

# Solid Base-Catalyzed Reaction of Nitriles with Methanol to Form $\alpha,\beta$ -Unsaturated Nitriles

## II. Surface Base Property and Reaction Mechanism

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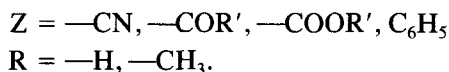
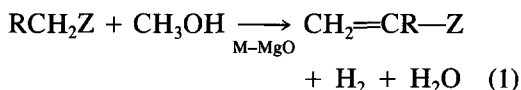
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Solid acid and base properties of magnesium oxides activated by transition metal ions, M–MgO, which are effective catalysts for the reaction of nitriles with methanol to form corresponding  $\alpha,\beta$ -unsaturated nitriles, were studied by temperature-programmed desorption of CO<sub>2</sub> and the reaction of isopropyl alcohol, and the reaction mechanism was studied by isotopic tracer methods. The surface base property of magnesium oxide was modified by the addition of a metal ion; the addition of a metal ion with larger ionic radius than Mg<sup>2+</sup> increases the amount of surface base site, whereas the addition of a metal ion with an ionic radius smaller than that of Mg<sup>2+</sup> induces surface acid sites without any appreciable changes in the amount of surface base site. Active catalysts were formed in the latter case but not in the former case. It was thought that a surface acid property as well as a surface base property played an important role in the course of the reaction. Reaction of deuterium-substituted acetonitrile and methanol revealed that the exchange reaction between hydroxyl hydrogen of methanol and methyl hydrogen of acetonitrile took place readily under the conditions of acrylonitrile synthesis and the isotopic distribution in acetonitrile after the reaction was very close to that of isotopic equilibrium. No exchange reaction between methyl hydrogen of methanol and that of acetonitrile was observed. It was found, on the other hand, that the isotopic exchange reaction between methyl hydrogen of deuterated methanol and light methanol can occur under the same conditions. The reaction mechanism appears to be dehydrogenation of methanol to adsorbed formaldehyde which then reacts with the acetonitrile anion and, after dehydration, yields acrylonitrile. © 1990 Academic Press, Inc.

### INTRODUCTION

As shown in Eq. (1), synthesis of  $\alpha,\beta$ -unsaturated compounds can be accomplished by reaction of methanol with an activated C–H-containing compound. This requires a series of sequential reactions (dehydrogenation, deprotonation, cross coupling, and dehydration) on the surface of the metal oxide catalyst:



To attain high selectivity, it is necessary to suppress undesirable reactions, such as decomposition of methanol to CO and H<sub>2</sub>, polymerization and hydrogenation of the products, and so forth. The roles of added metal ion and surface base sites of the promoted magnesium oxide catalyst are significant for the reaction as described in the first paper in this series (*I*).

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It can be assumed that the abstraction of the methyl or methylene hydrogen which is activated by inductive electron withdrawal by the adjacent unsaturated substituent will take place on the basic site of the oxide catalyst and this intermediate anion will then react with adsorbed formaldehyde or activated methanol to eventually give the product. The activated state of methanol in the reaction and the role of the added metal ion in the reaction are, however, unknown.

In this investigation, solid acid and base properties of the promoted magnesium oxide by metal ion were determined by temperature-programmed desorption (TPD) of  $\text{CO}_2$  and by the reaction of isopropyl alcohol (IPA), and deuterium tracer experiments were carried out in order to elucidate the reaction mechanism.

## EXPERIMENTAL

### *Catalyst*

The catalysts used in this investigation were  $\text{M-MgO}$  ( $\text{M} = \text{Al(III)}, \text{Cr(III)}, \text{Fe(III)}, \text{Mn(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{and Cd(II)}$ ), the preparation procedures of which were the same as those described in the first paper in this series (1). The number in parentheses represents the valency of the metal ion in the preparation solution. Unless noted otherwise, magnesium oxide was treated in water at an ambient temperature for 24 h, dried at 383 K overnight, and calcined at 873 K for 2 h in a nitrogen stream ( $50 \text{ ml} \cdot \text{min}^{-1}$ ) before it was used.

### *TPD of $\text{CO}_2$*

Amounts of surface base sites were estimated for the catalysts from their adsorption capacities of  $\text{CO}_2$ , determined by the temperature-programmed desorption method ( $20 \text{ K} \cdot \text{min}^{-1}$ ) using a flow system (He carrier,  $50 \text{ ml} \cdot \text{min}^{-1}$ ) equipped with a mass spectrometer. TPD spectra of  $\text{CO}_2$  were recorded after  $\text{CO}_2$  adsorption at an ambient temperature on the catalysts which were pretreated at 873 K for 2 h in a He stream.

