Surface Reactions on MoO_3 Induced by Tunable Pulse Infrared Free Electron Laser

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We have carried out ethanol conversion reactions on the MoO_3 under the pulse infrared irradiations (period = 2 s) with several wavelengths emitted from free-electron-laser. We found a piece of evidence to show the dependence of activities in the ethanol conversion rate on the infrared wavelengths. When the wavelength was tuned to $967\,cm^{-1}$, which corresponded to the absorption frequency of 0.167 nm Mo=O bond, C_2H_5OH was converted mainly to C_2H_4 with CH_3CHO as a minor product while no reaction occurred at $1200\,cm^{-1}$ where no resonant vibration mode of MoO_3 was present. The reaction products were different from those produced in thermal reactions.

Controlling the catalyses of solid surface is one of the interesting issues. In the solid catalysts the surface was composed of active sites with different structures. They undertake different reaction paths, which deteriorates the selectivity. Thus the design of the active site structure on an atomic scale is one way to attain a highly selective catalyst.[1] The other method may be the selective excitation of the specific chemical bond at the active site. For example Mo oxide is a key component for selective oxidation reaction of hydrocarbons.[2] The MoO_3 is the most fundamental Mo oxide, which has several Mo–O bond lengths. Two Mo=O bonds have different vibrational frequencies as shown in Figure 1. Each Mo–O bond shows different catalytic properties affected by its local structure.[3–7] In the ethanol conversion reaction, the Mo=O with the distance of 0.167 nm was claimed to yield aldehyde while both ethyl ether and aldehyde were expected to be formed from the local structure including Mo=O with the distance of 0.173 nm.[4] If we could excite the particular bond, we could initiate a single reaction path. The IR with the wave number in the region of $1000\,cm^{-1}$ may excite the Mo=O bond selectively and control the catalytic properties. However, as far as we know, there is no literature about dependence of catalytic activities on the IR frequencies. There are two problems. One is that the energy is easily dispersed to the lattice, heating up the whole sample, which activates catalysts thermally. In order to distinguish the thermal reaction from the photoreaction, one has to use a pulse and tunable IR source. Next problem is that we did not have appropriate pulse light source in this energy region. Free electron laser (FEL) is the unique solution to solve the problems and provides us a tunable, pulse and intense infrared light. In 2001 Tokyo University of Science has launched a FEL facility, FEL-SUT, which is dedicated to the mid-IR region.[8] We have carried out the irradiation of FEL-IR on the MoO_3 in the presence of ethanol. Our purpose of this study is to see the possibility that the FEL-IR can induce the chemical reaction distinguishable from the thermal one.

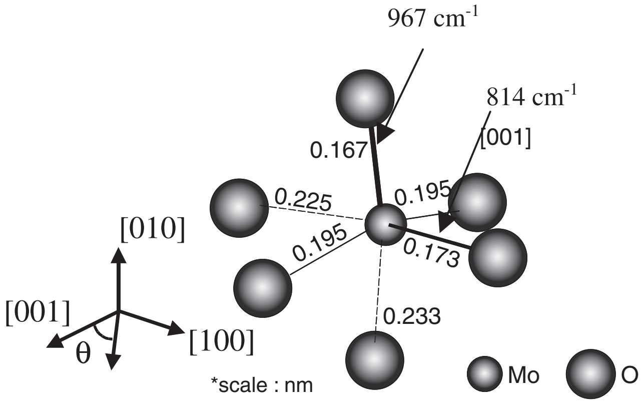

Figure 1. The molecular structure of MoO_3.[9]

