

Surface Property and Catalytic Activity of MgO-TiO₂

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The acid base and reducing properties of MgO-TiO₂ of various compositions—binary mixtures of a basic oxide (MgO) and an acidic oxide (TiO₂)—were studied and compared with their catalytic activities for the decomposition of diacetone alcohol, the dehydration of 4-methyl-2-pentanol, and the alkylation of phenol with methanol. The acidity of TiO₂ decreased upon addition of MgO, whereas the basicity of MgO was found to increase upon addition of 10 wt% TiO₂. The decomposition rate of diacetone alcohol was correlated well with the basicity of MgO-TiO₂ of different compositions, while the dehydration of 4-methyl-2-pentanol was correlated with the acidity. On the other hand, a maximum conversion of the alkylation was observed over MgO-TiO₂ (weight ratio, 1:1) which has both basicity and acidity. No correlation was found between the reducing property and catalytic activity. The hydrogen exchange reaction of propylene with D₂O or D₂ over MgO-TiO₂ (1:1) was shown by microwave spectroscopy to proceed via π -allyl carbanion or isopropyl carbenium ion intermediates, indicating that the active sites are basic and acidic, respectively.

INTRODUCTION

Titanium oxide is classified as a solid acid (1, 2), while magnesium oxide is classified as a solid base (1, 3, 4). How is a binary oxide, MgO-TiO₂, which consists of a solid base and a solid acid classified? How is the basic property of MgO and acidic property of TiO₂ changed by the addition of TiO₂ and MgO, respectively? The present work was initiated to answer these questions. The binary oxide was then applied as a catalyst to the decomposition of diacetone alcohol, the dehydration of a secondary alcohol, the alkylation of phenol with methanol, and the hydrogen exchange reaction of propylene with D₂O or D₂. The correlations of the surface property of TiO₂-MgO with catalytic activity are demon-

strated and the reaction intermediates of the exchange reactions are elucidated.

EXPERIMENTAL

Catalyst. MgO-TiO₂ was prepared by kneading magnesium oxide and titanate acid with a small amount of deionized water in a mortar for 2 h, followed by drying at 110°C for 8 h and by calcining in air at 300-700°C for 3 h. Magnesium hydroxide and titanate acid were precipitated by adding dropwise 28% of ammonia water to each aqueous solution of MgCl₂·6H₂O (Wako Pure Chemical Industries, Ltd., GR) and TiCl₄ (Wako Pure Chemical Industries, Ltd., EP), the final pHs being 9.6 and 9.4, respectively. Each precipitate was washed with deionized water, until no chlorine ion

was detected in the washings, and dried at 110°C for 14 and 8 h, respectively.

Differential thermal analysis-thermal gravimetric analysis and X-ray analysis. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were carried out simultaneously in air at a heating rate of 10°C/min. X-Ray diffraction patterns were measured over the range of $2\theta = 10-65^\circ\text{C}$ for the powdered samples which had been calcined in air at various temperatures for 3 h.

Surface area and acid-base and reducing properties. Surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at -196°C . Acidity and acid strength of solid surface were determined by Benesi's method (5), using various Hammett indicators. The indicators used were neutral red ($\text{p}K_a = +6.8$), methyl red (+4.8), phenylazonaphthylamine (+4.0), *p*-dimethylaminoazobenzene (+3.3), benzeneazodiphenylamine (+1.5), and dicinnamalacetone (-3.0). Basicity and base strength were determined by observing the color change of 2,4,6-trinitroaniline ($\text{p}K_{\text{BH}} = 12.2$), 2,4-dinitroaniline (15.0), 4-chloro-2-nitroaniline (17.2), and 4-nitroaniline (18.4) and by titrating with benzoic acid using the indicators, respectively (6, 7).

