Sulfated Mesoporous Alumina: A Highly Effective Solid Strong Base Catalyst for the Tishchenko Reaction in Supercritical Carbon Dioxide

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Heterogeneous strong base catalysis for the intramolecular Tishchenko reaction of aromatic 1,2-dicarbaldehydes to the corresponding phthalides in supercritical $CO_2 CscCO_2$ has been realized with mesoporous alumina containing SO_4^{2-} ions in the alumina framework ($meso$Al$_2$O$_3$/SO$_4^{2-}$). Infrared spectroscopy of pyrrole adsorbed on the alumina and strong poisoning by a weak Brönsted acid of methanol revealed that the SO_4^{2-} ions in the framework slightly suppressed the average strength of base sites (O^{2-}) on $meso$Al$_2$O$_3$/SO$_4^{2-}$, but there exists a small number of strong base sites that promote the Tishchenko reaction in scCO$_2$. Although the intramolecular Tishchenko reaction of phthalaldehyde to phthalide in scCO$_2$ was somewhat slower than those in organic solvents such as tetrahydrofuran (THF) and benzene, the addition of a small amount of THF as a cosolvent remarkably increased the reaction rate; the reaction in the scCO$_2$−THF system proceeded 1.5-fold faster than those in pure benzene and THF solvents.

Introduction

Supercritical fluids (SCFs) have been recognized as a unique reaction medium possessing the merits of both gases and liquids, because their physical properties can be continuously adjusted from those analogous to gases to those analogous to liquids by manipulating the pressure and temperature.[1] The high density required to dissolve and extract many organic compounds, the high diffusivity and the low viscosity enhancing mass transfer, and the high thermal conductivity eliminating reaction heat efficiently are suitable especially for heterogeneous catalytic reactions that take place in the pores of solids. Among the SCFs, supercritical carbon dioxide (scCO$_2$) is the most attractive because of its low cost, nontoxic and nonflammable nature, and mild critical temperature (304 K) and pressure (7.4 MPa). The Lewis acidity of CO$_2$, however, has restricted the use of scCO$_2$ medium in several homogeneous and heterogeneous acid- or transition metal-catalyzed reactions;[1] to our knowledge, no attempts have been carried out on strong base-catalyzed reactions in scCO$_2$.

Infrared spectroscopic studies revealed that on contact of CO$_2$ with solid bases, carbonate species, such as monodentate or bidentate carbonate ions, and bicarbonate ions were readily formed on the surface, which inevitably led to strong inhibition of solid base catalysis.[2] Therefore, it is a challenging task to perform solid base-catalyzed organic reactions in the scCO$_2$ medium. Development of solid strong base catalysts utilizable in scCO$_2$ would expand the potential of scCO$_2$ as a safe and environmentally benign reaction medium for chemical synthesis. Recently, we have successfully synthesized a new solid strong base material of mesoporous alumina containing SO_4^{2-} in the framework (designated as $meso$Al$_2$O$_3$/SO$_4^{2-}$), and preliminarily reported its strong base catalysis for the Tishchenko reaction[3]

in scCO$_2$.[4] In this article, we report a full account on the strong base catalysis of $meso$Al$_2$O$_3$/SO$_4^{2-}$ for the Tishchenko reaction in scCO$_2$ (Scheme 1) and on unique properties of the surface and bulk of $meso$Al$_2$O$_3$/SO$_4^{2-}$.

Experimental Section

Preparation of *meso*Al₂O₃. Pure mesoporous alumina ($meso$Al$_2$O$_3$) was synthesized according to Davis' report:[5] into a polypropylene vessel containing a stirring bar were added Al-(O-*sec*-Bu)$_3$ (21.9 g, 89.0 mmol), 1-propanol (120 g, 2.00 mol), and deionized water (5.15 g, 286 mmol), followed by vigorous stirring at room temperature. After 1 h, a solution of lauric acid (5.40 g, 27.0 mmol) in 1-propanol (17.5 g, 290 mmol) was added under vigorous stirring, and the mixture was further stirred vigorously at room temperature for 24 h. The resulting white liquid was placed in a 300-mL autoclave and heated at 383 K for 48 h without stirring to afford a white precipitate. The precipitate was washed on a filter paper with a large amount of ethanol and dried at room temperature under an N$_2$ flow. The white solid thus obtained was heated from room temperature to 873 K at a ramping rate of 10 K min^{-1} under an N$_2$ flow, and then calcined under an air flow at 873 K for 5 h to burn out the organic species to give pure $meso$Al$_2$O$_3$. After several repetitions of the synthesis, it was found that the synthesized $meso$Al$_2$O$_3$ had surface areas in the range of 474−523 m^2 g^{-1}. In the present study, we employed two lots of $meso$Al$_2$O$_3$: the one with the largest surface area of 523 m^2 g^{-1} was designated as $meso$Al$_2$O$_3$(#1) and the other with the smallest surface area of 474 m^2 g^{-1} as $meso$Al$_2$O$_3$(#2).

