

Modification Effect of La on the Adsorption Behavior of CH₄ on MgO

by Tohru KANNO*, Takashi HANZAWA** and Masayoshi KOBAYASHI*

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Abstract

The modification effect of La on CH₄-adsorption was examined. In the presence of surface OH, exposure of CH₄ caused the production of RCO species on MgO, while olefinic species was mainly produced on La-doped MgO. In the case of CH₄-pretreated surface, ammonia formed NCO species on MgO, not on La-doped MgO.

We conclude that the higher selectivity of C₂ compounds in oxidative coupling of methane on La-doped MgO is ascribed to La's inhibition effect on breaking olefinic C-C bond produced from CH₄; this breaking forms RCO species leading to CO_x species.

1. INTRODUCTION

CH₄ is one of primary components of natural gas and, therefore, its oxidative coupling into C₂ compounds such as C₂H₄ and C₂H₆ is important both industrially and environmental-ly. This reaction is usually operated over basic metal oxide-based catalysts. High selectivity of C₂ compounds needs the process of coupling of methyl radicals and then dehydrogenation, competing with conversion into CO_x species¹⁾.

A large number of researches on this reaction over MgO and metal-modified MgO have been done so far²⁾. Choudhary et al.^{3,4)} reported that a dose of La onto MgO enhanced C₂ selectivity up to 80% at 850°C. They mentioned that one of the features of La/MgO catalysts was the high melting of La, which worked to promote the catalytic activity and C₂ selectivity. In our laboratory also, a dose of 0.01 molar La on MgO increased the selectivity by 11.5%, using a membrane reactor made of porous Al₂O₃ tube⁵⁾.

In this paper, comparison of CH₄-derived species was made between MgO and La-doped MgO by IR spectroscopy, and the scheme of modification of La was suggested, which was related to oxidative coupling of CH₄.

2. EXPERIMENTAL

2-1 Preparation of the Samples.

The samples were prepared as follows; 10 g of MgO powder (Merck Corp.) was suspended by 100 ml of redistilled water in a beaker on a hot plate. This suspension was decanted three times to remove as much metal-ion impurities as possible, and then put in an oven at

* Department of Chemical System Engineering

** Chemical Environmental Engineering

90°C for 12 hrs after rough-dry. Addition of La was done by aqueous lanthanum nitrate solution, which had been prepared to be 1 wt%-La to MgO.

50 mg of the powder thus obtained was compressed to be a thin disk of 20 mm in diameter. The disk was put in an IR cell made of quartz glass and preheated *in vacuo* at 350°C, at which $\text{Mg}(\text{OH})_2$ decomposes, for 4 hrs; for both samples: MgO and La-doped MgO (designate as La-MgO), three kinds of surface were prepared by the following pretreatments *in vacuo*;

- (1), at 350°C for 1 hr, followed by 800°C for 3 hrs
- (2), at 350°C for 1 hr, followed by 550°C for 3 hrs
- (3), at 350°C for 1 hr, followed by 800°C for 3 hrs, and then exposure of 1-torr H_2O at room temp. for 20 min. (designate as the hydrated surface)

2-2 Equipments.

The equipment with vacuum line and the IR cell in this study were similar to one in the previous paper⁶⁾. The gases were commercially packed in a glass container by Takachiho Chemical Corp. except for H_2O . The purities of them were 99.99% (CH_4) and 99.9% (C_2H_4 and C_3H_6), respectively. The IR spectrometer was Shimadzu FT-IR 8100, and measurement was done at room temp.

3. RESULTS AND DISCUSSION

3-1 Adsorption Behavior on the Three Kinds of Surface for MgO and La-MgO.

3-1-1 Adsorption Behavior of CH_4 .

Fig. 1 shows IR spectra after exposure of CH_4 at room temp. followed by raising temp. on the three kinds of surface for MgO and La-MgO. The frequencies of the peaks obtained and their assignments are listed in Table 1. On the surface evacuated at 800°C (a), bidentate carbonate (designate as bi. c.) and weakly adsorbed CH_4 were observed for both samples. The intensity of the peak of bi. c. grew up to 500°C and then decreased. This peak disappeared at 700°C. This phenomenon was, maybe, caused by carbonized sample due to the decomposition of the adsorbed species.

