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Physical and Catalytic Properties of MgO Prepared Using Citric Acid

Tomohiro Nakayama, Satoshi Sato,*,† and Fumio Nozaki†

Graduate School of Science and Technology, Chiba University, Yayoi, Inage, Chiba 263

†Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263

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The physical properties, particularly the pore structure and specific surface area, of MgO prepared using citric acid was investigated. Both the specific surface area and the pore volume increased steeply with the weight loss at around 600 K at which citric acid was decomposed. The pore size distribution of the sample was controlled by the ratio of citric acid and the temperature of heat treatment. In a catalytic decomposition of 4-hydroxy-4-methyl-2-pentanone into acetone, the reaction rate was proportional to the specific surface area of the sample, and the catalysts prepared by this technique had high reaction rates because of their high specific surface areas.

Citric acid is utilized to prepare a ceramics powder through a technique known as an amorphous citrate process.[1—6] High crystallinity of the ceramics is provided by the citrate process because highly mixed citrates are decomposed at lower temperatures. The technique, however, has not been applied to the preparation of catalysts, except for composite oxide catalysts containing copper.[7—10] In contrast to studies concerning composite oxides, there has been no study about a metal oxide catalyst having a single component. Then, in our previous work,[11] various metal oxides having a single component prepared through the same citrate process using various organic acids were investigated. Hydroxycarboxylic acids such as citric acid and lactic acid as well as an amino acid such as glycine were effective in providing metal oxides with a high specific surface area. High specific surface areas of 142, 47, 40, and 16 $m^2 g^{-1}$ were obtained using citric acid for MgO, CeO_2, La_2O_3, and NiO samples calcined at 773 K, respectively.

In addition to a high specific surface area, it is also important to control the pore size distribution in order to obtain a high catalytic activity. The particular pore size of the catalyst has been reported to be effective for hydrodesulphurisation.[12] In a case of alumina, pore size distribution was changed with calcination temperature.[13] Ono et al. reported that both the pore size distribution and the pore volume in alumina were sharply controlled by a rapid swing of the pH of the solution during the gelation process.[14] There, however, have been few studies on pore size distribution of the MgO catalyst.

In this study, we prepared MgO catalysts using citric acid with various molar ratios of the citric acid to magnesium ions. We also performed thermal gravimetric analyses of the magnesia precursor containing citric acid, a control in the pore structure of the MgO, and the catalytic activity of MgO samples for a reaction catalysed by bases.

Experimental

MgO samples were prepared using magnesium nitrate and citric acid. This procedure was essentially the same as the amorphous citrate process, which was introduced by Marcilly et al.[1] We prepared samples without using solvents in order to clarify a static thermogravimetry (TG) analysis. A prescribed amount of magnesium nitrate was melted with citric acid at 343 K; the resulting mixture was named A-stage sample. The A-stage mixture was evacuated under a pressure of 1 kPa at 343 K. During the evacuation, the mixture was gradually solidified, and then expanded; the resulting solid was named B-stage sample. After the B-stage solid had been heated in air at 433 K for 1 h, it was calcined in air at a prescribed temperature for 3 h to give a catalyst sample.

A static TG analysis of the A-stage sample was examined by the weight loss of the sample during the heat treatment at various prescribed temperatures. Each of the samples was heated in air at a temperature range from 343 to 973 K for 3 h.

The thermogravimetry and mass analysis (TG-MS) of the B-stage sample were recorded using a Shimadzu, TG50H thermogravimeter and a Shimadzu, QP1000EX quadra-pole mass spectrometer with a sample weight of 0.025 g. The sample was heated from 298 to 973 K at a rate of 5 $K min^{-1}$ under a helium flow of 50 $ml min^{-1}$.

Specific surface areas of the samples were determined by the BET method using nitrogen as an adsorbate at 77 K with the aid of a conventional volumetric gas adsorption apparatus. The pore size distribution was calculated by a method of Cranston and Inkley[15] using the adsorption isotherm of nitrogen at 77 K.

The decomposition of 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol, DAA) into acetone was carried out with a conventional pulse-reaction apparatus under hydrogen flow as a carrier gas at 298 K. The weight of the catalyst sample was 1.0 mg, and the pulse size was 0.1 μL at a hydrogen flow rate of 150 $ml min^{-1}$. Prior to the reaction, samples were heated in a hydrogen stream at 623 K for 1 h. The reaction products were analysed by on-line gas chromatography using a polyethylene glycol 1500 column (1 m).