Preparation of *meso*Al₂O₃/SO₄²⁻-I and -II. To a mixture of Al(O-*sec*-Bu)$_3$ (21.9 g, 89.0 mmol) and 1-propanol (120 g, 2.00 mol) was added deionized water (5.15 g, 286 mmol) containing 96% H$_2$SO$_4$ (0.1 g, 1 mmol and 0.2 g, 2 mmol for $meso$Al$_2$O$_3$/SO$_4^{2-}$-I and -II, respectively). The resultant solution was vigorously stirred for 1 h at room temperature. Lauric acid (5.40 g, 27.0 mmol) in 1-propanol (17.5 g, 290 mmol) was then added, and the mixture was further stirred for 24 h at room

SCHEME 1: Intramolecular Tishchenko Reaction of Aromatic 1,2-Dicarbaldehydes to Phthalides in ScCO$_2$
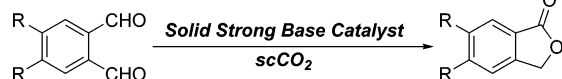
temperature. The resulting white liquid was placed in a 300-mL autoclave and heated at 383 K for 48 h without stirring to afford a white precipitate. The precipitate was washed on a filter paper with a large amount of ethanol and dried at room temperature under an N$_2$ flow. The white solid thus obtained was heated from room temperature to 873 K at a ramping rate of 10 K min^{-1} under an N$_2$ flow and calcined under an air flow at 873 K for 5 h to burn out the organic species to yield $meso$Al$_2$O$_3$/SO$_4^{2-}$-I or -II. Bedilo and Klabunde employed this method to synthesize sulfated zirconia: the use of a small amount of H$_2$SO$_4$ resulted in the incorporation of SO$_4^{2-}$ ions into the zirconia framework.[6]

Preparation of $meso$Al$_2$O$_3$/SO$_4^{2-}$-III. A mixture of Al(O-sec-Bu)$_3$ (19.5 g, 79.0 mmol), Al$_2$(SO$_4$)$_3$ (1.7 g, 5.0 mmol), 1-propanol (120 g, 2.00 mol), and deionized water (5.15 g, 286 mmol) was vigorously stirred for 1 h at room temperature. Lauric acid (5.40 g, 27.0 mmol) in 1-propanol (17.5 g, 290 mmol) was then added, and the resulting mixture was further stirred for 24 h at room temperature. The resulting white liquid was placed in a 300-mL autoclave and heated at 383 K for 48 h without stirring to afford a white precipitate. The precipitate was washed on a filter paper with a large amount of ethanol and dried at room temperature under an N$_2$ flow. The white solid thus obtained was heated from room temperature to 873 K at a ramping rate of 10 K min^{-1} under an N$_2$ flow, and calcined under an air flow at 873 K for 5 h to burn out the organic species to give $meso$Al$_2$O$_3$/SO$_4^{2-}$-III.

Sulfur Content. The sulfur content in $meso$Al$_2$O$_3$/SO$_4^{2-}$ was determined by the infrared absorption method after combustion in an induction furnace with an EMIA-520 (HORIBA). A sample was burned under oxygen atmosphere with a mixture of metallic iron, tungsten, and tin that served as a combustion assistant to generate SO$_2$, the amount of which was determined by infrared spectroscopy. The sulfur contents in $meso$Al$_2$O$_3$/SO$_4^{2-}$-I, -II, and -III were 0.23, 0.48, and 1.30 wt %, respectively.