For 550°C pretreated-surface (b), unidentate carbonate (designate as uni. c.) as well as bi. c. were observed. The appearance of uni. c. corresponds to the increase of the amount of surface OH species, which cover bare Mg^{2+} sites and this coverage is favor of producing uni. c. because Mg^{2+} is indispensable for bi. c. production.

On the hydrated surface (c), any peaks at 1300-1800 cm^{-1} weren't observed, indicating no formation of carbonate species. In the region of 800-1100 cm^{-1} , the difference of IR spectra was seen between MgO and La-MgO. The details will be shown in 3-2.

3-1-2 Adsorption Behavior of C_2H_4 .

Fig. 2 shows IR spectra after exposure of C_2H_4 at room temp. followed by raising temp. The frequencies of the peaks obtained and their assignments are listed in Table 2. On the

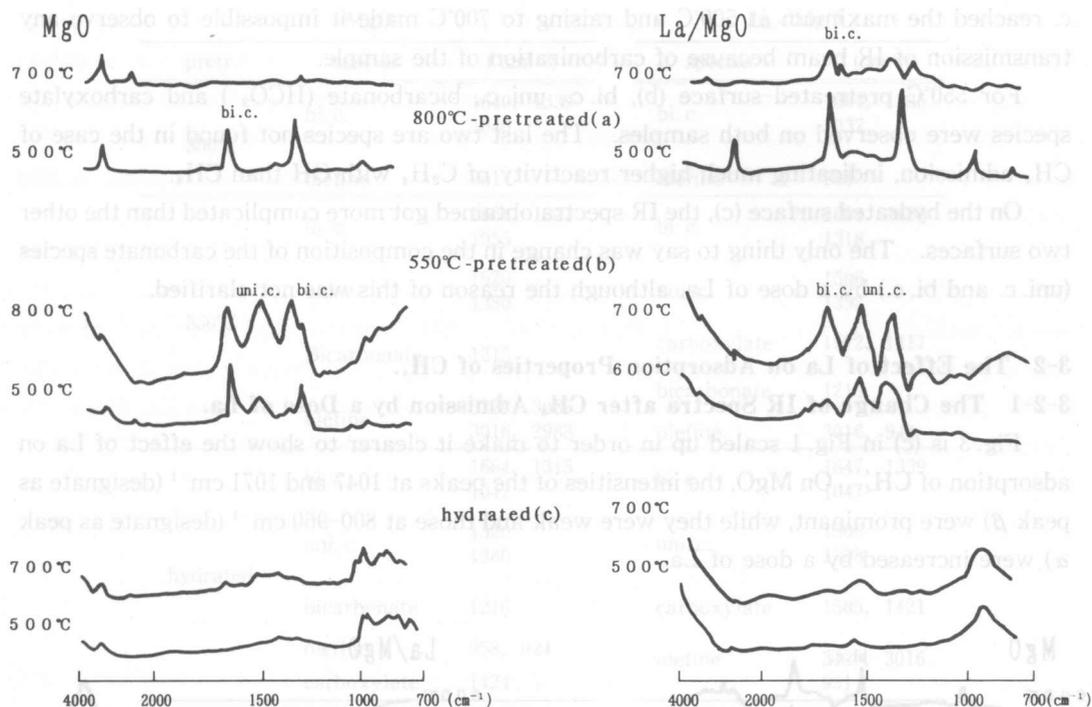


Fig. 1 Dependency of IR spectra of 13 torr CH₄-derived species on the pretreatment condition on MgO and La-MgO.

Table.1 The IR frequencies and assignments of CH₄-derived species.

MgO			La/MgO	
pretr.	species	f (cm ⁻¹)	species	f (cm ⁻¹)
800°C	bi. c.	1645, 1340 1044	bi. c.	1654, 1332 1030, 859
	CH ₄	3018 1310	CH ₄	3028
	bi. c.	1663, 1316 1047	bi. c.	1661, 1342 854
550°C	uni. c.	1516 1379	uni. c.	1514 1375
	CH ₄	3016	CH ₄	3016
	C-O species	1071 1047	olefine	962, 927 835
hydrated	CH ₄	3011 1304	CH ₄	3023 1304
	olefine	958, 924 824		

(hydrated; evacu. at 800 °C → 1 Torr-H₂O)

(bi. c.; bidentate carbonate,
uni. c.; unidentate carbonate)

surface evacuated at 800°C (a), bi. c. and olefinic species were observed. The intensity of bi. c. reached the maximum at 500°C and raising to 700°C made it impossible to observe any transmission of IR beam because of carbonization of the sample.