Results and Discussion

1. TG-MS Analysis. In order to detect the gasses produced during the thermal decomposition of the MgO precursor, a TG-MS analysis of a B-stage sample which was prepared using the equimolar ratio of citric acid and magnesium nitrate was examined (Figs. 1 and 2). The weight loss associated with a thermal decomposition of the B-stage sample was divided into two major steps (Fig. 1). The weight was lost in the first step between 473 and 573 K and in the second step above 573 K. Various gasses were simultaneously detected together with the weight loss. In the gasses evolved during the first step within a temperature range from 473 to 573 K, CH_4 (*m*/*z* 16), H_2O (18), NO (30), C_3H_6 (42), CO_2 (44), and NO_2 (46) were observed (Fig. 2). These gasses resulted in a decomposition of the nitrate roots and citrates. During the second step within a temperature range from 600 to 800 K, CH_4, C_3H_6, CO_2, and a small amount of NO_2 were observed. These gasses were speculated to be derived mainly from the decomposition of citrates, and a small portion from the decomposition of nitrates.

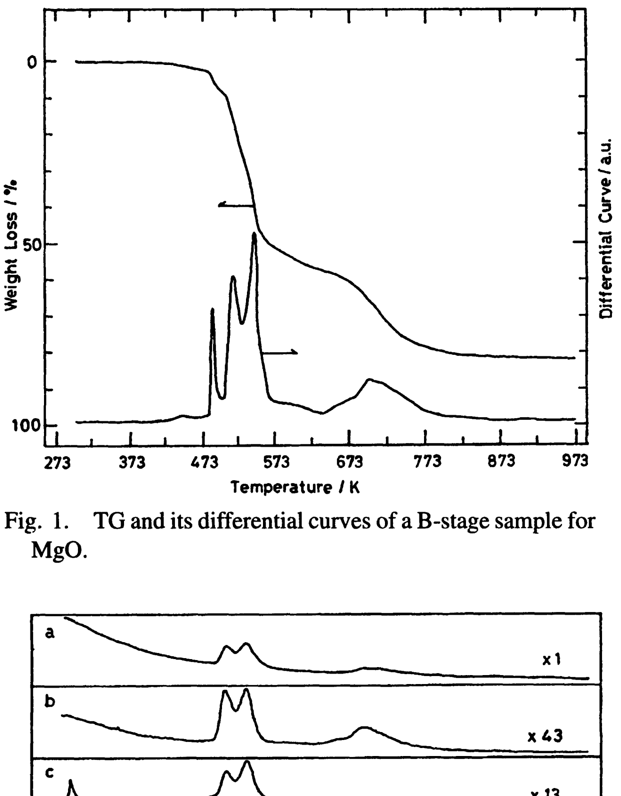

Fig. 1. TG and its differential curves of a B-stage sample for MgO.

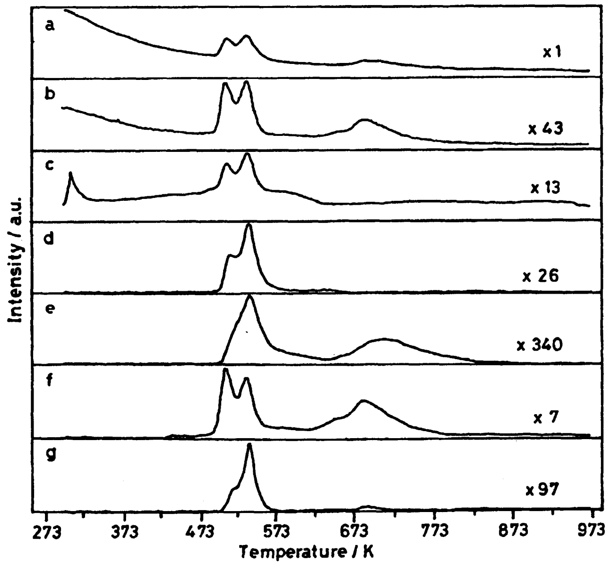

Fig. 2. MS data with a decomposition of the B-stage sample shown in Fig. 1. a, TIC (total ion chromatogram); b, *m*/*z* 16.0 (CH_4); c, *m*/*z* 18.0 (H_2O), d, *m*/*z* 30.0 (NO); e, *m*/*z* 42.0 (C_3H_6); f, *m*/*z* 44.0 (CO_2); g, *m*/*z* 46.0 (NO_2).