BET surface area was determined by nitrogen adsorption at 77 K.

### *Reaction of IPA*

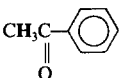




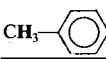
Dehydration and dehydrogenation of isopropyl alcohol were performed at 528 K in a micropulse reactor constructed of quartz glass. Isopropyl alcohol ( $0.5 \mu\text{l}$ ) was injected into a nitrogen carrier gas ( $20 \text{ ml} \cdot \text{min}^{-1}$ ). Products were analyzed with a gas chromatograph. The powdered catalyst (15 mg) was pretreated under the same conditions as in the pretreatment of the TPD measurement.

### *Apparatus and Reaction Procedure*

The reaction of various reagents with methanol was carried out in a continuous flow reactor. Details of the apparatus and reaction procedure have been described earlier (1). The same apparatus was employed for the reaction of deuterium-substituted methanol and acetonitrile. Methanol- $d_1$  ( $\text{CH}_3\text{OD}$ ), methanol- $d_4$  ( $\text{CD}_3\text{OD}$ ), and acetonitrile- $d_3$  ( $\text{CD}_3\text{CN}$ ) were obtained from Merck and ISSOTEC (Matheson). After the reaction had been in progress for 1 h, the materials which passed through a catalyst bed (0.2 g at 603 K) in the next hour were collected in a cold trap (dry ice-methanol) used for the determination of isotopic compositions with a Hitachi M-80 double-focused mass spectrometer equipped with a field ionizer. The field ionization method allows us to determine the isotopic composition directly from signal intensities without any disturbances of fragmentation, so that column separation by gas chromatography was not used. Since the H-D exchange reaction between the hydroxyl hydrogen of methanol and the water that existed in a mass spectrometer took place during measurement, analysis of the deuterated chemicals indicated isotopic purities of 90 ~ 95% for methanol- $d_1$ , 90 ~ 96% for methanol- $d_4$ , and 98 ~ 100% for acetonitrile- $d_3$  which were slightly lower than the certified puri-

TABLE 1

Comparison between the Approximate Acidity ( $pK_a$ ) of  $\alpha$ -Hydrogen of Reactant and the Rate of Reaction with Methanol over Cr-MgO and Fe-MgO Catalysts<sup>a</sup>

Reactant	$pK_a$	Reaction rate ( $\mu\text{mol} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1}$ )	
		3 wt% Cr-MgO	3 wt% Fe-MgO
	19	8.2 <sup>c</sup>	34.9
	20	11.9	11.6
	25	3.8	4.5
	>25	1.9	1.6
	>25	0.1	- <sup>c</sup>
	37	tr	tr

<sup>a</sup> The reactions were run at 623 K with 1.3 kPa of substrate in  $\text{N}_2$  carrier; the methanol/substrate molar ratio was 10 and the space velocity (methanol + substrate +  $\text{N}_2$ ) was  $80 \text{ ml} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1}$ .

<sup>b</sup> Taken from H. O. House, "Modern Synthetic Reactions," 2nd ed. p. 494, Benjamin, California, 1972.

<sup>c</sup> Steady-state activities were not attained.

ties. No other type of H-D exchange reaction took place in a mass spectrometer.

## RESULTS

### Reaction Rate of Various Reagents with Methanol

The reaction rates of methanol with six substrates (acetophenone, acetone, acetonitrile, propionitrile, methyl propionate, and toluene) using Cr-MgO and Fe-MgO catalysts were determined at 625 K and compared with the  $pK_a$  values of their  $\alpha$ -hydrogen. Results are given in Table 1. The reactions were conducted under the same reaction conditions for each substrate as described in the footnote to the table, and the rates listed were calculated for the formation of corresponding  $\alpha,\beta$ -unsaturated compounds.

Acetophenone reacts with methanol at the highest rate; virtually no reaction of toluene was observed. We find that there is a

correlation between the rates of reaction and the  $pK_a$  values of substrates; the reaction rate is higher for the substrate with the lower  $pK_a$  value. Undesirable reactions of methanol such as the decomposition to  $\text{H}_2$  and CO were negligible in the reaction of each substrate except toluene. The reaction of toluene with methanol was accompanied by appreciable decomposition of methanol. Interestingly, the decomposition of methanol became a major reaction when only methanol was reacted over the promoted MgO catalysts. Such reactions did not occur over the unpromoted catalyst.