For 550°C pretreated-surface (b), bi. c., uni. c., bicarbonate (HCO_3^-) and carboxylate species were observed on both samples. The last two are species not found in the case of CH_4 admission, indicating much higher reactivity of C_2H_4 with OH than CH_4 .

On the hydrated surface (c), the IR spectra obtained got more complicated than the other two surfaces. The only thing to say was change in the composition of the carbonate species (uni. c. and bi. c.) by a dose of La, although the reason of this was not clarified.

3-2 The Effect of La on Adsorption Properties of CH_4 .

3-2-1 The Change of IR Spectra after CH_4 Admission by a Dose of La.

Fig. 3 is (c) in Fig. 1 scaled up in order to make it clearer to show the effect of La on adsorption of CH_4 . On MgO, the intensities of the peaks at 1047 and 1071 cm^{-1} (designate as peak β) were prominent, while they were weak and those at 800–960 cm^{-1} (designate as peak α) were increased by a dose of La.

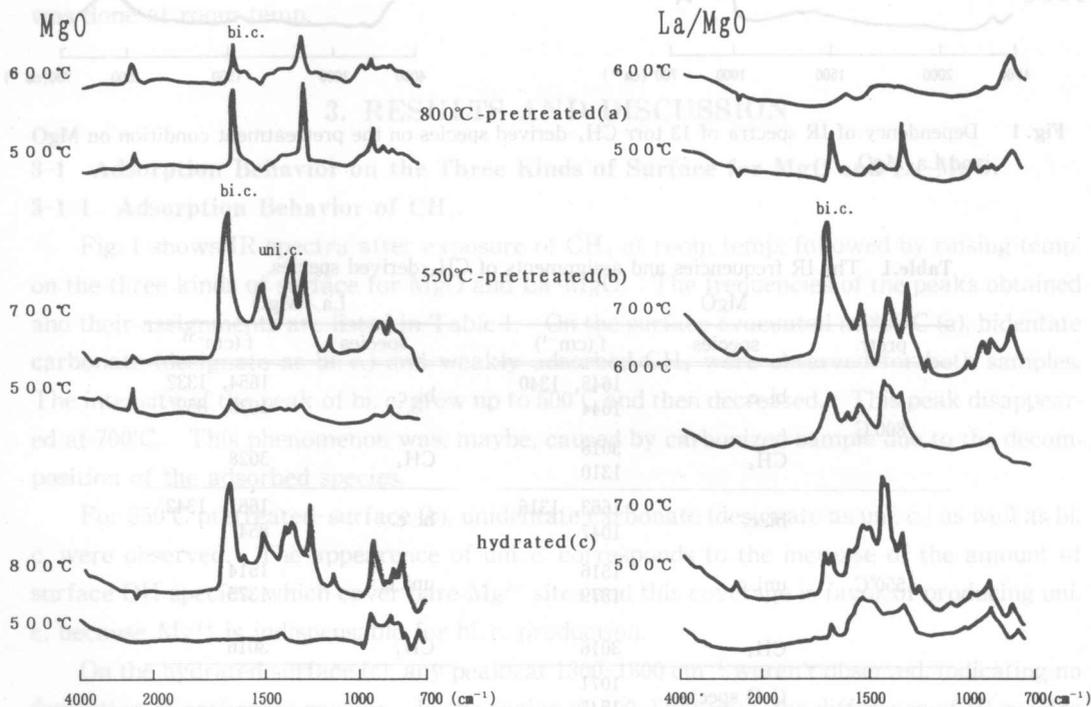
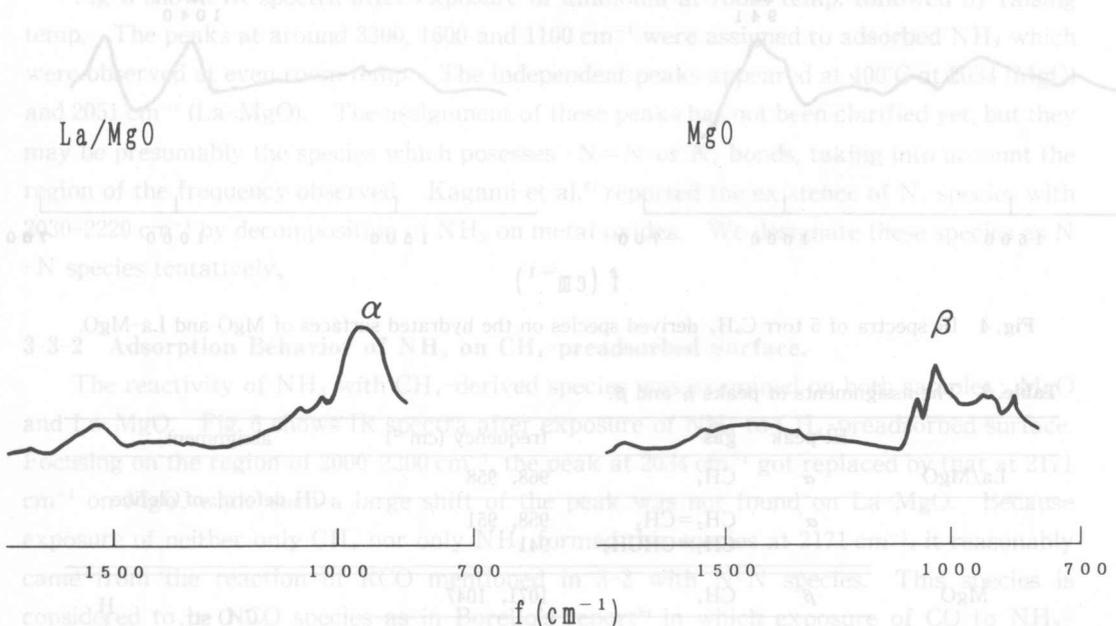