There have been a few studies on the TG analysis of metal oxides having a single component prepared by this method.[3,4] Baythoun and Sale analyzed the TG of manganese oxide precursors obtained from citric acid and manganese nitrate at a heating rate of 6 K min^{-1}.[4] Mn_2O_3 was obtained below 673 K, and the elimination of H_2O, CO_2, and NO was observed. There is no significant difference between their report and this study. We, however, detected CH_4 and C_3H_6, which originated from citric acid.

2. Relationship between the Heat-Treatment Temperature and the Specific Surface Area. In addition to the results of the TG-MS, a static TG and a change in the specific surface area along with the variation in the heat-treatment temperature were investigated in detail in order to examine the process of pore formation of samples prepared by this method. A static TG curve of an A-stage sample together with the change in the specific surface areas with the heat temperature for a MgO sample prepared using a mixture of citric acid and magnesium nitrate with a molar ratio of 1.33 : 1 is shown in Fig. 3. In contrast to the results from TG-MS, the static TG curve is directly suitable for the change in the specific surface area at the specified heat-treatment temperature, because the same sample was provided for the measurements.

The weight loss of the sample with a citric acid ratio of 1.33 : 1 occurred through three steps (Fig. 3). In the first step below 433 K, the weight loss was anticipated to arise mainly from the elimination of water and the decomposition of liberated nitrate roots, which resulted from the formation of citrate salts. This speculation was supported by the fact that the production of a reddish-brown NO_2 gas was observed below 433 K. When a sample prepared from magnesium

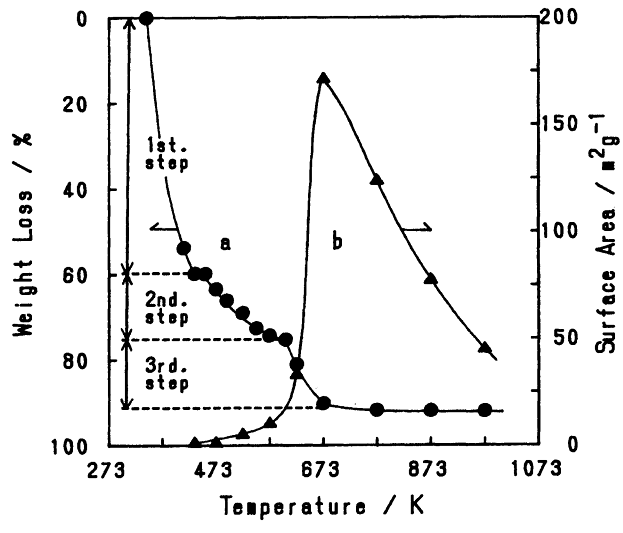

Fig. 3. Changes in sample weight and specific surface area with heat temperature for a A-stage sample of MgO by using citric acid and magnesium nitrate with a molar ratio of 1.33 : 1. a, weight loss; b, specific surface area.

nitrate without using citric acid was heated, NO_2 gas was observed up to 623 K. Both in the second step from 433 to 573 K and in the third step above 573 K (Fig. 3), the elimination of CO_2 was observed. In addition, it was found that the weight loss of the second step was equal to the third-step weight loss. Furthermore, as shown in Fig. 3, the specific surface area was found to be 11 $m^2\,g^{-1}$ at the end of the second step at 573 K; then, a steep increase in the specific surface area (172 $m^2\,g^{-1}$) was observed during the third step at around 673 K. Above 673 K, however, the surface area decreased along with an increase in the heat-treatment temperature. Since the weight loss was completed below 673 K, it can be concluded that the small pores providing high specific surface areas were constructed by the elimination of citric acid from the samples at temperatures of around 673 K.

For a sample with a small molar ratio of citric acid of 0.67 : 1, there were only two steps in the static TG curve.[11] The 0.67 : 1 ratio corresponds to a composition of $Mg_3(C_6H_6O_7)_2$ as magnesium citrate, which has no excess citric acid. This sample did not have the second-step weight loss which was observed in a sample with a molar ratio of 1.33 : 1 (Fig. 3). It can be said that the excess citric acid caused the second-step weight loss. Since the extent of the increase in the specific surface area of a sample with a molar ratio of 1.33 : 1 (from 11 to 172 $m^2\,g^{-1}$ in Fig. 3) was higher than that of 0.67 : 1 (from 18 to 137 $m^2\,g^{-1}$ in Ref. 11), we could infer that the excess of citric acid played an important role in the increase in the specific surface area.