### Temperature-Programmed Desorption of $\text{CO}_2$

The number of accessible surface base sites on the promoted magnesium oxides with various metal ions was estimated by the amount of chemisorbed  $\text{CO}_2$  molecules. The TPD spectra for chemisorbed  $\text{CO}_2$  are shown in Fig. 1. Table 2 summarizes the

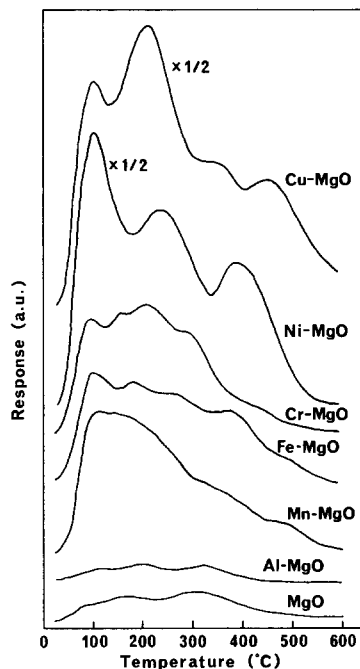


FIG. 1. TPD spectra of adsorbed  $\text{CO}_2$  on various M-MgO catalysts.

TABLE 2  
Amount of Surface Base on Various M-MgO Catalysts

Catalyst (3 wt%)	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Amount of surface base		Fraction <sup>a</sup> (%)
		$10^{-4} \text{ mol} \cdot \text{g}^{-1}$	$10^{-6} \text{ mol} \cdot \text{m}^{-2}$	
MgO <sup>b</sup>	11	0.2	1.9	10.2
MgO	137	3.3	2.4	12.9
Al-MgO	106	0.3	0.2	1.3
Fe-MgO	103	2.1	2.0	10.7
Cr-MgO	105	2.1	2.0	10.7
Mn-MgO	168	5.8	3.5	18.7
Ni-MgO	143	11.4	8.0	42.8
Cu-MgO	124	13.6	11.0	58.8

<sup>a</sup> Calculated by assuming that the amount of total lattice oxide ion per unit surface area is  $1.87 \times 10^{-5} \text{ g-atm}$  for every catalyst.

<sup>b</sup> Commercial oxide (Soekawa Rika, 99.92%).

surface area of each catalyst, the total amount of surface base per gram or per unit surface area, and the fraction of the amount of surface base against that of total surface lattice oxide ions. The desorption of  $\text{CO}_2$  began near 323 K and substantially slowed at about pretreatment temperature (873 K) for every catalyst. Unfortunately, the TPD spectra for the catalysts showed multiple desorption peaks with unidentifiable maxima in the whole temperature-programmed region. It is, therefore, difficult to see clear differences among the TPD spectra obtained for each catalyst. No substantial change seems to occur in the distribution of surface basicity on MgO by the addition of various metal ions. On the other hand, the adsorption capacity of  $\text{CO}_2$  for each catalyst was found to depend strongly on the kind of metal ion added.

A comparison of the amount of surface base site per unit surface area for each catalyst (Table 2) reveals that  $\text{Cu}^{2+}$  ion and  $\text{Ni}^{2+}$  ion show the pronounced effect of increasing the amount of surface base of MgO. The amounts of surface base on these catalysts were 4–5 times as high as that on MgO and correspond to about 50% of the total surface oxide ion. Such an increase was also observed for the  $\text{Cd}^{2+}$  ion- or  $\text{Mn}^{2+}$  ion-containing MgO catalyst but was not so remarkable as that for the Cu or Ni ion-containing

one. The addition of  $\text{Fe}^{3+}$  ion or  $\text{Cr}^{3+}$  ion had no effect on the surface basicity. In contrast to the above results, the amount of surface base per square meter was drastically decreased by the addition of  $\text{Al}^{3+}$  ion.

The amount of surface base was plotted against the ionic radius of added metal ion in Fig. 2. MgO has a nondirectional simple ionic crystal with NaCl structure, and coordination numbers of both  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  are 6. The values of ionic radius in Fig. 2 are those for the metal ion with coordination number of 6 (2), considering that the metal ion introduced into the lattice of MgO may settle down to the same circumstance as  $\text{Mg}^{2+}$ . The valencies of metal ions are based on the starting materials in the preparation of catalysts. For Fe-MgO and Cr-MgO catalysts, the valencies of Fe and Cr were confirmed to be 3+ by ESR measurements and not to change after the heat treatment. Similarly, the valency of Cu ion in Cu-MgO after the heat treatment was confirmed to be 2+ by ESR signal. Since for the Mn-MgO catalyst the valency of surface Mn ion was 4+ as ascertained by XPS analysis, the amount of surface base obtained for Mn-MgO was plotted against the ionic radius of both  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  in the figure.