The reducing property of solid surface was measured by observing the anion radicals of nitrobenzene which had been formed by adsorption on the surface by X-band ESR spectra. The amount of anion radicals was estimated by using DPPH as a standard. The nitrobenzene used was purified by repeating a freezing-thawing cycle *in vacuo*.

Reaction procedure. The decomposition of diacetone alcohol was carried out at $32 \pm 0.5^\circ\text{C}$ in a static system. Twenty-five milliliters of diacetone alcohol, purified by repeating a vacuum distillation three times, was reacted over a powdered catalyst calcined at 400°C with vigorous stirring, and the amount of acetone, which was the

only product, was determined by gas chromatography. The reaction obeyed the first-order rate equation and the rate constant was taken as catalytic activity.

The alkylation of phenol with methanol was carried out at 400°C by using a conventional flow method apparatus. A mixture of phenol and methanol (molar ratio = 1:1) was passed together with nitrogen through a catalyst bed, the flow rate being 0.375 ml/sec. About 0.5 g of a catalyst (20-30 mesh) which had been calcined in air at 500°C for 3 h was further calcined in the catalyst bed under a stream of nitrogen at reaction temperature for 30 min. The reaction products were trapped with ice and analyzed by gas chromatography on a column containing 25% DC-550 on Shimalite. The catalytic activity and selectivity were expressed by [(mole percentage of all alkylated products per mole percentage of supplied phenol) $\times 100$] and [(mole percentage of particular product per mole percentage of all alkylated products) $\times 100$], respectively.

The reaction of 4-methyl-2-pentanol was carried out by a conventional flow method using nitrogen as carrier gas at 250°C. Alcohol vapor, the pressure (25 mm Hg) of which was kept constant in an alcohol saturator, was passed together with nitrogen through a reaction tube containing 2 g of catalyst (16-24 mesh). The reaction products were collected in a liquid nitrogen trap and analyzed by gas chromatography, as reported previously (8). Catalytic activity was obtained from the linear plot of conversion percentage against contact time (W/F ; W :catalyst weight, F :flow rate of alcohol).

The hydrogen exchange reaction of propylene with irreversibly adsorbed heavy water or deuterium was carried out at 182°C under the initial pressure of propylene (122 Torr) or at -80°C under the initial pressures of propylene (106 Torr) and deuterium (124 Torr). Heavy water of 99.75% purity and propylene purified by

TABLE 1
Specific Surface Areas of MgO-TiO₂ Calcined at Various Temperatures

| Calcination temperature (°C) | Surface area (m ² /g) | | | | |
|------------------------------|----------------------------------|----------------------------|----------------------------|----------------------------|------------------|
| | MgO | MgO-TiO ₂ (9:1) | MgO-TiO ₂ (1:1) | MgO-TiO ₂ (1:9) | TiO ₂ |
| 300 | 25.9 | 46.6 | 98.2 | 148 | 129 |
| 400 | 140 | 151 | 109 | 91.1 | 85.6 |
| 500 | 25.0 | 60.2 | 61.6 | 66.4 | 44.4 |
| 600 | 35.6 | 39.1 | 42.9 | 58.0 | 28.9 |
| 700 | 32.7 | 28.1 | 30.6 | 21.4 | 10.8 |

vacuum distillation were used. The mass analysis of deuterated propylene was made by mass spectroscopy, and the deuterium distribution in propylene-*d*₁ and -*d*₂ species during the exchange was determined by microwave spectroscopy.

RESULTS AND DISCUSSION

DTA-TGA and X-Ray Diffraction

Magnesium hydroxide and titanate acid showed endothermic peaks at 400 and 78°C, respectively, in their DTA diagrams. The hydrogel of MgO-TiO₂ (9:1) showed a large endothermic peak at 400°C and a small one at 78°C, while the hydrogel of MgO-TiO₂ (1:9) showed a small endothermic peak at 400°C and a large one at 78°C. In the case of MgO-TiO₂ (1:1), the heat absorption peaks were almost comparable. These diagrams indicate that the dehydrations of magnesium hydroxide and titanate acid in the hydrogel of MgO-TiO₂ occur at 400 and 78°C, respectively.