The static TG analysis summarizes the fact that the first-step weight loss comes from the elimination of water and the decomposition of liberated nitrate roots, that the second-step weight loss corresponds to the decomposition of excess citric acid, and that the third-step weight loss arises from the decomposition of the citrate salts which were produced in the first step. The decomposition of the citrate salts provided the small pores and high specific surface areas.

The static TG is different from the TG-MS results (Figs. 1 and 2). The weight loss shown in Fig. 3 occurred at temperatures lower than that in Fig. 1. Because the static TG is done in air in contrast to the fact that the TG-MS is operated dynamically under non-oxidized conditions in a helium flow, both the decomposition of citrate and nitrate as well as the oxidation of CH_4, C_3H_6, and NO must occur at lower temperatures.

3. Pore Size Distribution. Figure 4 shows the changes in the pore size distribution of MgO, which was prepared at the equimolar ratio of citric acid with a variation in the temperature of the heat treatment. A sample heated at a low temperature of 523 K was not porous. At a heat-treatment temperature of 623 K, many pores at pore diameters of about 7 nm were formed with a pore volume of 0.21 $cm^3\,g^{-1}$. The pore volumes of the samples calcined at 523, 773, and 873 K were 0.01, 0.14, and 0.10 $cm^3\,g^{-1}$, respectively. At higher heat-treatment temperatures ranging from 773 to 873 K, the pore size distribution moved to the smaller diameter side. These samples had a sharp pore size distribution at a pore diameter of 4 nm. MgO samples prepared by this method had different pore size distributions, being controlled by the temperature of the heat treatment.

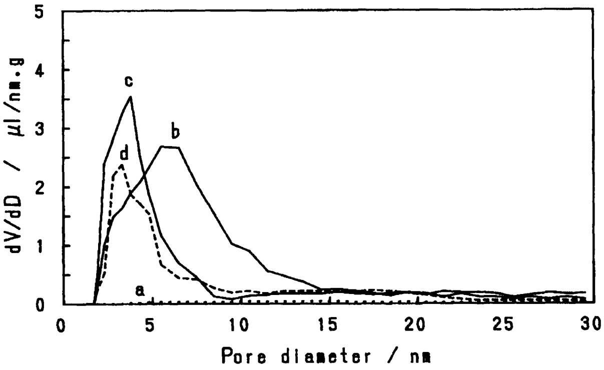

Fig. 4. Changes in a pore size distribution of MgO with heat treatment temperature. a, 523 K; b, 623 K; c, 773 K; d, 873 K. MgO was prepared with an equimolar ratio of citric acid and magnesium nitrate.

Figure 5 shows the changes in the pore size distribution of MgO calcined at 773 K with different molar ratios of citric acid to magnesium nitrate in the sample preparation (curves a, b, and d are reported in Ref. 11). A sample prepared with the equimolar ratio of citric acid and magnesium nitrate had many pores having pore diameters of around 4 nm. When the ratio of citric acid was increased to 1.33 : 1, the pore size was enlarged and pores of around 7 nm increased. On the other hand, at a small ratio of citric acid of 0.33 : 1, those pores having a size of about 4 nm decreased, resulting in a small specific surface area of 88 $m^2\,g^{-1}$. The pore volumes of those samples with citric acid ratios of 0.33 : 1, 0.67 : 1, 1 : 1, 1.17 : 1, and 1.33 : 1 were 0.14, 0.20, 0.21, 0.24, and 0.22 $cm^3\,g^{-1}$, respectively. Thus, it can be said that the pore size distribution of the samples prepared by this method is controlled by the molar ratio of citric acid as well as by the temperature of the heat treatment.

4. Decomposition of DAA into Acetone. The curve (a) in Fig. 6 shows a change in the conversion of DAA with the heat-treatment temperature of the MgO samples. The conversion of DAA showed a maximum at a heat-treatment

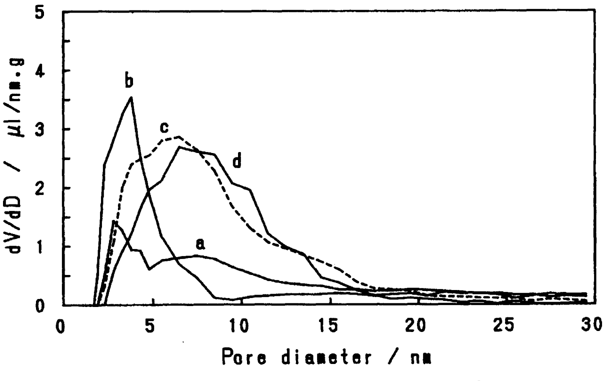

Fig. 5. Changes in the pore sized distribution of MgO samples calcined at 773 K with different molar ratios of citric acid to magnesium nitrate in the sample preparation. a, 0.33 : 1; b, 1 : 1; c, 1.17 : 1; d, 1.33 : 1.