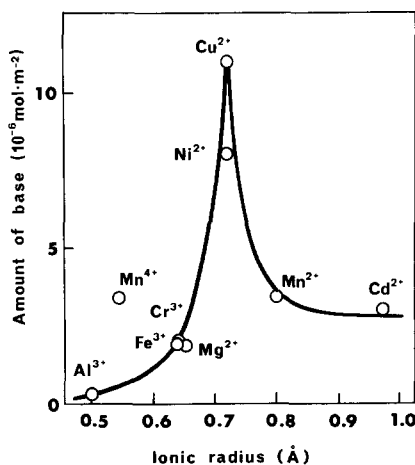


FIG. 2. Relationship between the amount of surface base of metal ion-containing MgO and the ionic radius of added metal ion.

As can be seen in Fig. 2, the amount of surface base drastically increased with the addition of a metal ion with an ionic radius slightly larger than that of  $Mg^{2+}$ , whereas the amount of base either decreased or remained unchanged when a metal ion with an ionic radius smaller than that of  $Mg^{2+}$  was added to MgO. The addition of metal ion with a far larger ionic radius, such as  $Cd^{2+}$ , is clearly ineffective for the enhancement of surface basicity.

The relationship obtained between the amount of surface base of metal ion containing MgO and the ionic radius of added metal ion is explained as follows. When the metal ion with a radius larger than that of  $Mg^{2+}$  is incorporated into the MgO lattice, a distortion occurs in the lattice which surrounds the added metal ion. The distortion may result in the expansion of the Mg-O bond length and in the localization of an electron on the oxygen atom. Consequently, the solid base property may appear or increase. That the addition of a metal ion with a far larger ionic radius showed the smallest effect may be ascribed to the fact that the metal ion is not able to incorporate into the lattice because of its larger ionic radius. It has already been clarified by IR study that the surface base site on alkaline-earth oxide was ascribed to lattice oxide ion (3), but there are many ambiguous points concerning its basic property. The above novel enhancement effect of added metal ion on surface basicity may prove an important structural factor for the solid base.

#### IPA Conversion

In order to confirm the above results, isopropyl alcohol conversion was studied to test the dehydrogenation abilities of the catalysts, as the dehydrogenation of IPA is a well-known base-catalyzed reaction. Results are shown in Table 3. All catalysts mainly catalyze the acetone formation. MgO and Al-MgO showed a dehydrogenation activity low for forming acetone. Fe-MgO, Cr-MgO, and Mn-MgO showed high activities for IPA conversion. Since the

TABLE 3

Dehydrogenation and Dehydration of Isopropyl Alcohol over the Various M-MgO Catalysts

Catalyst (3 wt%)	Conversion (%)	Selectivity (%)	
		Acetone	Propylene
MgO <sup>a</sup>	2.9	100	0
Al-MgO	2.3	~100	tr
Fe-MgO	29.3	95.1	4.9
Cr-MgO	30.5	92.4	7.6
Mn-MgO	47.9	~100	tr
Ni-MgO	44.5	100	0
Cu-MgO	81.2	100 <sup>b</sup>	0

<sup>a</sup> Commercial oxide.

<sup>b</sup> Produced acetone partly condensed to give mesityl oxide.

surface area of these catalysts is about 10 times larger than that of MgO tested here, their activities per unit surface area are virtually the same level as that of MgO. The Cu-MgO catalyst showed the highest activity for the IPA conversion, as expected from Table 2. In the case of Ni-MgO catalyst, the conversion of IPA was slightly lower than the value which can be expected from the amount of surface base of the catalyst. Nevertheless, the above activity order of catalysts almost parallels the results on surface basicity determined by  $CO_2$  adsorption, confirming the enhancement of surface base property of MgO by the combination of metal ion.

#### Catalytic Activity and Surface Basicity

We measured the catalytic activity of MgO promoted by manganese ion with different metal ion loadings for the reaction of propionitrile with methanol and compared the activity with the amount of surface base sites. The latter were determined by temperature-programmed desorption of adsorbed  $CO_2$ . Results are illustrated in Fig. 3. The catalytic activity of magnesium oxide is dramatically improved by the addition of up to 5 wt%. Above this the activity decreases.