X-Ray diffraction showed a pattern of Mg(OH)₂ when it was calcined at 300°C, but only a pattern of MgO when calcined above 400°C. Titanate acid dried at 110°C showed a peak of anatase, but showed peaks of both anatase and rutile when calcined in the range of 300-500°C. In any composition of MgO-TiO₂ calcined at 400-500°C, only the patterns of MgO and TiO₂ appeared; any other patterns such as Mg₂TiO₄ were not observed. This indicates

that MgO-TiO₂ consists of the mixture of each oxide crystal and amorphous part.

Surface Area and Acid-Base and Reducing Properties

Specific surface areas of MgO, MgO-TiO₂, and TiO₂ are shown in Table 1. MgO, MgO-TiO₂ (9:1), and MgO-TiO₂ (1:1) showed the maximum surface areas when calcined at 400°C, while the surface areas of MgO-TiO₂ (1:9) and TiO₂ decreased with the rise in calcination temperature. The surface areas of any compositions of MgO-TiO₂ were larger than that of each component oxide.

The acidity and acid strengths of the catalysts calcined at 300, 500, and 700°C are listed in Table 2. Only TiO₂ showed an acid strength of $H_0 = -3.0$. The highest acid strengths of MgO-TiO₂ (1:9 and 1:1) were $H_0 = +3.3$ and $H_0 = +4.8$, respectively, indicating that the acid strength of TiO₂ is weakened by the addition of MgO. Magnesium oxide itself did not show any acidic property. The acidity at $H_0 = +4.8$ and $+1.5$ of MgO-TiO₂ calcined at 500°C decreased with the increase in MgO content as shown in Fig. 1. The acidity and acid strength of MgO-TiO₂ prepared by the coprecipitation method were reported to be higher than those of the component oxide, MgO or TiO₂ (9), though the simultaneous coprecipitation is difficult due to the big difference between the pH

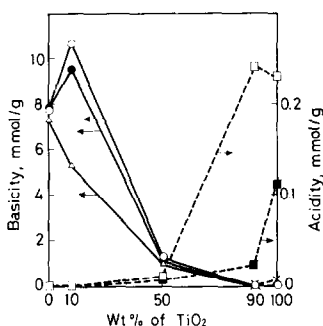


FIG. 1. Acidity and basicity of MgO-TiO₂ of different compositions: (O) $pK_{BH} = 12.2$; (●) $pK_{BH} = 15.0$; (Δ) $pK_{BH} = 17.2$; (□) $pK_a = 6.8$; (■) $pK_a = 4.8$; (X) $pK_a = 1.5$.

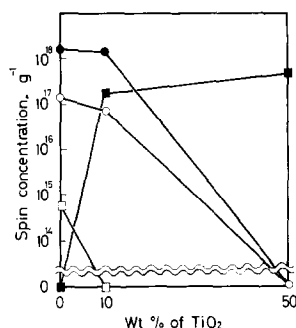


FIG. 2. Amounts of anion radicals of nitrobenzene on MgO-TiO₂ (O) calcined in air at 400°C; (□) calcined in air at 500°C; (●) evacuated at 400°C; (■) evacuated at 500°C.

of the solution necessary for the precipitation of magnesium hydroxide and that of titanic acid. In this case, a little increase in the acidity at $H_0 = +6.8$ was observed only for MgO-TiO₂ (1:9) as seen in Fig. 1. Thus, the acidic property of MgO-TiO₂ prepared by mechanical mixing is lower than that prepared by coprecipitation. Similar results were reported for SiO₂-Al₂O₃ by Hall *et al.* (10). The acidity increase of MgO-TiO₂ (1:9) can be interpreted in

terms of the change in the coordination number of the oxygen of MgO due to mixing, which was proposed in general form by Tanabe *et al.* (11).