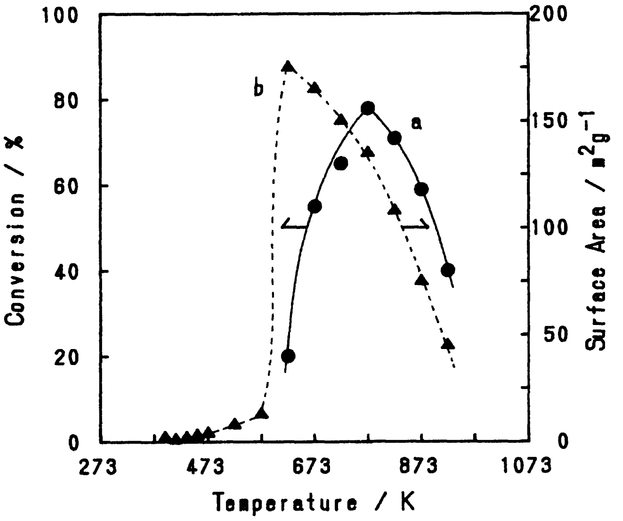

Fig. 6. Changes in the conversion of DAA with heat treatment temperature of MgO. a, the conversion of DAA; b, specific surface area.

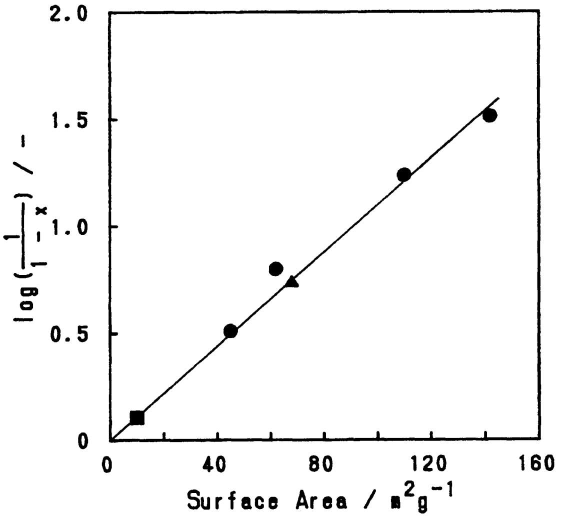

Fig. 7. The influence of the specific surface area of various MgO samples on the first-order rate constant. ●, this method; ■, thermal decomposition; ▲, commercially available reagent.

temperature of 773 K. Although the specific surface area increased steeply at around 600 K (curve (b) in Fig. 6, which has been reported in Ref. 11), the catalytic activity of those samples heated below 623 K was low. It is supposed that this low activity can possibly be ascribed to contamination due to a residual carbon. At heat-treatment temperatures higher than 773 K, the catalytic activity decreased along with a decrease in the specific surface area.

Since the pulse sizes in the injecting DAA did not change the conversion, this reaction was supposed to be a first-order reaction.[16] Thus, the influence of the specific surface area of various MgO samples on the first-order rate constant is shown in Fig. 7. The circle symbols in Fig. 7 are for those samples heated at temperatures of 773 K and higher than 773 K, while the data for samples heated at temperatures below 773 K were excluded from Fig. 7 because of carbon contamination. Figure 7 also contains the data for a sample prepared by the pyrolysis of magnesium nitrate and for a commercial MgO sample. Since MgO samples prepared by this method have higher specific surface areas than those of the other reference samples, their catalytic activities are superior to those of the reference catalysts. Although the MgO samples had different pore distributions, as shown in Figs. 4 and 5, the reaction rate is directly proportional to the specific surface area of the samples.

In conclusion, the static TG and pore size distribution analyses served to clarify the formation process of a porous MgO prepared using citric acid. The pore size distribution could be controlled by the ratio of citric acid and the temperature of heat treatments of the samples.

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