A similar maximum was also observed

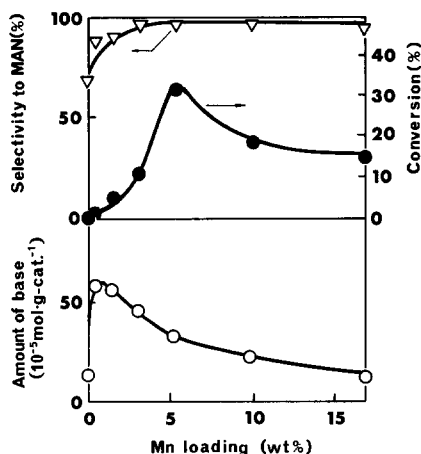


FIG. 3. Effects of the manganese ion loading on the catalytic activity, the selectivity of Mn-MgO catalyst in the reaction of propionitrile with methanol, and the basicity. The reaction was run at 623 K with 0.4 kPa of propionitrile in  $N_2$  carrier; the methanol/propionitrile molar ratio was 10 and the space velocity was  $73 \text{ ml} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1}$ . The surface basicity was determined by  $CO_2$  adsorption.

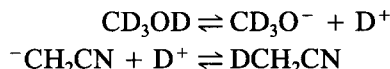
with the amount of surface base sites with variation of the Mn loading. The maximum, however, appeared at a loading lower than that observed in the activity. It is apparent that the loading which gave the maximum amount of surface base does not result in a catalyst showing the highest activity: The catalytic activity for the reaction is not necessarily proportional to the number of basic sites on the catalyst surface.

#### Deuterium Tracer Experiments

Deuterium isotope effects on the rate of acrylonitrile formation in the reaction of acetonitrile with methanol were investigated. The results are shown in Table 4. Under the reaction conditions shown in the footnotes to the table, the conversion of acetonitrile was less than 1% and the reaction was nearly quantitative. The kinetic isotope effect on the rate was clearly observed only when the methanol deuterated at the methyl group was allowed to react at 603 K, giving  $k(\text{CH}_3\text{OH})/k(\text{CD}_3\text{OD}) = 2.2$ . No kinetic isotope effects were caused by deuterium sub-

stitution at hydroxyl hydrogen of methanol and acetonitrile.

The isotope distributions in *d*-methanol and *d*-acetonitrile were measured by mass spectrometry after the reactions over 3 wt% Mn-MgO and MgO catalyst; these experimental results are summarized in Tables 5 and 6, respectively. When a mixture of methanol- $d_4$  and acetonitrile- $d_0$  (10:1) was passed over Mn-MgO catalyst at 603 K, variously deuterated methanol and acetonitrile were formed. The acetonitrile consists of four deuterated isomers and its isotopic distribution was very close to that calculated for the isotopic equilibrium. The fraction of methanol- $d_3$  increased in step with a decrease of the fraction of methanol- $d_4$ ; the contents of methanol- $d_0$ , methanol- $d_1$ , and methanol- $d_2$  were almost unchanged. It is evident that the methanol- $d_3$  formed is  $CD_3OH$  and the hydrogen of acetonitrile is scrambled almost exclusively with the O-D group of the  $CD_3OD$ :



The ratio of methanol- $d_3$  to methanol- $d_4$  (0.36) is equal to the calculated ratio (0.36) of the number of hydrogen atoms in acetonitrile to the number of deuterium atoms in the O-D group of the deuterated methanol (after taking impurities into account). These results clearly show that the exchange reaction

TABLE 4

Kinetic Isotope Effect on the Rate of Acrylonitrile Formation in the Reaction of Acetonitrile with Methanol over 3 wt% Mn-MgO Catalyst<sup>a</sup>

Reactants	Rate of formation ( $\times 10^{-6} \text{ mol} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1}$ )
$CH_3OH + CH_3CN$	2.6
$CD_3OD + CH_3CN$	1.2
$CH_3OD + CD_3CN$	2.4

<sup>a</sup> Reaction conditions: reaction temperature, 603 K; the methanol/acetonitrile molar ratio, 10; catalyst weight, 0.2 g; and space velocity ( $CH_3OH + CH_3CN + N_2$ ),  $315 \text{ ml} \cdot \text{min}^{-1} \cdot \text{g-cat}^{-1}$ .