The basicity and basic strength of the catalysts are listed in Table 3. MgO, MgO-TiO₂ (9:1 and 1:1) showed a basic strength of $H_- = 17.2$, whereas MgO-TiO₂ (1:9) and TiO₂ did not show any basic property. The change in basicity of MgO-TiO₂ with MgO content is shown in Fig. 1. It is

TABLE 2
Acidity and Acid Strength of MgO-TiO₂

| | Calcination temperature (°C) | Acidity (mmol/g) | | | | | |
|----------------------------|------------------------------|------------------|-------|-------|-------|-------|-------|
| | | pK_a | | | | | |
| | | +6.8 | +4.8 | +4.0 | +3.3 | +1.5 | -3.0 |
| MgO | 300-700 | 0 | 0 | 0 | 0 | 0 | 0 |
| MgO-TiO ₂ (9:1) | 300-700 | 0 | 0 | 0 | 0 | 0 | 0 |
| MgO-TiO ₂ (1:1) | 300 | 0.058 | 0 | 0 | 0 | 0 | 0 |
| | 500 | 0.010 | 0.010 | 0 | 0 | 0 | 0 |
| | 700 | 0.014 | 0.014 | 0 | 0 | 0 | 0 |
| MgO-TiO ₂ (1:9) | 300 | 0.31 | 0.020 | 0 | 0 | 0 | 0 |
| | 500 | 0.24 | 0.024 | 0.024 | 0.024 | 0 | 0 |
| | 700 | 0.085 | 0.024 | 0.024 | 0 | 0 | 0 |
| TiO ₂ | 300 | 0.15 | 0.021 | 0.021 | 0.004 | 0.004 | 0.004 |
| | 500 | 0.23 | 0.11 | 0.11 | 0.004 | 0.004 | 0.004 |
| | 700 | 0.026 | 0.015 | 0.015 | 0.005 | 0.005 | 0.005 |

TABLE 3
Basicity and Basic Strength of MgO-TiO₂

| | Calcination temperature (°C) | Basicity (mmol/g) pK _{BH} | | | |
|----------------------------|------------------------------|------------------------------------|-------|------|------|
| | | 12.2 | 15.0 | 17.2 | 18.4 |
| MgO | 300 | 0.22 | 0.13 | 0 | 0 |
| | 400 | 7.66 | 7.80 | 7.28 | 0 |
| | 500 | 0.47 | 0 | 0 | 0 |
| | 600 | 0.18 | 0 | 0 | 0 |
| | 700 | 0.17 | 0.12 | 0 | 0 |
| MgO-TiO ₂ (9:1) | 300 | 0.61 | 0.29 | 0 | 0 |
| | 400 | 10.6 | 9.50 | 5.26 | 0 |
| | 500 | 9.86 | 3.11 | 2.92 | 0 |
| | 600 | 0.62 | 0.57 | 0 | 0 |
| | 700 | 0.21 | 0 | 0 | 0 |
| MgO-TiO ₂ (1:1) | 300 | 0 | 0 | 0 | 0 |
| | 400 | 1.27 | 1.18 | 1.10 | 0 |
| | 500 | 1.38 | 1.19 | 1.14 | 0 |
| | 600 | 0.22 | 0.033 | 0 | 0 |
| | 700 | 0 | 0 | 0 | 0 |
| MgO-TiO ₂ (1:9) | 300-700 | 0 | 0 | 0 | 0 |
| TiO ₂ | 300-700 | 0 | 0 | 0 | 0 |

interesting that the basicities at $H_- = 12.2$ and 15.0 of MgO-TiO₂ (9:1) calcined at 400°C are higher than that of MgO. A more pronounced basicity maximum was observed for MgO-TiO₂ (9:1) calcined at 500°C. The basicity maxima of MgO-TiO₂ (9:1) calcined at 400 and 500°C become sharper when the basicity per unit surface area is plotted. The basicity increase of MgO produced by the addition of a small amount of TiO₂ is hard to interpret. This is the second example of the basicity increase of binary oxides. The first example was found for MgO-Al₂O₃ (12).