Fig. 2 Dependency of IR spectra of 5 torr C_2H_4 -derived species on the pretreatment condition on MgO and La-MgO.

Table 2 The IR frequencies and assignments of C₂H₄-derived species.

	MgO		La/MgO	
	pretr.	species	species	f (cm ⁻¹)
800°C		bi. c.	bi. c.	1664, 1335 1037
		olefine	olefine	951
		bi. c.	bi. c.	1664, 1630 1055 1318
550°C		uni. c.	uni. c.	1506 1398
		Bicarbonate	carboxylate	1572, 1417
		olefine	bicarbonate	1219
			olefine	3016, 944
		bi. c.	bi. c.	1664, 1339 1047
		uni. c.	uni. c.	1506 1398
hydrated		bicarbonate	carboxylate	1565, 1421
		olefine	olefine	3129, 3016 951
		carboxylate		1424

(hydrated; evacu. at 800°C → 1 Torr-H₂O)(bi. c.; bidentate carbonate,
uni. c.; unidentate carbonate)**Fig. 3** IR spectra of 13 torr CH₄-derived species on the hydrated surfaces of MgO and La-MgO.

3-2-2 The Assignments of Peaks α and β from Adsorption of Olefine.

Fig. 4 shows IR spectra after exposure of C_3H_6 on the $800^\circ C$ -pretreated (a) and the hydrated (b) surfaces. Two spectra showed a large difference. The adsorption behavior seemed to depend upon how much OH exists; the peak at 941 cm^{-1} (designate as peak α') was observed on $800^\circ C$ -treated surface (a) in the presence of little OH and this peak can be assigned to CH deformation vibration of olefinic species. Under much OH species (b), the peak at 1040 cm^{-1} (designate as peak β') was found.

Comparison was made among CH_4 - and olefine-derived IR peaks in Table 3. From this Table, peak α , which was obtained from CH_4 admission, clearly shows the existence of olefinic species. On $V_2O_5-Al_2O_3$, C_3H_6 reacts with OH to form $(CH_3)_2-CH-CO$ species with the IR peak of 1095 cm^{-1} assigned to CO stretching vibration. Peaks β and β' have the similar range of IR frequencies and so were assigned to the similar RCO species, where the existence of carbonate can be ruled out because of the lack of the peaks at $1300-1800\text{ cm}^{-1}$ as mentioned before.