TABLE 5

H-D Isotope Exchange between Methanol and Acetonitrile over 3 wt% Mn-MgO Catalyst<sup>a</sup>

Reactant	Acetonitrile conversion (%)	Sampling <sup>b</sup>	Isotope distribution (%)								
			Methanol					Acetonitrile			
			<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>
10CD <sub>3</sub> OD + CH <sub>3</sub> CN	0.5	Inlet	0	0	6	4	90	100	0	0	0
		Outlet	0	0	6	25	69	3	25	42	30
							(4)	(22)	(44)	(30) <sup>c</sup>	
10CH <sub>3</sub> OD + CD <sub>3</sub> CN	1.1	Inlet	4	94	1	1	0	0	0	0	100
		Outlet	5	90	2	3	0	0	0	0	100

<sup>a</sup> Reaction conditions are the same as those shown in the footnotes to Table 2.<sup>b</sup> Mass spectrometric analysis was carried out for the samples in the inlet and outlet of the reactor.<sup>c</sup> The values in parentheses are calculated deuterium distributions in acetonitrile at the isotopic equilibrium.

between hydroxyl hydrogen of methanol and hydrogen of acetonitrile takes place readily and is part of the overall methanol-acetonitrile reaction. Similarly, a mixture of methanol-*d*<sub>4</sub> and acetonitrile-*d*<sub>0</sub>, when passed over MgO catalyst at 603 K, also gave various deuterated products as shown in Table 6. The isotopic distribution in acetonitrile, however, did not reach equilibrium.

Tables 5 and 6 yield other important information. When a mixture of methanol-*d*<sub>1</sub>(CH<sub>3</sub>OD) and acetonitrile-*d*<sub>3</sub> was passed over Mn-MgO catalyst under the same reaction conditions, almost identical isotopic distributions for both methanol and acetonitrile

were obtained before and after the reaction within experimental error. Exactly the same result was observed with the MgO catalyst as shown in Table 6. The facts imply that the exchange reaction between methyl hydrogen of methanol and of acetonitrile is a far more difficult process relative to the above-mentioned exchange reaction.

Additional experiments were carried out with a mixture of methanol-*d*<sub>4</sub> and methanol-*d*<sub>1</sub>(CH<sub>3</sub>OD). The results are listed in Table 7. It was found that methanol-*d*<sub>2</sub> and methanol-*d*<sub>3</sub> were formed when the mixture was passed over Mn-MgO catalyst at 603 K. A H-D material balance, before vs after the

TABLE 6

H-D Isotope Exchange between Methanol and Acetonitrile over MgO Catalyst<sup>a</sup>

Reactant	Acetonitrile conversion (%)	Sampling <sup>b</sup>	Isotope distribution (%)								
			Methanol					Acetonitrile			
			<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>
10CH <sub>3</sub> OD + CD <sub>3</sub> CN	tr	Inlet	8	88	1	3	0	0	0	0	100
		Outlet	8	88	1	3	0	0	0	2	98
10CH <sub>3</sub> OH + CD <sub>3</sub> CN	tr	Inlet	97	2	1	0	0	0	0	0	100
		Outlet	83	16	1	0	0	23	23	19	35

<sup>a</sup> Reaction conditions are the same as those shown in the footnotes to Table 2.<sup>b</sup> Mass spectrometric analysis was carried out for the samples in the inlet and outlet of the reactor.

TABLE 7

H-D Isotope Exchange Reaction of Methyl Group of Methanol over Mn-MgO and MgO

Catalyst	Reaction condition <sup>a</sup>	Acetonitrile conversion (%)	Isotope distribution (%)								Deuterium content in methyl group(%)	Percentage exchanged	
			Methanol				Acetonitrile						
			d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>			d <sub>3</sub>
Mn-MgO (3 wt%)	A	(Inlet)	3	48	5	4	40	0	0	0	100	45.3	52.0
		1.0 (Outlet)	0	30	22	20	28	0	0	0	100	48.7	
	B	(Inlet)	5	46	1	5	43					48.3	70.2
		— (Outlet)	1	22	27	27	23					50.3	
MgO	A	(Inlet)	4	48	1	4	42	0	0	0	100	46.3	38.9
		0 (Outlet)	1	39	15	12	33	0	0	0	100	46.3	
	B	(Inlet)	4	46	1	4	45					49.3	50.0
		— (Outlet)	1	29	18	21	31					51.3	

<sup>a</sup> Two reaction conditions were employed: condition A, reaction temperature, 603 K; feed gas composition, N<sub>2</sub>: CD<sub>3</sub>OD: CH<sub>3</sub>OD: CD<sub>3</sub>CN = 52:5:5:1; space velocity (including N<sub>2</sub>), 315 ml · min<sup>-1</sup> · g-cat<sup>-1</sup>; condition B, feed gas composition, N<sub>2</sub>: CD<sub>3</sub>OD: CH<sub>3</sub>OD = 52:5:5; others are the same as those of condition A.

reaction, showed no net gain or loss of H or D. Therefore, it can be concluded that the d<sub>2</sub>- and d<sub>3</sub>-methanol do not result from the uptake of hydrogens present originally on the surface of the catalyst.