Figure 1 reveals that MgO and MgO-TiO₂ (9:1) have only the basic property and TiO₂ and MgO-TiO₂ (1:9) have only the acidic property, whereas MgO-TiO₂ (1:1) possesses both acidic and basic properties.

The number of anion radicals of nitrobenzene formed per gram of catalyst is shown in Fig. 2. The number of the reducing sites on MgO calcined in air or *in vacuo* at 400°C decreased on the addition of TiO₂ and became zero for MgO-TiO₂ containing 50% TiO₂. The number is about

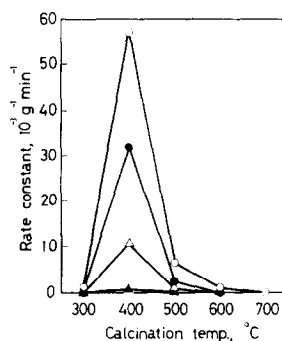


FIG. 3. Specific rate of decomposition of diacetone alcohol at 32°C vs calcination temperature of MgO-TiO₂. (●) MgO; (○) MgO-TiO₂ (9:1); (△) MgO-TiO₂ (1:1); (▲) MgO-TiO₂ (1:9).

ten times higher in evacuated catalysts than in the catalysts calcined in air. The number becomes small or zero when MgO is calcined in air or *in vacuo* at 500°C. However, MgO-TiO₂ (9:1 and 1:1) evacuated at 500°C showed a considerably large number of the reducing sites. The appearance of reducing sites on MgO and MgO-TiO₂ (9:1) calcined in air or evacuated at 400°C is considered to be due to point defects or dislocation formed on the surface by analogy with CaO (3). On the other hand, the reducing sites on MgO-TiO₂ (9:1 and 1:1) evacuated at 500°C are apparently the Ti³⁺ on the surface, since the amount of Ti³⁺ on TiO₂ is known to increase to its largest value when evacuated at 500°C (13).

Decomposition of Diacetone Alcohol, Dehydration of 4-Methyl-2-pentanol, and Alkylation of Phenol with Methanol

The decomposition of diacetone alcohol to form acetaldehyde is known to be catalyzed by basic catalysts (14, 15). MgO and MgO-TiO₂ (9:1, 1:1, and 1:9) showed maximum activities for the reaction when calcined in air at 400°C (Fig. 3). The activities of those catalysts calcined in air at 400°C were plotted against the TiO₂ content in Fig. 4. MgO-TiO₂ (9:1) showed the highest activity out of MgO and

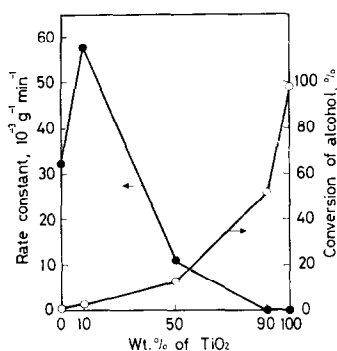


FIG. 4. Change in catalytic activity of MgO-TiO₂ with the catalyst composition. (●) Decomposition of diacetone alcohol at 32°C over MgO-TiO₂ calcined at 400°C. (○) Dehydration of 4-methyl-2-pentanol at 250°C over MgO-TiO₂ calcined at 500°C.

MgO-TiO₂ (1:1 and 1:9). The activity change in Fig. 4 is well correlated with the change in basicity at $pK_{BH} = 12.2$ and $pK_{BH} = 15.0$ (cf. Fig. 1). This indicates that relatively weak basic sites are active for the reaction.

