

論文 / 著書情報  
Article / Book Information

題目(和文)	赤外分光法を用いたZSM-5ゼオライト上で進行するメタノールからの炭化水素生成に関わる炭素-炭素結合の形成機構に関する研究
Title(English)	Infrared study on mechanisms of C-C bond formation during methanol-to-hydrocarbons reaction over ZSM-5 zeolite
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出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9412号, 授与年月日:2014年3月26日, 学位の種別:課程博士, 審査員:野村 淳子,北村 房男,酒井 誠,馬場 俊秀,原 亨和
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9412号, Conferred date:2014/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

専攻 : Department of	物質電子化学	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 (理学) Doctor of
学生氏名 : Student's Name	山崎 弘史		指導教員 (主) : Academic Advisor(main)	野村 淳子
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

The aim of this study is to investigate the mechanism of C-C bond formation during methanol to hydrocarbons reaction over ZSM-5 zeolite using infrared (IR) spectroscopy. Main purpose of this study is to clarify the reactivity of surface alkoxy species such methoxy species and ethoxy species on acidic OH groups.

In Chapter I, the introduction of zeolite chemistry and methanol to hydrocarbons reaction is described.

In Chapter II, experimental apparatus in this study and a new concept of the estimation of real temperature of sample in IR cell are described. The peak top frequency of the stretching vibration of OH groups on amorphous silica reversibly changes accompanied by the change of the sample in temperature under the constant concentration. Using this phenomenon, the estimation of the real temperatures of samples in IR cell can be achieved.

In Chapter III, the reaction of surface methoxy species on ZSM-5 and ethene was investigated as one of the elementary step of MTH reactions. The formed methoxy species on acidic sites of ZSM-5 are thermally stable under evacuation even at 673 K. Methoxy groups are regarded as methylation reagents of light olefins from IR observation and GC-MS analysis. Carbene-like intermediate for the methylation of light olefins by methoxy species was proposed on zeolite, which is based on the IR observation that the recovered acidic hydroxyl groups after the reaction of d3-methoxy groups with light olefin molecules are all deuterated.

In Chapter IV, the reaction of methoxy species with methanol and dimethyl ether (DME) was studied to in relation to the initial C-C bond formation in MTH reaction. In other words, products as hydrocarbons in the initial step of MTH reaction were investigated. The direct production of propene from methoxy groups and DME is evidenced on H-ZSM-5 zeolite by isotopic studies of IR observation of surface species and gas chromatograph-mass spectroscopy (GC-MS) analysis of products. Stepwise reactions of DME to ethene and water followed by methylation of ethene by methoxy groups were negligible during the generation of propene by the reaction of methoxy groups and DME.

In Chapter V, the kinetics of the methylation of olefins by methoxy species was investigated. The activation energies of the reaction of methoxy species with ethene and propene were estimated at  $111 \pm 7$  and  $41 \pm 7$  kJ mol<sup>-1</sup> over H-ZSM-5. The activation energies of methylation of olefins by methoxy species decrease with increasing carbon number of olefins. Additionally, the kinetics of the formation of methoxy species on H-ZSM-5 was investigated. Activation energies of the formation of methoxy species from methanol and dimethyl ether were estimated at  $95 \pm 14$  and  $69 \pm 6$  kJ mol<sup>-1</sup> over H-ZSM-5 zeolite, and that of the formation of dimethyl ether from methanol was obtained at  $86 \pm 4$  kJ mol<sup>-1</sup>. Dimethyl ether is considered to be the important source of methoxy species.

In Chapter VI, The oligomerization of ethene over H-ZSM-5 at 303 K was studied as one of the elementary step of MTH reactions using IR spectroscopy. Ethene oligomerization at 303 K proceeds on the basis of a concerted mechanism, and not by a stepwise mechanism as the reaction of ethoxy species and ethene. The mechanism of the decomposition of ethoxy species to ethene was additionally discussed. The decomposition of ethoxy species also occurred on the basis of a concerted mechanism, not a carbenium cation mechanism.

In Chapter VII, I summarized this thesis.

備考 : 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).