The Other Catalysts. CaO was obtained from thermal decomposition of Ca(OH)$_2$ at 873 K under vacuum (10^{-4} Torr) for 2 h. ALO-2, -3, and -4 are the reference alumina catalysts supplied from the Catalysis Society of Japan, and contain the following impurities: ALO-2: 0.03% Fe$_2$O$_3$, 0.22% SiO$_2$, 0.04% Na$_2$O, 1.72% SO$_4^{2-}$; ALO-3: 0.01% Fe$_2$O$_3$, 0.01% SiO$_2$, 0.3% Na$_2$O, 0.01% TiO$_2$; and ALO-4: 0.01% Fe$_2$O$_3$, 0.01% SiO$_2$, 0.01% Na$_2$O. $meso$Al$_2$O$_3$/SO$_4^{2-}$-IV was prepared by the same procedures as that employed for the synthesis of $meso$Al$_2$O$_3$/SO$_4^{2-}$-I and -II, but (NH$_4$)$_2$SO$_4$ (0.35 g, 2.6 mmol) was used as a sulfate ion source in place of H$_2$SO$_4$.

Organic Reagents. Phthalaldehyde (**1a**) (Aldrich) and 2,3-naphthalenedicarbaldehyde (**2a**) (Aldrich) were distilled under vacuum before use. 4,5-Dimethylbenzene-1,2-dicarbaldehyde (**3a**) and 4,5-dichlorobenzene-1,2-dicarbaldehyde (**4a**) were synthesized by Farooq's procedure:[7] the reduction of 4,5-dichlorobenzene-1,2-dicarboxylic acid (Aldrich) to the corresponding aromatic 1,2-dimethanol with LiAlH$_4$, followed by Swern oxidation. 4,5-Dimethylbenzene-1,2-dimethanol (Wako) was oxidized by the Swern method. All the aromatic 1,2-dicarbaldehydes were well dried under vacuum at room temperature for several hours and stored in a vial under N$_2$ atmosphere.

Benzene, tetrahydrofuran (THF), acetic acid, and methanol were purified by distillation, and stored in an N$_2$-filled vial with MS 4A, which had been activated at 773 K for 2 h under vacuum (10^{-4} Torr).

Pyrrole for the infrared spectroscopy was distilled under vacuum, then passed through a column of MS 4A, which had been activated at 773 K for 2 h under vacuum (10^{-4} Torr), and stored in vacuo, all the procedures of which were performed in a vacuum-line apparatus.

Measurement of Surface Area and Pore Diameter. N$_2$ adsorption−desorption measurements were performed at 77 K with a BELSORP 28SA (BEL Japan), using static adsorption procedures. The samples were pretreated under the same conditions as employed for the reactions (Ca(OH)$_2$: 873 K, 10^{-4} Torr, 2 h; aluminas: 773 K, 10^{-4} Torr, 2 h) prior to analysis. Adsorption data were analyzed by the Brunauer−Emmett−Teller (BET) method[8a] for surface areas, and the Dollimore−Heal (DH) method[8b] to obtain pore-size distribution curves.

Infrared Spectroscopy of Adsorbed Pyrrole and Phthalaldehyde. Infrared (IR) spectra were recorded at room temperature on an FT/IR-550 (JASCO) with a resolution of 4 cm^{-1}. The catalyst pressurized into a thin disk at 200 kg cm^{-2} was pretreated in a quartz-made IR cell equipped with an optical path window made of KBr under the same conditions as employed for the reaction (Ca(OH)$_2$: 873 K, 10^{-4} Torr, 2 h; aluminas: 773 K, 10^{-4} Torr, 2 h). Gaseous pyrrole at 5 Torr or **1a** at its vapor pressure at room temperature was then introduced into the IR cell at room temperature for 30 min and 4 h, respectively, followed by evacuation at 10^{-4} Torr at room temperature for 30 min. The sample thus obtained was transferred to the optical path part and infrared spectra were recorded.

X-ray Diffraction Analysis. X-ray powder diffraction measurement was performed with a MultiFlex (Rigaku) under ambient atmosphere. The sample was pretreated at 773 K at 10^{-4} Torr for 2 h, mounted on an XRD sample cell as fine powder under ambient atmosphere, and analyzed at a current of 40 mA and a voltage of 40 kV in the 2θ range 1° to 80° with a scanning rate of 1.0 deg min^{-1}.

Reaction Procedures. SAFETY WARNING! Operators handling high-pressure equipment for reactions in scCO$_2$ should take proper precautions to minimize the risk of personal injury.