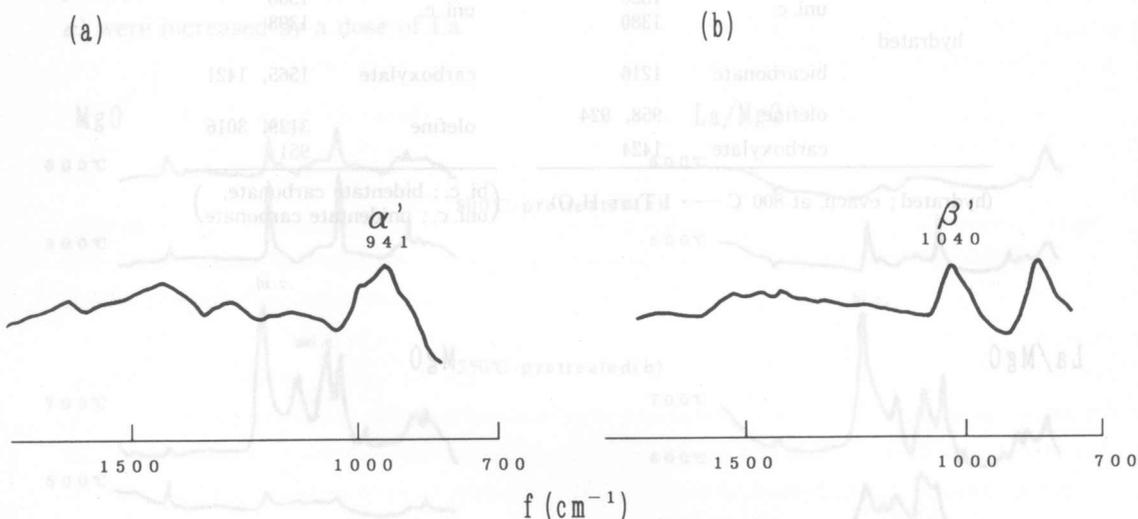
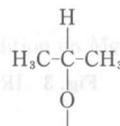


Fig. 4 IR spectra of 5 torr C_3H_6 -derived species on the hydrated surfaces of MgO and La-MgO.

Table 3 The assignments of peaks α and β .

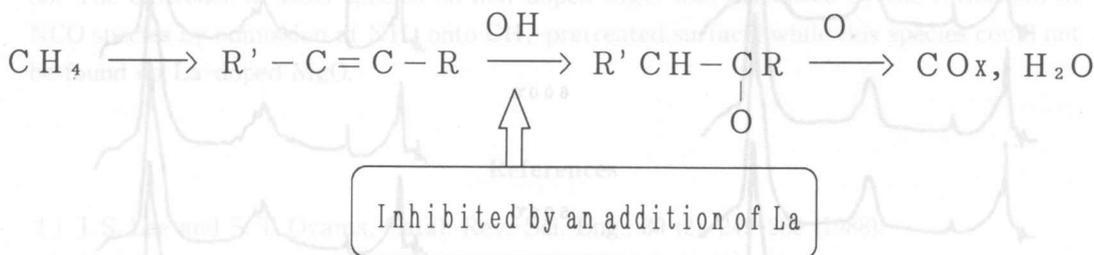
	IR peak	gas	frequency (cm^{-1})	assignment
La/MgO	α	CH_4	968, 958	CH deform. of olefine
	α'	$CH_2=CH_2$	958, 951	
		$CH_2=CHCH_3$	941	
MgO	β	CH_4	1071, 1047	C-O str.
	β'	$CH_2=CHCH_3$	1040	
$V_2O_5/Al_2O_3^*$		$CH_2=CHCH_3$	1095	C-O str.



* A. A. Davydov, "Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxide", Edited by C. H. Rochester, John Wiley & Sons Ltd. (1990)

3-2-3 The Scheme of the Effect of La on Adsorption Properties of CH₄.

