Study on the Acidity and the Catalytic Activity of the Metal Ion-exchanged Silica Gel*

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Summary: Solid acidities created in metal ion-exchanged silica gels have been investigated. Total acidities of these silica gels evacuated at 100°C were predominantly Brönsted type and approximately proportional to the amount of the exchanged metal ions. The acidities of these samples decreased in order of $\text{Zn} \gg \text{Cd} > \text{Co} > \text{Ni} \sim \text{Cu} > \text{Mn} \sim \text{Ca} \sim \text{Mg}$.

On the other hand, Lewis acidities were created by evacuation at higher temperature than 250°C and these acidities varied in order of $\text{Zn} > \text{Cu} > \text{Cd} \sim \text{Ni} > \text{Co} > \text{Mn} > \text{Ca} \sim \text{Mg}$. Their maximum acid strength decreased qualitatively in order of $\text{Cd} > \text{Zn} \sim \text{Cu} > \text{Ni} \sim \text{Co} > \text{Mn} \sim \text{Ca}$. These orders closely correlate with the electron affinities of metal ions and also with the charge densities at metal ions, especially in the cases of Zn and Cd.

Furthermore, isomerization reactions of *cis*-2-butene to 1-butene and *trans*-2-butene and of 1-butene to 2-butenes were investigated with some metal ion-exchanged silica gel catalysts. The isomerization activities varied in order of $\text{Zn} > \text{Co} \gg \text{Ni} > \text{Mn}$ and were enhanced by evacuation at higher temperature than 200°C, and the selectivities to produce *cis*-2-butene from 1-butene and 1-butene from *cis*-2-butene were in relatively high range.

From these results, it was elucidated that Lewis acid site, metal ion, on silica gel acted as active center for this isomerization reaction and that the influence of the crystal field surrounding the metal ion should be taken into account in addition to its Lewis acidity for understanding the catalytic activity.

1 Introduction

The authors previously investigated the acidities and the catalytic activities of the halogenated silica gels and proposed the mechanism of enhancement of the acidities in silica gels by halogenation¹⁾, and further studied the exchange reaction of the surface protons in silica gel with some metal ions and the coordination states of these exchanged metal ions^{2),3)}.

This paper deals with the acidities and the catalytic activities of these metal ion-exchanged silica gels to elucidate the nature of acid sites created by metal ion exchange in connection with the halogenated silica gel and the cationated zeolite. Besides the study on the activities and selectivities of metal ion-exchanged alumina catalysts conducted by Okada and Shirasaki⁴⁾ for disproportionation and hydrogenation of toluene and dehydrogenation of cyclohexane, other investigations along this line are very few.

2 Experimental

2.1 Silica Gel

Silica gel prepared by decomposition of purified ethyl silicate was stored in drying bottle

after calcination at 500°C for 3 hrs. Its BET surface area measured by N_2 at -183°C was 660 m²/g¹⁾.

2.2 Exchange by Metal Ion

The silica gel was impregnated in mixed aqueous solution of desired metal nitrate (0.05 mol/l) and ammonium acetate (0.5 mol/l) under stirring at room temperature for several hours²⁾.

The metal ion content of silica gel was measured by EDTA titration method using indicators; murexide for Ni, Co and Mn; eriochrome black T for Cu and Zn; PAN for Cd.

2.3 Acidity

The total acidity of sample was determined by the Tamele's method with dimethyl yellow ($\text{p}K_a = +3.3$) as indicator and the distribution pattern of acid strength was also investigated with Hammett's indicators of $\text{p}K_a +4.8$, $+4.0$, $+3.3$, $+1.5$ and $+0.8$ respectively.

Furthermore, relative amounts of Lewis acidity and Brönsted acidity by analyses of infrared spectra of pyridine adsorbed on the samples. The pyridine treatments were carried out in the *in situ* cell at 100°C, and the spectra were recorded on a Nihonbunko IR-S type spectrometer after evacuation of excess pyridine at room temperature.

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2.4 Catalytic Activity for Butene Isomerization

Isomerizations of 1-butene to 2-butenes and of *cis*-2-butene to 1-butene and *trans*-2-butene were followed by static method under an atmospheric pressure. Reacted gas was analysed by gas chromatography (4.5 m column of 30% dimethylsulfolane on C-22, carrier gas; H₂, room temp.).

