

Catalytic Deoxygenation of Oleic Acid over Ceria-Zirconia Catalysts

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Abstract

The catalytic deoxygenation of oleic acid was studied over ceria-zirconia mixed metal oxide (CZMMO), $Ce_{1-x}Zr_xO_2$ ($x = 0, 0.25, 0.50, 0.75$ and 1.0), and Fe, Ni, Cu and Rh loaded on the CZMMO catalysts. Experiments were carried out in a continuous flow reactor within the temperature range of 325-425°C. The gaseous products mainly are CO and CO₂ while the main compositions in liquid products are C₁₇ and C₁₈ hydrocarbons. The difference in the product distribution was insignificant for all types of the catalysts used in this work. Surprisingly, $Ce_{0.75}Zr_{0.25}O_2$ exhibits the highest catalytic activity for the deoxygenation of oleic acid with high selectivity toward C₁₇ hydrocarbons. The catalytic activities of metal supported on $Ce_{0.75}Zr_{0.25}O_2$ catalysts are lower than that of $Ce_{0.75}Zr_{0.25}O_2$. This is due to a product hindrance. A kinetic study of deoxygenation of oleic acid over $Ce_{0.75}Zr_{0.25}O_2$ support was further carried out. First order kinetic was well fitted for the deoxygenation of oleic acid and the estimated activation is ca. 23 kcal mol⁻¹.

Introduction

It has been reported that the liquid products from pyrolysis of sewage sludge consist mainly of a long chain carboxylics [1]. This fraction could be upgraded by deoxygenation reaction and potentially be used as a diesel fuel additive for the cetane number booster [2]. Therefore, the catalytic deoxygenation unit seems reasonable to be implemented in the sequence with the pyrolysis unit. The deoxygenation of carboxylic acids such as acetic acid [4], benzoic acid [5, 6] and octanoic acid [7] has been studied over the several types of the metal oxide catalysts. From these reports, the metal oxide catalysts illustrate good catalytic activity. Therefore, our aim is to study the deoxygenation of oleic acid as a model of high carbon number carboxylic acid obtained from sewage sludge. The ceria-zirconia mixed metal oxide (CZMMO) catalysts with various compositions were tested for their catalytic activity here under steady-state conditions in a continuous flow reactor within the temperature range of 325-425°C. Moreover, the kinetic studies of deoxygenation were also carried out.

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Results and discussion

Deoxygenation of oleic acid (OA), $C_{17}H_{35}COOH$, can take place via two pathways. The first one is the direct decarboxylation forming C_{17} hydrocarbons and the second one is the ketonization forming symmetrical ketones of C_{35} and CO was then removed by the decarbonylation converting to aliphatic hydrocarbons of C_{17} and C_{18} . The gaseous products from thermal and catalytic deoxygenation of OA are CO and CO_2 and the liquid products contain hydrocarbons ranging from C_6 - C_{18} . The conversion of OA was calculated from CO and CO_2 production. The effect of reaction temperature was illustrated in Fig. 1. For example at $385^\circ C$, the highest OA conversion of 20.8% was observed for $Ce_{0.75}Zr_{0.25}O_2$ followed by 15.7% for CeO_2 . For $Ce_{0.50}Zr_{0.50}O_2$, $Ce_{0.25}Zr_{0.75}O_2$ and ZrO_2 , the OA conversions were comparable at 10.9 and 12.8 and 11.9%, respectively. The results were found to relate with the redox property of the CZMMO catalysts. This is confirmed by the CO-TPR results, where $Ce_{0.75}Zr_{0.25}O_2$ showed the highest reducibility [8]. The liquid products are hydrocarbon ranging from C_6 to C_{18} and the main products are C_{17} and C_{18} hydrocarbons. The composition distribution in liquid fraction is similar in all catalysts studied. However, $Ce_{0.75}Zr_{0.25}O_2$ and CeO_2 was found to be more selective toward C_{17} and C_{18} hydrocarbons.