Let us consider more the difference of the adsorption properties of CH₄ on MgO and La-MgO in Scheme 1. On MgO, the olefinic species reacts with OH to form RCO species, leading to CO_x which must decrease the selectivity of C₂ compounds. A dose of La inhibits this path and more olefinic species exist on the surface. We, therefore, conclude that La makes olefinic species, which was produced from CH₄, more stable.



Scheme. Modification effect of La on the adsorption property of CH₄ on MgO.

3-3 Reactivity of CH₄-derived Species with Ammonia.

3-3-1 Adsorption Behavior of Ammonia.

Fig. 5 shows IR spectra after exposure of ammonia at room temp. followed by raising temp. The peaks at around 3300, 1600 and 1100 cm⁻¹ were assigned to adsorbed NH₃ which were observed at even room temp. The independent peaks appeared at 400°C at 2034 (MgO) and 2051 cm⁻¹ (La-MgO). The assignment of these peaks has not been clarified yet, but they may be presumably the species which possesses -N=N- or N₃ bonds, taking into account the region of the frequency observed. Kagami et al.⁹⁾ reported the existence of N₂ species with 2030-2220 cm⁻¹ by decomposition of NH₃ on metal oxides. We designate these species as N-N species tentatively.

3-3-2 Adsorption Behavior of NH₃ on CH₄-preadsorbed Surface.

The reactivity of NH₃ with CH₄-derived species was examined on both samples: MgO and La-MgO. Fig. 6 shows IR spectra after exposure of NH₃ to CH₄-preadsorbed surface. Focusing on the region of 2000-2200 cm⁻¹, the peak at 2034 cm⁻¹ got replaced by that at 2171 cm⁻¹ on MgO, while such a large shift of the peak was not found on La-MgO. Because exposure of neither only CH₄ nor only NH₃ formed this species at 2171 cm⁻¹, it reasonably came from the reaction of RCO mentioned in 3-2 with N-N species. This species is considered to be NCO species as in Borello's report⁹⁾ in which exposure of CO to NH₃-preadsorbed MgO surface formed NCO species with 2187 cm⁻¹. This result can be, in other words, a strong support of the presence of RCO species on MgO and its absence on La-MgO.

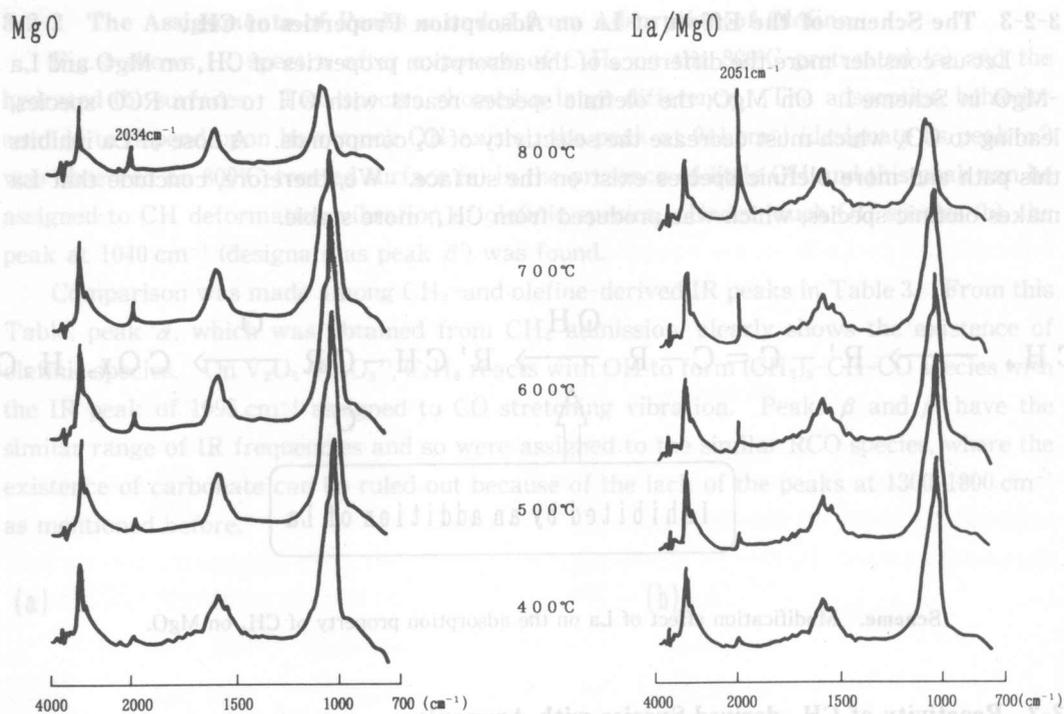


Fig. 5 IR spectra of 5 torr NH_3 -derived species on the hydrated surfaces of MgO and La-MgO.