The Tishchenko reaction was performed with an scCO$_2$ reactor system of SCF-Get, SCF-Bpg, and SCF-Sro (JASCO). A typical reaction procedure for the experiment of entry 9 in Table 1 is as follows: into a 10-mL stainless steel autoclave (SUS316, TAIATSU TECHNO) containing a stirring bar and freshly distilled phthalaldehyde (**1a**, 1.00 mmol) was added $meso$Al$_2$O$_3$/SO$_4^{2-}$-III (50 mg) preactivated at 773 K under vacuum (10^{-4} Torr) for 2 h in a nitrogen-filled glovebag. Liquid CO$_2$ cooled to 263 K was introduced into the autoclave, which had been heated to 313 K, using an HPLC pump, and the pressure was adjusted to 8.0 ± 0.2 MPa. The resultant mixture was stirred for 2 h at 313 K with the CO$_2$ pressure constantly maintained at 8.0 ± 0.2 MPa. The autoclave was cooled in an ice bath, and the pressurized CO$_2$ was gradually released. The resulting solid mixture was washed from the autoclave with THF. The THF slurry was filtered through a Celite pad. Evaporation of the THF filtrate gave a crude solid mixture, and the solid was dissolved in CDCl$_3$ with Ph$_3$CH (internal standard substance) and applied to NMR analysis. The yield of phthalide (**1b**, 73%) was determined with ^{1}H NMR (270 or 500 MHz) by the comparison between the peak area of Ph$_3$CH and that of $-$CH_2- in phthalide. The products, phthalide (**1b**), naphthalide

TABLE 1: Catalytic Activities of CaO, Aluminas, and Sulfated Aluminas for the Intramolecular Tishchenko Reaction of Phthalaldehyde (1a) to Phthalide (1b)[a]

entry	catalyst[b]	surface area ($m^2\ g^{-1}$)[c]	pore diameter (nm)[d]	yield (%)[e]
1	CaO[f]	48		1
2	ALO-2	312		62 (64[g])
3	ALO-3	129		<1
4	ALO-4	173		12 (15[g])
5	$meso$Al$_2$O$_3$(#1)	523	2.7	62
6	$meso$Al$_2$O$_3$(#2)	474	2.7	51 (59[g])
7	$meso$Al$_2$O$_3$/SO$_4^{2-}$-I	532	2.9	66
8	$meso$Al$_2$O$_3$/SO$_4^{2-}$-II	567	2.4	62
9	$meso$Al$_2$O$_3$/SO$_4^{2-}$-III	570	3.4	73 (81[g])
10	$meso$Al$_2$O$_3$/SO$_4^{2-}$-IV	571	2.9	56

[a] Reaction conditions are as follows: reactor, a 10-mL stainless steel autoclave; catalyst, 50 mg; **1a**, 1.00 mmol; CO_2 pressure, 8.0 ± 0.2 MPa; reaction temperature, 313 K; reaction time, 2 h. [b] Each catalyst was pretreated at 773 K for 2 h under vacuum (10^{-4} Torr). [c] Determined by the BET method. [d] Determined by the DH method. [e] Determined by ^{1}H NMR, using Ph$_3$CH as an internal standard. [f] Prepared from Ca(OH)$_2$ at 873 K for 2 h under vacuum (10^{-4} Torr). [g] Reaction time was 4 h.

(**2b**), 5,6-dimethylphthalide (**3b**), and 5,6-dichlorophthalide (**4b**), were confirmed by comparison with ^{1}H NMR data in refs 9a, 9b, 9c, and 9d, respectively.

For reaction in an scCO$_2$-cosolvent system, cosolvent (0.1 mL) was added with a syringe into the autoclave containing **1a** and $meso$Al$_2$O$_3$/SO$_4^{2-}$-III in a nitrogen-filled glovebag, followed by the introduction of liquid CO$_2$.

The reaction procedures described above gave experimentally reproducible data for several runs.

Observation of Phase Behaviors. Into a 10-mL autoclave equipped with sapphire windows (TAIATSU TECHNO) was added 1.00 mmol of freshly distilled **1a** or **1b** and/or 0.1 mL of THF with a stirring bar, followed by the introduction of liquid CO$_2$. The mixture was stirred at 313 K for 15 min, and then the phase behavior was visually inspected through the windows.