3 Experimental Results and Discussion

3.1 Acidity of Metal Ion-exchanged Silica Gel

Solid acidity was created by metal ion exchange of the surface silanol of silica gel. The total acidities ($pK_a = +3.3$) of some metal ion-exchanged silica gels ($\text{Me}(\text{NO}_3)_2\text{-SiO}_2^*$) increased with their metal ion contents as shown in **Fig. 1**. However, their created acidities were relatively small in comparison with amounts of metal ions in these samples. The ratios of acidities to metal ion contents were ca. 0.5 for $\text{Zn}(\text{NO}_3)_2\text{-SiO}_2$, ca. 0.25 for $\text{Cd}(\text{NO}_3)_2\text{-SiO}_2$, ca. 0.09 for $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$ and $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ respectively.

The total acidities of these samples varied with temperature of heating under vacuum for several hours. The correlations between total acidities and heating temperature for some samples were shown in **Fig. 2** (Co, Cd and Zn) and **Fig. 3** (Ni).

In general, acidity was enhanced by heating at higher temperature than 200°C, but the

Fig. 1 Variation of Total Acidity of $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ Evacuated at 100°C with Metal Ion Content

*) In this paper, metal ion-exchanged silica gel prepared in nitrate solution is abbreviated as $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$.

Fig. 2 Variation of Acidity with Heating Temperature under Vacuum

Fig. 3 Variation of Acidity with Evacuation Temperature and Ni Ion Content for $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$

variation feature was characteristic of the kind of metal ion. Especially, in the case of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ evacuated at high temperature, 400°C, the correlation curve between acidity and Ni ion content was very complex and two peaks of acidities were observed at 0.43 and 1.6 (mmol/g) of Ni ion contents as shown in

Fig. 3.

The authors studied previously the behaviors of the anions in these evacuated samples and found that nitrate anion could be removed by evacuation at 300°C, but it was difficult to remove chlorine ions from the surface under the same condition. Therefore, it was deduced that the nature of acid site created on these $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ samples by evacuation at higher temperature than 300°C differs from that evacuated at lower temperature.

This was examined by infrared spectra of pyridine adsorbed on these samples. The infrared spectra of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ (Ni; 1.4 mmol/g)-pyridine system were shown in **Fig. 4(a)** and the variations of absorption intensities at 1,450 cm^{-1} and 1,540 cm^{-1} with evacuation temperature were also shown in **Fig. 4(b)**.

1. Evacuated at 100°C before pyridine adsorption
2. Evacuated at 250°C before pyridine adsorption
3. Evacuated at 350°C before pyridine adsorption

Fig. 4(a) Infrared Spectra of $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ -Pyridine System

Fig. 4(b) Variation of Absorption Intensities* at 1,450 cm^{-1} and 1,540 cm^{-1} with Evacuation Temperature

* The differences of the absorptions at respective wave numbers before and after the pyridine adsorption were adopted as their relative absorption intensities

As reported by Parry⁵⁾ and Ward⁶⁾, absorption bands at 1,447~1,460 cm^{-1} and 1,600~1,633 cm^{-1} are due to pyridine adsorbed on Lewis acid site, those at 1,485~1,500 cm^{-1} and 1,540~1,550 cm^{-1} to pyridinium ion caused by Brönsted acid site and those at 1,440~1,447 cm^{-1} and 1,580~1,600 cm^{-1} to hydrogen bonded pyridine.

So, these spectra for $\text{Ni}(\text{NO}_3)_2\text{-SiO}_2$ indicate that Brönsted acid sites are predominant for the sample evacuated at lower temperature and Lewis acid sites are created by evacuation at temperature above 250°C with decreasing of Brönsted acid sites. In the cases of $\text{Zn}(\text{NO}_3)_2\text{-SiO}_2$ and $\text{Co}(\text{NO}_3)_2\text{-SiO}_2$, similar results were also observed.

The total acidities of some $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ (metal ion content; 0.37~0.55 mmol/g) evacuated at 100°C and 300°C respectively were lumped in **Table 1** together with the electronegativities of metal ions.

The acidities of the samples evacuated at 100°C, mainly Brönsted type ones, decreased in order of $\text{Zn} \gg \text{Cd} > \text{Co} > \text{Ni} \sim \text{Cu} > \text{Mn} \sim \text{Ca} \sim \text{Mg}$. On the other hand, Lewis acidities created by evacuation at 300°C varied in order of $\text{Zn} > \text{Cu} > \text{Cd} \sim \text{Ni} > \text{Co} \geq \text{Mn} > \text{Ca} \sim \text{Mg}$.