The isotope distribution in methanol did not reach the equilibrium distribution, suggesting that the rate of this exchange reaction is not as fast as that of the exchange reaction of hydroxyl hydrogen of methanol. This novel exchange reaction was further confirmed by the use of MgO catalyst. It can be seen from Table 7 that the exchange reaction proceeds over unpromoted MgO catalyst but the rate is slightly lower than that over the Mn-MgO catalyst. In addition, when a small amount of CD<sub>3</sub>CN was added to the reactant feed, the rate of the exchange reaction decreased slightly because of the strong adsorption of acetonitrile; however, no hydrogen atom was found in acetonitrile, although the exchange reaction of hydrogen between the methyl group of acetonitrile and the hydroxyl group of methanol occurs readily under the present reaction conditions.

#### DISCUSSION

In the solid base-catalyzed reaction with methanol, the C-H bond of the methyl or

methylene groups of other reactants must be activated by electron withdrawing groups such as carbonyl, cyano, or phenyl. The intermediate carbon anion, formed after the abstraction of acidic hydrogen by a surface basic site, reacts with adsorbed methanol to give the product. Therefore, one of important factors in the mechanistic consideration is the activated state of methanol on the oxide surface. By analogy with Aldol type reactions and with the proposed mechanism for the alkylation of toluene over solid bases to give styrene and ethylbenzene (4-6), it is likely that the present reaction may proceed via a formaldehyde intermediate formed from methanol by dehydrogenation, followed by condensation with the carbon anion.

The exchange reaction between the hydroxyl hydrogen of methanol and the methyl hydrogen of acetonitrile (Table 5) takes place readily and the isotopic distribution in acetonitrile is close to that at the isotopic equilibrium, indicating that the dissociation step of acetonitrile on the surface basic site to form a proton and carbon anion is an equilibrium reaction. It is, therefore, evident that the dissociation of the C-H bond of acetonitrile is not a rate determining step.

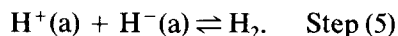
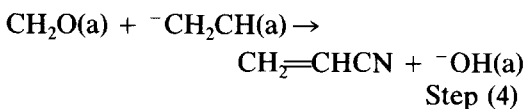
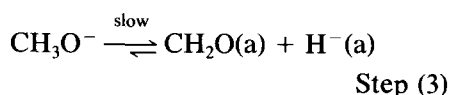
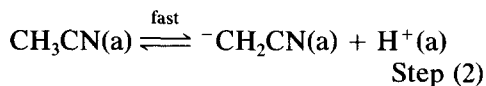
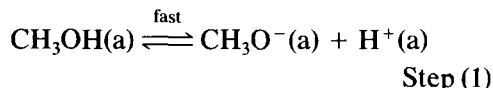


Table 5 also shows that the isotopes are scrambled completely in the methyl group of acetonitrile and the hydroxyl group in methanol. This shows that the dissociation step in O–H bond of methanol is not involved in the rate determining step. This situation is almost independent of the presence of the added metal ion in the catalyst (Tables 5 and 6), so that these two dissociation steps may be promoted only by the surface base sites.

No exchange reaction between the methyl hydrogen of methanol and that of acetonitrile was observed, on the other hand (Table 5), and a clear kinetic isotope effect was observed as shown in Table 4. These facts strongly suggest that the rate determining step is dissociation of the C–H bond of methanol. However, it was also found that the isotopic exchange reaction of methyl hydrogens between deuterated methanol and light methanol can occur readily under the same condition (Table 7). This novel exchange reaction is very interesting but its reaction mechanism is not fully understood. Nevertheless, a probable mechanism can be deduced by assuming that the reaction is analogous to the transfer hydrogenation of ketones with alcohol (7–11). Thus, once an adsorbed formaldehyde species is formed by dehydrogenation of methanol over the oxide surface, the methyl hydrogen of adsorbed methanol can transfer to such adsorbed species. The adsorbed methanol then changes to another adsorbed formaldehyde and the initially adsorbed formaldehyde changes to an adsorbed methanol after the hydrogen transfer. When deuterated methanol and light methanol are reacted, one can observe the hydrogen exchange at the methyl group of methanol as the reaction cycle is repeated. Since the transfer hydrogenation usually takes place rapidly over the oxide surface (7–11), the isotope exchange might proceed at a considerable rate with the presence of a small amount of adsorbed formaldehyde without the production of formaldehyde in gas phase. Hence the occurrence of such an exchange reaction may

not rule out but rather support the assumption that the dissociation of C–H bond of methanol is the rate determining step.