1a-scCO$_2$ system: at the CO$_2$ pressure of 8.0 ± 0.2 MPa, **1a** dissolved almost completely in scCO$_2$, but a small amount of **1a** existed at the bottom of the vessel as a yellow liquid. Increasing the CO$_2$ pressure led to the increase in the solubility of **1a**, and **1a** completely dissolved at 10.0 ± 0.2 MPa. The scCO$_2$ phase was colorless and transparent under all the above conditions.

1a−THF−scCO$_2$ system: the addition of THF enhanced the solubility of **1a**, and **1a** completely dissolved even at the CO$_2$ pressure of 8.0 ± 0.2 MPa. The light yellow homogeneous fluid was then turbid, implying that local density enhancement occurred by the formation of **1a**−THF−CO$_2$ clusters.

1b−scCO$_2$ system: compared with **1a**, **1b** was far less soluble in scCO$_2$. Even at the CO$_2$ pressure of 13.0 ± 0.2 MPa, the white solids of **1b** remained at the bottom of the vessel. The scCO$_2$ phase was colorless and transparent in this system.

1b−THF−scCO$_2$ system: no drastic increase in the solubility of **1b** was observed by the addition of THF at the CO$_2$ pressure of 8.0 ± 0.2 MPa. The colorless fluid phase was somewhat turbid, indicative of the formation of **1b**−THF−CO$_2$ clusters in a slight amount.

Results and Discussion

Catalytic Activities of Various Solid Strong Base Catalysts. We first tested CaO, which had been prepared by thermal treatment of Ca(OH)$_2$, in the reaction of **1a** to **1b** in scCO$_2$ (Table 1, entry 1), because CaO exhibited the highest activity

for the reaction in benzene solvent.[3c,d] However the activity of CaO was quite low in scCO$_2$, presumably owing to the instantaneous formation of inactive CaCO$_3$ on the CaO surface in the dense CO$_2$. This result clearly indicates that representative solid strong base catalysts of alkaline earth oxides are inadequate for base-catalyzed reactions in acidic scCO$_2$ medium.

In our previous studies γ-alumina was found to be able to promote the intramolecular Tishchenko reaction in benzene solvent.[3d] Therefore, we applied three types of γ-aluminas, ALO-2, -3, and -4, to the reaction. ALO-2 contains a few weight percent of SO$_4^{2-}$ ions, ALO-3 includes Na$^+$ ions, and ALO-4 is almost pure γ-alumina. The three aluminas exhibited remarkable differences in the activity depending on the kind of impurities: ALO-2 showed quite high activity (Table 1, entry 2), while more basic aluminas of ALO-3 and -4 gave poor catalysis (entries 3 and 4).

It is assumed that the surface basicity of ALO-2 is weaker than that of ALO-3 and -4 through the electron-withdrawing inductive effects of included SO$_4^{2-}$ ions,[2a,10] which leads to less adsorption of acidic CO$_2$ onto the surface. The nature of alumina impeding the formation of the corresponding carbonate and our capability to adjust the surface basicity by incorporated SO$_4^{2-}$ ions gave us a fruitful guide to develop a new type of solid strong base catalyst that would efficiently function even in acidic scCO$_2$.

Interestingly, we found that the reaction was promoted by mesoporous alumina ($meso$Al$_2$O$_3$) possessing uniform nanosized pores 2.7 nm in diameter prepared from Al(O-sec-Bu)$_3$ through the sol−gel process[5] (entries 5 and 6), even though the $meso$Al$_2$O$_3$ contained no sulfate ions. The yield of 62% with $meso$Al$_2$O$_3$(#1) was much higher than that of 12% with pure γ-alumina, ALO-4. In this study we tested two lots of mesoporous alumina, $meso$Al$_2$O$_3$(#1) and $meso$Al$_2$O$_3$(#2), which had been prepared separately. Any difference in the catalytic activity between $meso$Al$_2$O$_3$(#1) and $meso$Al$_2$O$_3$(#2) would arise from a difference in the surface area.