99.5% MoO_3 was purchased from Kanto Chemicals and was used without further purification. The sample was placed in the reaction chamber and was pretreated at 623 K for 1 h in the presence of dry air and evacuated using a rotary pump with a liquid nitrogen trap. Then the sample was cooled to room temperature. The 6 Torr ethanol vapor was introduced to the sample at room temperature. FEL-IR was emitted from a MIR-FEL machine of IR-FEL Research Center in Tokyo University of Science (FEL-SUT). The FEL was operated with the acceleration energy of 30.8 MeV. FEL macro pulse has its duration time 2 μs with a period = 2 s, which was composed of a train of micropulses (durations = 2 ps with a period of 350 ps). Three IR wavelengths were used to excite the sample. One was $1200\,cm^{-1}$, (Power = 3.5 mJ per macropulse) at which MoO_3 has no absorption band. The others were $967\,cm^{-1}$ (Power = 3.2 mJ per macropulse) and $814\,cm^{-1}$ (Power = 1.9 mJ per macropulse), which corresponds to the stretching mode of the two Mo=O bonds. The pulse interval was 2 s in order to prevent the sample from being warmed. The FEL was introduced into the chamber through a ZnSe window. The sample was horizontally shifted every 5 pulses in order to reduce the effect of radiation damages. The products were analyzed with a gas chromatograph (Shimadzu 8A) using Porapak Q (for C_2H_5OH and CH_3CHO) and active carbon (for CO_2) columns. The gas phase was sampled using 6 way valves connected to the gas chromatograph. After the irradiation at $967\,cm^{-1}$ and the gas phase analyses, we evacuated the cell at room temperature and reintroduced C_2H_5OH at 6 Torr and proceeded the IR irradiations at $1200\,cm^{-1}$. Likewise we carried out the IR irradiation at $814\,cm^{-1}$ and gas phase analyses sequentially. For comparison we carried out the thermal reaction of ethanol on the MoO_3. The temperature was 453 K. The products were analyzed after the 180 min reaction.

In our previous work we found remarkable color changes of MoO_3, when the sample was irradiated at 967 cm^{-1}. We inferred that the following change might take place on the MoO_3 surface.[10]

$$2MoO_3 + C_2H_5OH \rightarrow Mo_2O_5 + CH_3CHO + H_2O, \quad (1)$$

where the reduced Mo species (Mo_2O_5) is black and Mo^{6+}(MoO_3) is white. Actually we observed Mo^{5+} by XPS at dark portion.[11] Since the power at 967 cm^{-1} was 1.1 times larger than that of 1200 cm^{-1}, the change of the Mo chemical state occurred not owing to the difference of the IR power but to the different irradiated wavelength.

Table 1. Reaction products converted from C_2H_5OH by IR irradiations

	C_2H_4 10^{-11}/mol/pulse	CH_3CHO 10^{-11}/mol/pulse
1200 cm^{-1}	trace amount	ND
967 cm^{-1}	13	5.5
814 cm^{-1}	1	0.1
thermal reaction	ND	6.6*

ND=not detected
*unit = 10^{-11} /mol/s

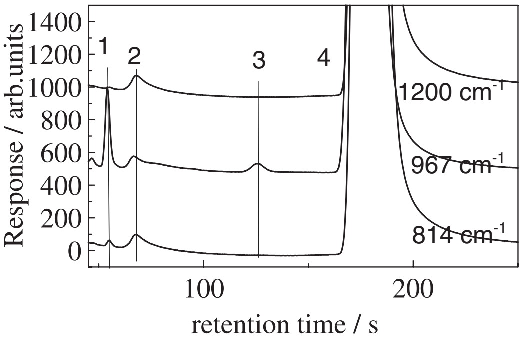

Figure 2. The gas chromatograph of the products after the infrared laser irradiations at several wavelengths. 1; C_2H_4, 2; H_2O, 3; CH_3CHO, 4; C_2H_5OH.

Figure 2 shows the results of gas chromatography using Porapak Q column. When the sample was irradiated with 1200 cm^{-1}, we found peaks appearing at 70 and 180 s (indicated as peak 2 and 4 in the figure, respectively) corresponding to water contamination and C_2H_5OH. This chromatogram indicates that little reaction occurred at this wavelength. On the other hand, we found peaks at 56 s (peak 1) and at 130 s (peak 3) in the chromatogram after 60 min irradiation at 967 cm^{-1} which corresponded to C_2H_4 and CH_3CHO, respectively. We also found that the formation of C_2H_4 from C_2H_5OH at another resonant frequency of 814 cm^{-1}.

Table 1 shows the amount of products. In the thermal reaction, MoO_3 produced CH_3CHO from the ethanol. On the other hand, IR irradiation induced the dehydration reaction in addition to the dehydrogenation. The facts that reaction occurs only at the resonant frequencies of Mo–O vibrational modes and the selectivity is completely different from the thermal reaction clearly demonstrate that the FEL-IR has opened a new photoreaction path different from the thermal reaction. Further studies must be necessary concerning frequency dependence and intensity dependence of the activity and the selectivity but we can safely say "yes" to the question whether the pulse IR can induce a chemical reaction that is distinguishable from the thermal reaction. Our next target is to see the possibility to activate the IR-induced photoreaction path for the conversion of saturated hydrocarbons selectively to unsaturated hydrocarbons or oxygenates.

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