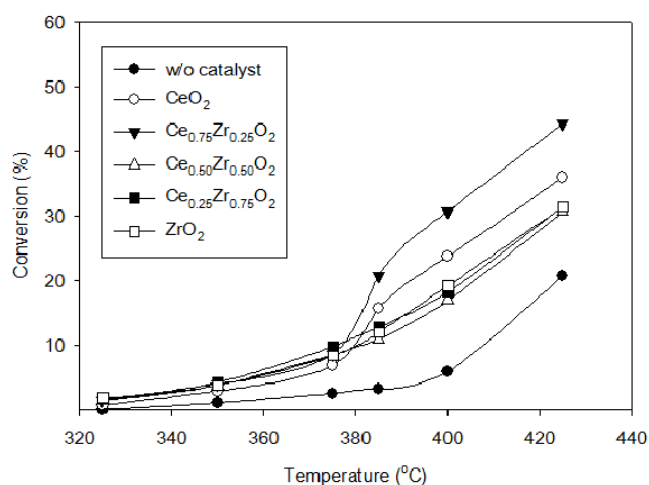


Fig. 1. Conversion versus temperature of deoxygenation reaction of oleic acid

Effects of doped metal were studied on the $Ce_{0.75}Zr_{0.25}O_2$. CO and CO_2 evolution rate from the deoxygenating reaction of oleic acid over Fe, Ni, Cu and Rh supported on $Ce_{0.75}Zr_{0.25}O_2$ at $385^\circ C$ were shown in Fig. 2. CO production rates were found to be constant at ca. $3.0 \times 10^{-6} \text{ mol s}^{-1} \text{ g}^{-1}_{\text{CAT}}$ for all catalysts. The maximum CO_2 production rate was ca. $2.52 \times 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}_{\text{CAT}}$ for $Ce_{0.75}Zr_{0.25}O_2$ catalysts. Doping of metals on the $Ce_{0.75}Zr_{0.25}O_2$ was found to reduce the OA deoxygenation rate. This might be due to CO produced from the reaction may strongly adsorb on the metal surface, leading to a loss in the catalytic activity.

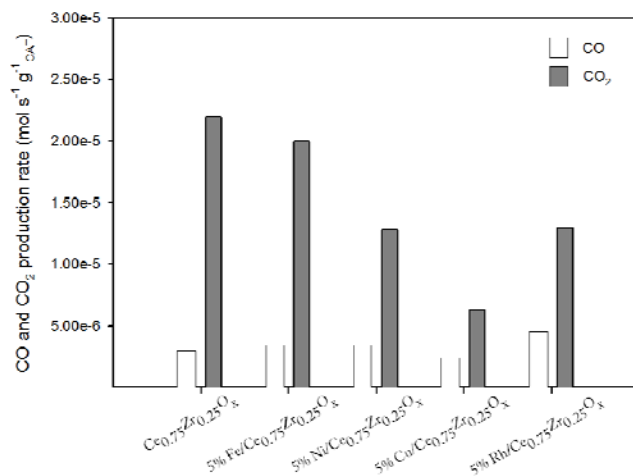


Fig. 2. CO and CO₂ evolution rate from the deoxygenation of oleic acid over metal supported on Ce_{0.75}Zr_{0.25}O₂ at 385°C

A first order kinetic model was applied for the deoxygenation of oleic acid over Ce_{0.75}Zr_{0.25}O₂. The initial rate and rate constant are summarized in Table 1. And subsequently the activation energy (E_a) were determined to be 23 kcal mol⁻¹ and the Arrhenius constant (A) is 1.3×10^9 l h⁻¹ g_{CAT}⁻¹.

Table 1. Initial rate of reaction and reaction constant at 375, 385 and 400°C

T (°C)	r_0 (mol s ⁻¹ g _{CAT} ⁻¹)	k (l h ⁻¹ g _{CAT} ⁻¹)
375	8.29×10^{-7}	1.14
385	1.05×10^{-6}	1.45
400	1.60×10^{-6}	2.20

Conclusions

In conclusion, the deoxygenation of oleic acid can be achieved via catalytic decarboxylation. The products obtained are mainly C₁₇ and C₁₈ for the case of ceria-zirconia catalysts. With the presence of metals, the deoxygenation is achieved via decarboxylation and ketonization. Ce_{0.75}Zr_{0.25}O₂ was found to be the most active and stable catalyst for oleic acid deoxygenation. A first order kinetic model was found to fit perfectly with experimental data. The calculated activation energy is ca 23 kcal mol⁻¹.

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References

- [1] C. Jindarom, V. Meeyoo, T. Rirksomboon, P. Rangsunvigit, (2007), Thermochemical decomposition of sewage sludge in CO₂ and N₂ atmosphere, *Chemosphere*, 67, 1477–1484.
- [2] S. Zhang, Y. Yan, T. Li, Z. Ren, (2005), Upgrading of liquid fuel from the pyrolysis of biomass, *Bioresource Technol.*, 96, 545–550.
- [3] K. Parida, H. K. Mishra, (1999), Catalytic ketonisation of acetic acid over modified zirconia 1. Effect of alkali-metal cations as promoter, *J. Mol. Catal A*, 139, 73-80.
- [4] M.W. de Lange, J.G. van Ommen, L. Lefferts, (2001), Deoxygenation of benzoic acid on metal oxides 1. The selective pathway to benzaldehyde, *Appl. Catal. A: General*, 220 41-49.
- [5] M.W. de Lange, J.G. van Ommen, L. Lefferts, (2002), Deoxygenation of benzoic acid on metal oxides 2. Formation of byproducts, *Appl. Catal. A: General*, 231, 17-26.
- [6] F. Billaud, Y. Guitard, A.K. Tran Minh, O. Zahraa, P. Lozano, D. Pioch, (2003), Kinetic studies of catalytic cracking of octanoic acid. *J. Mol. Catal. A: General*, 192 281-288.
- [7] S. Pengpanich, V. Meeyoo, T. Rirksomboon, K. Bunyakiat, (2002), Catalytic oxidation of methane over CeO₂-ZrO₂ mixed oxide solid. *Appl. Catal. A: General*, 234 221-233.
- [8] M. Thammachart, V. Meeyoo, T. Rirksomboon, S. Osuwan, (2001), Catalytic activity of CeO₂-ZrO₂ mixed oxide catalysts prepared via sol-gel technique: CO oxidation. *Catal. Today*, 68 53-61.