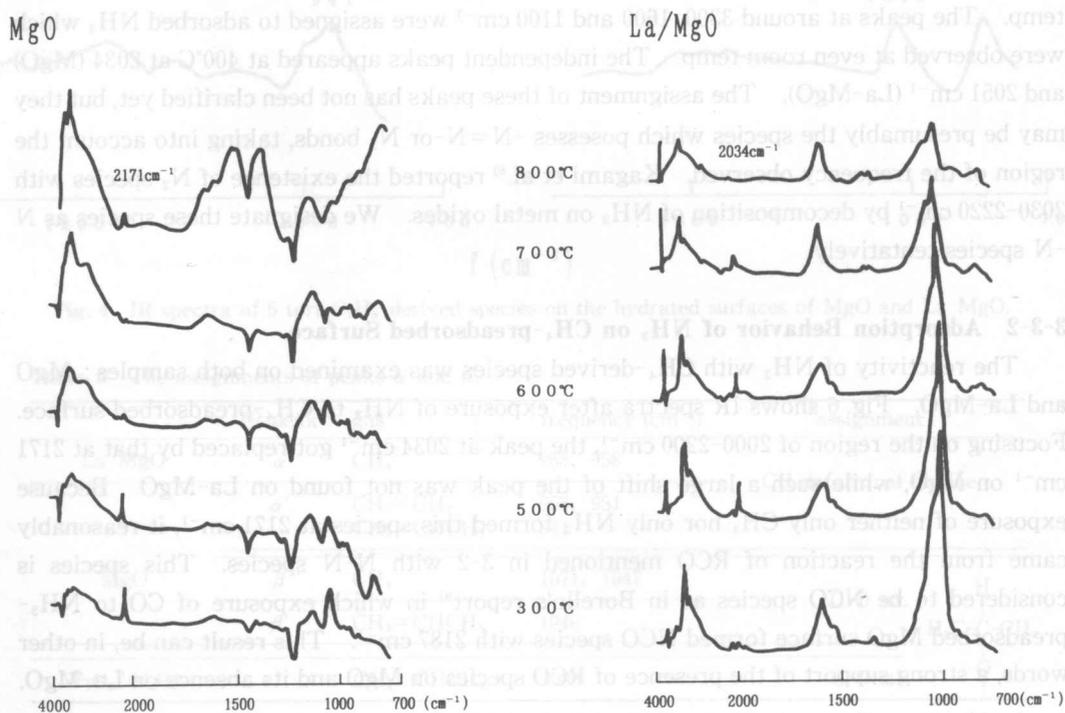


Fig. 6 IR spectra of NH_3 -derived species on CH_4 -preadsorbed surfaces on MgO and La-MgO.

4. CONCLUSIONS

- (1). On non-doped MgO, olefinic species from CH₄ easily reacts with OH to form RCO species, possibly causing the decrease in the selectivity of C₂ compounds in the oxidative coupling of methane.
- (2). La on MgO works to stabilize this olefinic species on the surface and to inhibit the path to formation of RCO species.
- (3). The existence of RCO species on non-doped MgO was evidenced by the formation of NCO species by admission of NH₃ onto CH₄-pretreated surface, while this species could not be found on La-doped MgO.

References

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2. EXPERIMENTAL

Preparation of the Samples

10 g of MgO powder (Merck Corp.) was suspended by red-distilled water of 200 ml with three-time decantations. This suspension was dried on a hot plate under agitation and put in an oven at 363 K overnight. The starting material for addition of alkali metal was aqueous alkali-hydroxide (Special Grade, Wako Pure Pharmaceutical Corp.) solution; the added weight was 1, 5 or 10% to MgO.

* Department of Chemical System Engineering

** Chemical Environmental Engineering