4-Methyl-2-pentanol was dehydrated to

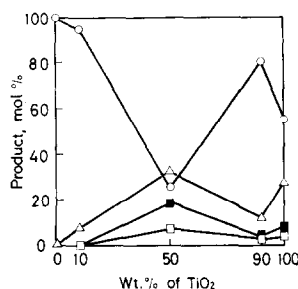


FIG. 5. Alkylation of phenol with methanol over MgO-TiO₂ of different compositions. Reaction temperature: 400°C. (○) Phenol; (△) *o*-cresol; (■) 2,6-xyleneol; (□) 2,4-xyleneol.

form mainly olefins over MgO-TiO₂, a very small amount (1–2%) of the ketone being formed by dehydrogenation. The percentage conversion of the alcohol was 98.3% in the case of TiO₂ calcined at 500°C, decreasing with the increase in MgO content, and only 0.8% in the case of MgO (Fig. 4). The change in the conversion correlated with the acidity change at $H_0 = 4.8$ as shown in Fig. 1. This

TABLE 4

Deuterium Distribution in Propylene-*d*₁ and -*d*₂ Species during the Exchange Reaction between Propylene and D₂O Adsorbed on TiO₂-MgO (1:1) at 182°C

| | Deuterium distribution (%) | | | | | | |
|--|----------------------------|--------|---------|----------|----------|--------|--------|
| | 50 min ^a | 90 min | 210 min | 1050 min | 1550 min | 3 days | 6 days |
| <i>Cis</i> -1- <i>d</i> ₁ | 0 | 2.3 | 3.0 | 6.2 | 7.6 | 11.3 | 14.3 |
| <i>Trans</i> -1- <i>d</i> ₁ | 0 | 3.2 | 3.4 | 7.1 | 8.4 | 13.3 | 15.6 |
| 3- <i>d</i> ₁ | 100 | 94.5 | 93.6 | 86.7 | 84.0 | 75.1 | 70.1 |
| 2- <i>d</i> ₁ | 0 | 0 | 0 | 0 | 0 | 0.3 | 0 |
| 1,1- <i>d</i> ₂ | | | | | 3.5 | 5.7 | 6.7 |
| <i>Cis</i> -1,3- <i>d</i> ₂ | | | | | 24.5 | 20.5 | 22.2 |
| <i>Trans</i> -1,3- <i>d</i> ₂ | | | | | 29.0 | 33.1 | 27.7 |
| 3,3- <i>d</i> ₂ | | | | | 43.0 | 40.7 | 41.5 |
| <i>Cis</i> -1,2- <i>d</i> ₂ | | | | | 0 | 0 | 1.3 |
| 2,3- <i>d</i> ₂ | | | | | 0 | 0 | 0.6 |
| <i>Trans</i> -1,2- <i>d</i> ₂ | | | | | 0 | 0 | 0 |
| Propylene- <i>d</i> ₁ | 97.2 | 96.2 | 91.2 | 71.8 | 63.0 | 41.7 | 24.6 |
| Propylene- <i>d</i> ₂ | 2.8 | 3.6 | 8.6 | 25.1 | 31.2 | 41.0 | 41.2 |
| Propylene- <i>d</i> ₃ | 0 | 0.2 | 0.2 | 2.9 | 5.3 | 14.6 | 25.4 |
| Propylene- <i>d</i> ₄ | | 0 | 0 | 0.2 | 0.5 | 2.5 | 7.4 |

^a Reaction time.