The acid strength of these samples evacuated at 300°C were qualitatively shown in **Table 2**

Table 1 Total Acidities ($\text{p}K_a = +3.3$) of $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ Samples

Metal Ion	Metal Ion Content (mmol/g)	Total Acidity (meq/g)		Electronegativity of Metal Ion ^{a)}
		Evacuated at 100°C	Evacuated at 300°C	
Mn(II)	0.43	trace	0.03	7.5
Co(II)	0.47	0.05	0.04	9.0
Ni(II)	0.42	0.03	0.08	9.0
Cu(II)	0.44	0.03	0.11	9.5
Zn(II)	0.45	0.19	0.15	8.0
Cd(II)	0.52	0.13	0.08	8.5
Ca(II)	0.55	trace	0	5.0
Mg(II)	0.37	trace	0	6.0

a) Catalysis Soc., "Shokubai Binran", 752, (1967) Chijin Shokan.

Table 2 The Acid Strength of $\text{Me}(\text{NO}_3)_2\text{-SiO}_2$ ^{a)}

Acid Strength $\text{p}K_a$	Indicator	Metal Ion						
		Ca	Mn	Co	Ni	Cu	Zn	Cd
+4.8	Methyl red	+	+	+	+	+	+	+
+4.0	Phenylazonaphthylamine	-	+	+	+	+	+	+
+3.3	Dimethyl yellow	-	-	+	+	+	+	+
+1.5	Phenylazodiphenylamine	-	-	-	-	+	+	+
+0.8	Crystal violet	-	-	-	-	-	-	+

a) Evacuated at 300°C.

+

 shows acidic color.

-

 shows basic or neutral color.

1. Zn (0.43 mmol/g)
2. Cd (1.60 mmol/g)
3. Ni (0.78 mmol/g)

Fig. 5 Variation Pattern of Acidity with pK_a of Indicator

and their maximum acid strength varied in order of $Cd > Zn \sim Cu > Ni \sim Co > Mn \sim Ca$. The variation patterns of acid strength of some samples were also shown in Fig. 5.

These orders of acid strength, especially of Lewis type one, correlate closely with the electronegativities of metal ions except Zn and Cd.

Now as the proton source of Brönsted acidity, (1) water polarized by coordination to metal ion and (2) polarized OH of silanol interacting with the nearest neighbour metal ion such as

may be proposed and case (1) is more probable, because Brönsted acidity decreases by evacuation at $250^\circ C$ as mentioned above, while OH of silanol is stable after evacuation at $400^\circ C$ as previously reported¹⁾.

Next, it is presumed that Lewis acidity is due to the ligand vacancy of metal ion resulted from removing of water or anion by high temperature evacuation.

It might be comprehensible from this presumption regarding acid sources that the acid strength of these metal ion-exchanged silica gels closely correlates with the electronegativities of their metal ions and especially in the cases of Zn and Cd, with the strength of electric fields caused by the charge densities of metal ions.

3.2 Catalytic Activity for Isomerization of Butene

Isomerization of *cis*-2-butene to *trans*-2- and 1-butene was investigated with $Ni(NO_3)_2-SiO_2$ (Ni; 0.24 mmol/g) catalyst.

As shown in Fig. 6, activity and total acidity ($pK_a = +3.3$) of this catalyst was remarkably increased by evacuation at higher temperature than $200^\circ C$. In this reaction, ratio of *trans*-2-butene to 1-butene was small; about 2, in comparison with about 10, in the case of chlorinated silica gel catalyst having only Brönsted acidity¹⁾.

Isomerization of 1-butene to 2-butenes was also investigated with some $Me(NO_3)_2-SiO_2$ (Me: Mn, Co, Ni and Zn) catalysts evacuated at $350^\circ C$. The results were shown in Table 3 together with total acidities and metal ion contents of used catalysts. Ratios of *cis/trans* in produced 2-butenes were in range of 0.7~0.8, larger than the equilibrium value (0.55) at $100^\circ C$.

Correlation between the nature of acid sites and the selectivities (*trans*/1- and *cis/trans*-ratios) in the butene isomerization is rather complex^{7),8)}. However, it might be accepted that the carbonium ion mechanism prevails on strongly acidic catalysts, resulting in high *trans*/1 ratio and that the concerted mechanism gives a predominantly low value of the ratio as reported by Misono et al⁹⁾.

