


Fig. 2. Nitrogen adsorption–desorption isotherm and pore size distribution of the SBA-15/AEAPMDMS/Rh.

Nitrogen adsorption-desorption isotherms were determined using a Micromeritics ASAP 2020 at -196 °C. The pore volume was obtained from t-plot method. Small-angle powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer.

The hydroformylation of 1-octene was performed as follows. The prepared catalyst, SBA-15/AEAPMDMS/Rh, was added to a SUS-316 autoclave reactor containing THF and 1-octene. Subsequently, the autoclave was sealed and flushed with N_2 gas. The syn-gas ($\text{CO}/\text{H}_2 = 1$) was introduced under pressure to bring the total pressure of 20 bar. The reaction condition was 120 °C and 20 bar. After the completion of the reaction, the products were analyzed by gas chromatography (GC-2014, Shimadzu).

3. RESULTS AND DISCUSSION

Fig. 1 shows that rhodium-immobilized aminated SBA-15 (SBA-15/AEAPMDMS/Rh) has an ordered structure. It also shows three well resolved peaks as as-made SBA-15. These well-defined peaks also prove that the two-dimensional hexagonal structure was retained after the rhodium immobilization. After the amine functionalization, it is postulated that the rhodium complex was immobilized to the free electron of the amine through a coordination bond between rhodium metal and amine group without any changes in the ordered pore structure of the SBA-15.

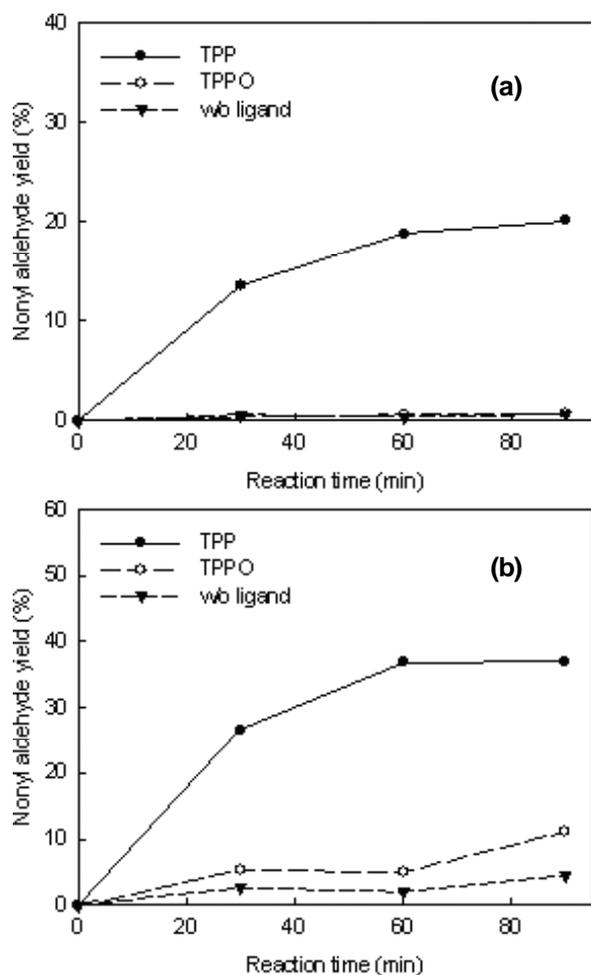


Fig. 3. Effect of ligand on nonyl aldehyde yield in the 1-octene hydroformylation over (a) SBA-15/AEAPMDMS/Rh, (b) homogeneous catalyst, $[\text{Rh}(\text{CH}_3\text{COOH})_2]_2$ (Reaction condition: 300 psi and 140 °C, rhodium amount: 0.035 mol.%, ligand/Rh ratio: 20).

Fig. 2 exhibits the N_2 adsorption–desorption isotherms and pore size distribution of the SBA-15/AEAPMDMS/Rh catalyst. The type IV hysteresis loop in accordance with IUPAC classification means that the pore shape may not be significantly changed through the silane functionalization process and additional rhodium immobilization processes. Moreover, the characteristic pore size distribution curve of SBA-15 [11] was not changed after the treatment.

The effects of ligand on the 1-octene hydroformylation were investigated using the SBA-15/AEAPMDMS/Rh catalyst and a homogeneous catalyst. In the case of homogeneous catalytic reaction, we used $(\text{Rh}(\text{CH}_3\text{COO})_2)_2$ as a precursor of a homogeneous Rh catalyst for octene hydroformylation [3]. Fig. 3 shows the effect of ligands on 1-octene hydroformylation.