TABLE 5
Distribution of Propylene-*d*₁ and -*d*₂ Species during the Exchange Reaction between Propylene and D₂ over TiO₂-MgO (1:1) at -80°C

| | Deuterium distribution (%) | | | | | | | | |
|--|----------------------------|--------|---------|---------|----------|----------|----------|---------------------|---------------------|
| | 19 min ^a | 59 min | 119 min | 189 min | 1339 min | 2904 min | 4089 min | 2 days ^b | 4 days ^b |
| <i>Cis</i> -1- <i>d</i> ₁ | 16.6 | 16.2 | 13.2 | 13.4 | 9.4 | 12.2 | 13.9 | 15.8 | 16.6 |
| <i>Trans</i> -1- <i>d</i> ₁ | 16.4 | 16.2 | 13.8 | 15.3 | 12.2 | 15.7 | 16.7 | 20.2 | 19.0 |
| 3- <i>d</i> ₁ | 67.0 | 67.6 | 73.0 | 71.3 | 78.4 | 72.1 | 69.4 | 64.0 | 64.4 |
| 2- <i>d</i> ₁ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1,1- <i>d</i> ₂ | | | | | 7.1 | | 9.2 | 9.4 | 9.4 |
| <i>Cis</i> -1,3- <i>d</i> ₂ | | | | | 25.0 | | 19.8 | 23.0 | 25.8 |
| <i>Trans</i> -1,3- <i>d</i> ₂ | | | | | 28.9 | | 33.6 | 29.7 | 30.3 |
| 3,3- <i>d</i> ₂ | | | | | 38.9 | | 37.5 | 37.9 | 34.5 |
| 2,3- <i>d</i> ₂ | | | | | 0 | | 0 | 0 | 0 |
| Propylene- <i>d</i> ₁ | 95.8 | | 91.2 | 87.3 | | 80.8 | 75.2 | 29.3 | 28.1 |
| Propylene- <i>d</i> ₂ | 0.8 | | 5.3 | 8.1 | | 16.0 | 20.3 | 41.2 | 47.6 |
| Propylene- <i>d</i> ₃ | 1.1 | | 1.6 | 2.9 | | 2.1 | 3.3 | 22.7 | 19.6 |
| Propylene- <i>d</i> ₄ | 1.7 | | 1.0 | 1.2 | | 0.8 | 0.6 | 6.0 | 4.3 |

^a Reaction time.

^b At room temperature.

indicates that the acid sites having $H_0 = 4.8$ are active for the dehydration reaction. The ratios of 4-methyl-1-pentene to 4-methyl-2-pentene were 0.92, 0.70, and 0.67 for MgO-TiO₂ (1:1 and 1:9) and TiO₂, respectively, and the ratios of 4-methyl-*cis*-2-pentene to 4-methyl-*trans*-2-pentene were 0.83, 0.81, and 1.07, respectively. The small values of the latter ratio also are evidence that the dehydration proceeds via carbenium ions on acid sites (16, 17).

The reaction of phenol with methanol over MgO-TiO₂ formed mainly *o*-cresol, 2,6-xyleneol, and 2,4-xyleneol as shown in Fig. 5, a small amount of anisole and *m*- and *p*-cresol was also formed. A maximum conversion of phenol was observed over MgO-TiO₂ (1:1), which has considerable amounts of both acidic and basic sites (cf. Fig. 1). This seems to indicate that the reaction takes place by an acid-base bifunctional mechanism (18). It should be noted that MgO-TiO₂ (1:1) is selective for the alkylation at *ortho* positions of phenol.

The Hydrogen Exchange Reaction of Propylene with Heavy Water or Deuterium

The deuterium distributions in propylene-*d*₁ and -*d*₂ species and mass analysis data during the exchange reaction between propylene and adsorbed D₂O or D₂ over MgO-TiO₂ (1:1) are shown in Tables 4 and 5.

The time variation of the distribution in propylene-*d*₁ and -*d*₂ species reveals that the reaction intermediates in the exchange reactions of propylene with D₂O and with D₂ are mainly π -allyl carbanions and isopropyl carbenium ions, respectively (19).¹ Therefore, the active sites for the reaction with D₂O are basic, while those for the reaction with D₂ are acidic.

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¹ In the case of the reaction of propylene with D₂, the possibility of a π -allyl mechanism followed by fast intramolecular 1,3-hydrogen transfer cannot be excluded.

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