On the basis of the above considerations the following reaction steps in the methylation of acetonitrile with methanol as a representative are depicted:



There is no doubt that steps (1) and (2) are in an equilibrium state. Step (3) is rate determining and forms an adsorbed hydride species. Step (4) is much faster than step (3) because a mixture of acetonitrile with formaldehyde, when passed over solid base catalyst, gives acrylonitrile readily (573–623 K). If the  $pK_a$  value of the reactant is too high as in the case of toluene, the rate-determining step becomes step (2).

The role of added metal ion is now discussed in relation to the above reaction mechanism. Since the rate determining step is the hydrogen abstraction from adsorbed methoxy anion species (step (3)), the improvement in catalytic activity and selectivity by the addition of metal ion may be attributed to the enhancement of the hydrogen abstracting ability of the oxide catalyst. Two reasons could exist for the rate enhancement: (1) modification of surface basic property, and (2) cooperative action of added metal ion and the basic site.

It is already evident from the tracer results that the solid base property plays an important role in the course of the reaction.

If the dehydrogenation of methanol which is the rate determining step is also controlled only by the surface base property, the order of the catalytic activity for the methylenation in various metal ion-containing MgO should coincide with that for both CO<sub>2</sub> adsorption capacity and IPA conversion. However, an apparent discrepancy arose, as can be seen in Tables 2 and 3: The addition of Fe<sup>3+</sup>, Cr<sup>3+</sup>, and Mn<sup>2+</sup> to MgO, which gave good catalysts for the reaction, did not result in the formation of any specific surface base site as determined by temperature-programmed desorption experiments with CO<sub>2</sub>. The addition also caused no increase in the rate of dehydrogenation of IPA to acetone. Furthermore, Fig. 3 shows that the catalytic activity to form  $\alpha,\beta$ -unsaturated compounds is not necessarily proportional to the concentration of basic sites. Therefore, these facts exclude the first possibility and suggest that some other catalytic property besides surface base should be taken into account.

Table 3 also gives us another important piece of information. One may note from Table 3 that some of the catalysts promote the dehydration of IPA to form propylene. The results are shown in the last column of the table. The catalysts which showed the activity for the formation of propylene were Al-MgO, Fe-MgO, Cr-MgO, and Mn-MgO. Since the surface acid property can be estimated from the formation of propylene in the conversion of IPA, the result indicates that these added metal ions can exist as acidic sites on the basic surface of MgO. Interestingly, the catalysts, except Al-MgO, active in the formation of propylene in the IPA conversion are effective for the reaction of acetonitrile with methanol. This coincidence strongly suggests that the second possibility is valid and that the surface acid property of the added metal ion as well as the base property is necessary for the active catalysts to promote the reaction of nitrile selectively. The reason for the poor activity of Al-MgO catalyst in spite of its acid property is a lack of

surface base property. The low activity of the Cu-MgO catalyst is due to a lack of acidic property. It can thus be said that the catalysts which have both acid and base properties are effective for the reaction and those which only show either acid or base property are ineffective.

On the basis of the above consideration, the correlation between the rate of reaction and the  $pK_a$  value (Table 1) is now discussed as follows: Methoxy anion formed by O-H dissociation on the surface base site may be adsorbed on the added metal ion site because the metal ion is a stronger Lewis acid than magnesium ion. Similarly an intermediate methylene anion formed by  $\alpha$ -hydrogen abstraction by the surface basic site may also be adsorbed on the added metal ion site. Methoxy anion is normally a much weaker base than intermediate carbon anion; these intermediate anions may be adsorbed more strongly on the added metal ion site than methoxy anion. The intermediate anion formed from the substrate with higher  $pK_a$  value can be adsorbed more stably with an electron donated to the metal ion site because the corresponding conjugated anion formed from the substrate with a higher  $pK_a$  value is a stronger base. Therefore, the hydride accepting ability of metal ions from adsorbed methoxy anions may be affected by the adsorption of intermediate methylene anions, depending strongly on the kind of substrate used. Since the hydride accepting ability of the metal ion is directly related to the rate determining step, the reaction rate must decrease with the increasing  $pK_a$  value of the substrate as observed in Table 1.

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