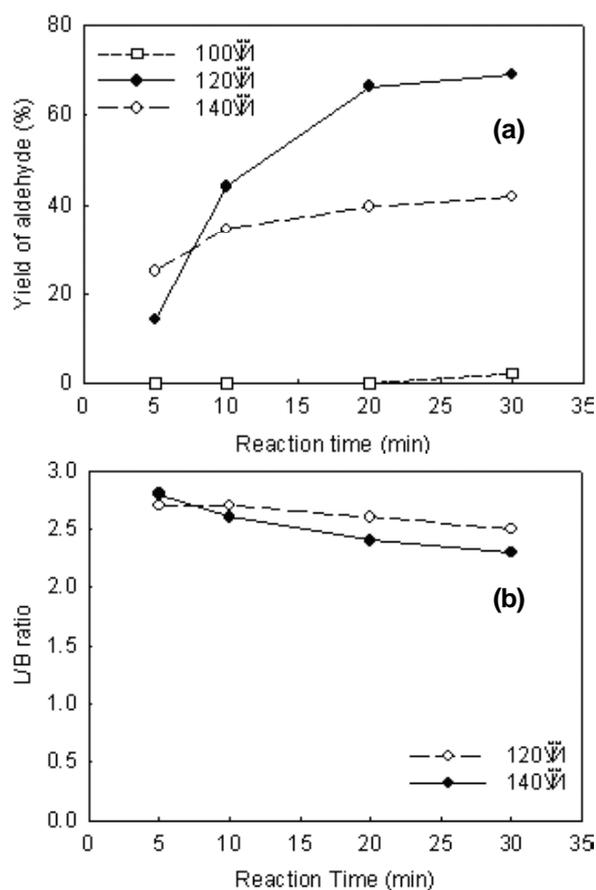


Fig. 4. Effect of reaction temperature on nonyl aldehyde yield and L/B ratio in the 1-octene hydroformylation. (Reaction condition: 300 psi, catalyst: 0.035 mol.-%-Rh of SBA-15/AEAPMDMS/Rh, TPP/Rh:20).

Triphenylphosphine (TPP) is commercially used as a ligand of homogeneous rhodium catalyst for the hydroformylation of propylene, and triphenylphosphine oxide (TPPO) for the hydroformylation of mixed octene [3]. In the hydroformylation of 1-octene using heterogeneous catalysts, nonyl aldehyde yield was considerably greater when TPP was used as the ligand in the immobilized rhodium catalyst than when TPPO or no ligand was put in (Fig. 3a). Such a tendency is similar to the hydroformylation results of a homogeneous catalyst (Fig. 3b). It is known that the TPP ligand increases the stability of the rhodium complex at a high temperature in the hydroformylation reaction with a homogeneous catalyst. Such a role seems to be applied to the rhodium catalyst fixed onto nanoporous silica as well.

Table 1 presents the comparison results of hydroformylation reaction with octene isomers with SBA-15/AEAPMDMS/Rh catalyst. They clearly

show that the hydroformylation reaction activity of 2-methyl-1-heptene, a branched terminal olefin, was considerably lower than that of 1-octene, a terminal olefin. In addition, there was low activity in the hydroformylation reaction of inner octene. Those findings indicate that the SBA-15/AEAPMDMS/Rh catalyst shows performance excellent enough to replace a homogeneous catalyst in the hydroformylation reaction of 1-octene but it needs to be still improved for the hydroformylation reaction of iso-octene.

Figs. 4a and 4b show the effects of reaction temperature on aldehyde yield and linear aldehyde/branched aldehyde ratio (L/B), respectively, in case of the hydroformylation reaction of 1-octene with the SBA-15/AEAPMDMS/Rh catalyst. There was almost no progress in the hydroformylation reaction until 100 °C, and 1-octene conversion increased as the temperature raised up to 140 °C. The isomerization reaction, however, took place faster than the hydroformylation reaction at 140 °C, resulting in low selectivity and yield for nonyl aldehyde. At 120 °C, hydroformylation was more prevailing than isomerization, and thus selectivity for nonyl aldehyde was high. The nonyl aldehyde yield reached a maximum at 120 °C, at which the 30-minute reaction led to 69.1% of nonyl aldehyde yield. At 120 °C, the linear aldehyde/branched aldehyde ratio (L/B) reached 2.5 after 30 minutes of reaction time, higher than 0.8, the L/B ratio with a homogeneous catalyst under the same conditions.

4. CONCLUSION

Rhodium was immobilized on the functionalized SBA-15 with an aminosilane in order to evaluate it as a heterogeneous catalyst for 1-octene hydroformylation. The triphenylphosphine ligand greatly improved the activity. Hydroformylation activity of 1-octene was higher than that of branched and/or inner octenes. At a reaction temperature of

120 °C, hydroformylation of 1-octene was more prevailing than isomerization, and thus the nonyl aldehyde yield reached a maximum.

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REFERENCES

- [1] L. Huang, Y. He and S. Kawi // *Appl. Catal. A:Gen.* **265** (2004) 247.
- [2] J.N. Armor // *Catal. Today* (2010), doi:10.1016/j.cattod.2009.11.019.
- [3] J.K. Jeon, Y.K. Park and J.M. Kim // *Chem. Lett.* **33** (2004) 174.
- [4] S.K. Sharma, P.A. Parikh and R.V. Jasra // *J. Mol. Catal. A:Chem.* **301** (2009) 31.
- [5] F. Hung-Low, G.C. Uzcátegui, M.C. Ortega, A.B. Rivas, J.E. Yanez, J. Alvarez, A.J. Pardey and C. Longo // *Catal. Today* **107–108** (2005) 273.
- [6] S.I. Fujita, S. Akihara, S. Fujisawa and M. Arai // *J. Mol. Catal. A:Chem.* **268** (2007) 244.
- [7] L. Yan, Y.J. Ding, H.J. Zhu, J.M. Xiong, T. Wang, Z.D. Pan and L.W. Lin // *J. Mol. Catal. A:Chem.* **234** (2005) 1.
- [8] N. Garcia, E. Benito, J. Guzman, P. Tiemblo, V. Morales and R.A. Garcia // *Micropor. Mater.* **3** (2007) 129.
- [9] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka and G.D. Stucky // *J. Am. Chem. Soc.* **120**, (1998) 6024.
- [10] J.A. Bae, S.H. Hwang, K.C. Song, J.K. Jeon, Y.S. Ko and J.H. Yim // *J. Nanosci. Nanotechnol.* **10** (2010) 290.
- [11] Y.S. Ko, J.S. Lee, J.H. Yim, J.K. Jeon and K.Y. Jung // *J. Nanosci. Nanotechnol.* **10** (2010) 180.