Selective adsorption of toluene on perovskite oxides for the organic hydride method

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Abstract: For application to the organic hydride method, selective adsorption of unreacted toluene is anticipated in the hydrogenation process. $La_{0.8}Ba_{0.2}CoO_{3-\delta}$ (LBCO), one of perovskite oxides, showed high adsorption selectivity for toluene. It was revealed that existence of both Ba and Co in the lattice is necessary for selective adsorption of toluene on LBCO. Moreover, results of the adsorption tests with several hydrocarbons indicated that aromatics with a methyl group is feasible for adsorption on LBCO.

Keywords: organic hydride method, selective adsorption, perovskite oxide.

1. Introduction

Hydrogen has attracted considerable attentions as a clean secondary energy. However, hydrogen is gaseous in ambient temperature and under atmospheric pressure, which is a disadvantage in storage and transportation. Therefore, a hydrogen carrier which can store hydrogen efficiently at an ambient condition is required. Organic hydrides are excellent hydrogen carriers in handleability, [1] and that have high hydrogen density.[2] Methylcyclohexane (MCH)-toluene system, one of the organic hydride-aromatic systems, is promising because of its physical property and low toxicity. However, hydrogenation of aromatics is restricted by the equilibrium, and unreacted aromatics remain in the product. Therefore, separation of aromatics from organic hydrides after hydrogenation is required for improvement in energy efficiency. We aimed to develop a separation system with an adsorbent that adsorbs toluene selectively after hydrogenation in MCH-toluene system.

Any adsorbents that selectively adsorb toluene from MCH have never been reported. However, Mukai *et al*. reported that $La_{0.7}Sr_{0.3}AlO_{3-\delta}$, one of perovskite oxides, adsorbed toluene strongly.[3] Therefore, we explored perovskite oxides which can selectively adsorb toluene, and investigated the factors which contribute to adsorption selectivity of toluene.

2. Experimental

Perovskite oxides were prepared using a citric acid complex method with metal nitrate precursors. The precursor solution was dried in a water bath. Then, the product was pre-calcined at 673 K for 2 h and calcined at 1123 K for 10 h.

Adsorption property of perovskite oxides was examined by adsorption tests with pulse feed of the mixture of toluene and MCH. Perovskite oxides were purged with Ar for 30 min at 773 K, and then were retained at 363 K. The pulse feed gas was Ar 92 % : toluene 4 % : MCH 4 %, and 0.4 mL was fed in each pulse. The outlet gas was analyzed by GC-FID (Shimadzu GC-14B).

To investigate effects of hydrocarbon structures on adsorption amounts, adsorption tests with several adsorbates, toluene, MCH, benzene, cyclohexane, 2,2,4-trimethylpentane and *p*-, *m*-, *o*- xylenes were conducted. The composition of feed gas was Ar 96 % : hydrocarbon 4 %, and the other conditions were the same to the adsorption test for the mixture of toluene and MCH.

3. Results and discussion

We explored perovskite oxides that adsorb toluene selectively by the adsorption tests. Amounts of perovskite oxides used in the adsorption tests were regulated so that surface areas were unified to 2.4 m^2. Results are presented in Table 1. On $La_{0.8}Ba_{0.2}CoO_{3-\delta}$ (LBCO) and $La_{0.8}Ba_{0.2}NiO_{3-\delta}$ (LBNO), detected amounts of toluene and MCH were small at initial stage, and then increased. Accordingly, toluene and MCH were adsorbed on LBCO and LBNO, but these perovskite oxides showed high adsorption selectivity for toluene. Because the larger amount of toluene was adsorbed to LBCO, we studied the factors that contribute to the adsorption property of LBCO.

Table 1. Adsorption tests on perovskite oxide

	Toluene adsorption / μmol g-cat^{-1}	MCHadsorption / μmol g-cat^{-1}
$La_{0.8}Ba_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$	0.0	0.0
$La_{0.8}K_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$	0.0	0.0
$La_{0.8}Cs_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$	0.0	0.0
$La_{0.8}Sr_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$	0.0	0.0
$La_{0.8}Ba_{0.2}MnO_{3-\delta}$	0.0	0.0
$La_{0.8}Ba_{0.2}FeO_{3-\delta}$	0.0	0.0
$La_{0.8}Ba_{0.2}YO_{3-\delta}$	0.0	0.0
$La_{0.8}Ba_{0.2}AlO_{3-\delta}$	0.0	0.0
$La_{0.8}Ba_{0.2}CoO_{3-\delta}$	4.5	0.6
$La_{0.8}Ba_{0.2}NiO_{3-\delta}$	2.5	0.1

Table 2. Adsorption amounts of toluene and MCH on A-site substituted $LaCoO_3$

	Toluene adsorption / μmol g-cat^{-1}	MCH adsorption / μmol g-cat^{-1}
LBCO	4.5	0.6
$LaCoO_3$	0.0	0.0
$BaCoO_3$	0.8	0.0
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	0.0	0.0
$La_{0.8}Ca_{0.2}CoO_{3-\delta}$	0.0	0.0

Then, the relationship between adsorption property and substitution ratio of A-site in $LaCoO_3$ was investigated. Table 2 shows results of the adsorption tests on LBCO, $LaCoO_3$, $BaCoO_3$, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and $La_{0.8}Ca_{0.2}CoO_{3-\delta}$. LBCO and $BaCoO_3$ adsorbed toluene selectively, whereas the other perovskite oxides adsorbed neither toluene nor MCH. Accordingly, the existence of both Ba and Co in the lattice is important for selective adsorption of toluene.

To elucidate the adsorption selectivity for toluene, we conducted adsorption tests on LBCO with several hydrocarbons. Table 3 shows results of the adsorption tests with toluene, MCH, benzene, cyclohexane and *p*-, *m*-, *o*- xylenes. Benzene, the simplest aromatic ring, was not adsorbed to LBCO, while cyclohexane was adsorbed about the same as MCH. Therefore, toluene adsorption to LBCO is not only due to an interaction between a simple aromatic ring and LBCO. Toluene adsorption to LBCO is also not due to an interaction between methyl group and LBCO because 2,2,4-trimethylpentane was not adsorbed to LBCO. Moreover, LBCO adsorbed more amounts of *p*-, *m*-, *o*-xylenes than that of toluene. Therefore, LBCO selectively adsorbs aromatic compounds with methyl groups. It was considered that the electronic state of the aromatic ring with a methyl group is important for adsorption on LBCO.

Table 3. Adsorption amounts of several kind of hydrocarbon on $La_{0.8}Ba_{0.2}CoO_{3-\delta}$

	Amount of adsorptio / μmol g-cat^{-1}
Toluene	3.7
MCH	1.1
Benzene	0.0
Cyclohexane	0.8
p-Xylene	4.8
m-Xylene	4.4
o-Xylene	3.8

4. Conclusions

Adsorption properties of perovskite oxides were examined, and $La_{0.8}Ba_{0.2}CoO_{3-\delta}$ showed high adsorption selectivity for toluene. The adsorption property of LBCO is induced by the existence of both Ba and Co in the lattice. An aromatic compound with a methyl group is selectively adsorbed on LBCO.

References

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