Our results with $Me(NO_3)_2-SiO_2$ catalysts indicate that relatively weak Lewis acid sites are predominant in these catalysts, and that the activities of these catalysts for the butene isomerization increase with their acidities and the ratios of *trans*/1 are considerably low.

Cata., $Ni(NO_3)_2-SiO_2$ (Ni, 0.24 mmol/g)
Reaction temperature, $100^\circ C$
Reaction time, 90 min

Fig. 6 Variation of Activity for Isomerization of *cis*-2-Butene and Acidity with Evacuation Temperature

Table 3 Isomerization of 1-Butene

Catalyst ^{a)} Me(NO ₃) ₂ -SiO ₂ Me	Metal Ion Content (mmol/g)	Total Acidity ^{b)} (meq/g)	Conversion ^{c)} of 1-Butene (%)	Ratio of <i>cis/trans</i> in Produced 2-Butene
Mn	0.52	0.05	32.0	0.73
Co	0.30	0.03	64.0	0.79
Ni	0.31	0.06	37.4	0.84
Zn	0.25	0.08	64.9	0.67

a) Evacuated at 350°C for 3 hrs. b) $pK_a = +3.3$. c) Reaction temperature: 100°C, Reaction time: 30 min.

Table 4 Change of Crystal Field Stabilization Energy (ΔE_c) with Butene Adsorption

Metal Ion	Number of <i>d</i> -Electron	Change of Crystal Field		$-\Delta E_c^{a)}$
		from	to	
Mn(II)	d^5	octahedral	pentagonal bipyramid	0
	d^4	"	"	-1.07 Dq ^{b)}
Ni(II)	d^8	"	"	-4.26 Dq ^{b)}
Co(II)	d^7	tetrahedral	"	+2.56 Dq ^{b)}
		"	square pyramid	+11 kcal/mol ^{c)}
			octahedral	+7.4 kcal/mol ^{c)}
Zn(II)	d^{10}	"	square pyramid	0
	d^9	"	"	+7.36 Dq ^{b)}

a) Weak field assumption was applied for calculation, because ligands were siloxane and oxygen anion in this case.

b) Bassolo, F., Pearson, R. G., "Mechanisms of Inorganic Reactions" 2nd Ed., 141, (1967) John Wiley and Sons, New York.

c) Dowden, D. A., Wells, D., "Actes 2 Congr. Int. Catal., Paris" 1499, (1961) Technip, Paris.

Therefore, in the cases of these catalysts, the coordination of butene to metal ion must be important in the isomerization mechanism.

For the isomerization of 1-butene, Zn(NO₃)₂-SiO₂ and Co(NO₃)₂-SiO₂ were found to be more active than Ni(NO₃)₂-SiO₂ and Mn(NO₃)₂-SiO₂ as shown in **Table 3**. This result may be interpreted as follows.

As previously reported³⁾, Mn(II) and Ni(II) ions are in octahedral ligand field, Zn(II) in tetrahedral, and Co(II) in both octahedral and tetrahedral ones respectively on these metal ion-exchanged silica gels evacuated at above 300°C. Further, in proceeding of the isomerization, butene is adsorbed on metal ion (Lewis acid site) and an increase of the crystal field stabilization energy ($|E_c|$: negative value) accompanied with this butene adsorption is favorable for this reaction. The estimated values of ΔE_c for several cases were shown in **Table 4**. ΔE_c of Co(II) is negative while that of Ni(II) is positive, so it is reasonable that Co(NO₃)₂-SiO₂ is more active than Ni(NO₃)₂-SiO₂. In the case of Zn(NO₃)₂-SiO₂, $|E_c|$ of Zn(II) (d^{10}) is zero, so it is difficult to explain its high activity. As previously reported²⁾, however, π -bonding considerably takes part for coordination bonds of Zn with siloxane of silica gel, and furthermore the electron of Zn(II) may be backdonated to the vacant π -orbital of butene in its coordina-

tion. When number of *d*-electron of Zn(II) decreases to d^9 by these bondings, $|E_c|$ grows to very large value, +7.36 Dq, and this may intensively contribute to high activity of Zn(NO₃)₂-SiO₂.

In conclusion, it was elucidated that the influence of the crystal field surrounding the metal ion should be taken into account in addition to its Lewis acidity for understanding the catalytic activity of the metal ion-exchanged silica gel for butene isomerization.

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