This finding encouraged us to further develop $meso$Al$_2$O$_3$-type solid base *intentionally modified with SO$_4^{2-}$ ions* to achieve higher catalytic performance. We introduced sulfate ions into the framework of $meso$Al$_2$O$_3$, not on its surface, in a similar way as in the preparation of sulfated zirconia aerogels,[6] because **1a** requires close contact with a metal oxide surface to initiate the Tishchenko reaction.[2,3] A mesoporous alumina of $meso$Al$_2$O$_3$/SO$_4^{2-}$-I incorporating SO$_4^{2-}$ with a sulfur content of 0.23 wt % was successfully synthesized by the hydrolysis of Al(O-sec-Bu)$_3$ with deionized water containing H$_2$SO$_4$, and it exhibited a higher yield of 66% than the nonsulfated $meso$Al$_2$O$_3$ (entries 5 and 6 vs entry 7). It is noteworthy that an increase in the amount of SO$_4^{2-}$ in $meso$Al$_2$O$_3$ with a sulfur content from 0.23 to 0.48 wt % in $meso$Al$_2$O$_3$/SO$_4^{2-}$-II brought about an increase in the surface area, but a decrease in the yield, presumably owing to some reduction of the surface basicity (entry 8). $meso$Al$_2$O$_3$/SO$_4^{2-}$-III with a sulfur content of 1.30 wt % was synthesized with a relatively large amount of Al$_2$(SO$_4$)$_3$ in place of H$_2$SO$_4$ as a sulfate ion source. $meso$Al$_2$O$_3$/SO$_4^{2-}$-III had a higher surface area of 570 m^2 g^{-1} than the other aluminas. With $meso$Al$_2$O$_3$/SO$_4^{2-}$-III, an introduction of sulfate ions into the alumina framework led to not only an expansion of the surface area of mesoporous alumina, but also the highest yield of **1b** (entry 9), indicating that $meso$Al$_2$O$_3$/SO$_4^{2-}$-III had the most suitable basic character for the Tishchenko reaction of **1a** in acidic scCO$_2$.

$meso$Al$_2$O$_3$/SO$_4^{2-}$-IV, in which sulfate ions were introduced by (NH$_4$)$_2$SO$_4$, possessed a high surface area of 571 m^2 g^{-1},

TABLE 2: Comparison of the Reaction Rates of the *meso*Al$_2$O$_3$/SO$_4^{2-}$-III-Catalyzed Intramolecular Tishchenko Reaction of Phthalaldehyde (1a) to Phthalide (1b) in Various Reaction Media[a]

entry	reaction medium	pK_a of the cosolvent[b]	yield (%)[c]
1	benzene[d]		38
2	tetrahydrofuran[d]		40
3	scCO$_2$[e]		31
4	scCO$_2$-benzene[f]	[g]	48
5	scCO$_2$-tetrahydrofuran[f]	[g]	58
6	scCO$_2$-acetic acid[f]	4.8	<1
7	scCO$_2$-methanol[f]	15.5	6

[a] Reaction conditions are as follows: reactor, a 10-mL flask for entries 1 and 2 and a 10-mL stainless steel autoclave for entries 3−7; catalyst (pretreated at 773 K for 2 h under vacuum (10^{-4} Torr)), 50 mg; **1a**, 1.00 mmol; reaction temperature, 313 K; reaction time, 15 min. [b] Data taken from the following: *Ionization Constants of Organic Acids in Aqueous Solution*; Serjeant, E. P., Dempsey, B., Eds.; IUPAC Chemical Data Series No. 23; Pergamon Press: Oxford, UK, 1979. [c] Determined by ^{1}H NMR, using Ph$_3$CH as an internal standard. [d] The reaction was carried out with 1 mL of benzene or THF under N$_2$ atmosphere. [e] CO$_2$ pressure, 8.0 ± 0.2 MPa. [f] CO$_2$ pressure, 8.0 ± 0.2 MPa; the amount of the cosolvent, 0.1 mL. [g] Not discussed here.

but exhibited relatively low activity, indicating that (NH$_4$)$_2$SO$_4$ is not a suitable SO$_4^{2-}$ ion source for the present purpose (entry 10).

The ^{1}H NMR spectra of the THF-extracted crude material after depressurization of scCO$_2$ in entries 1−10 only showed those of reactant **1a** and product **1b**.

Comparison of Reaction Rates in Various Reaction Media. To compare a pure scCO$_2$ medium with other reaction media, we carried out the *meso*Al$_2$O$_3$/SO$_4^{2-}$-III-catalyzed reaction of **1a** to **1b** not only in a pure organic solvent of benzene or THF, but also in scCO$_2$-cosolvent systems (Table 2).

Although the reaction in pure scCO$_2$ was somewhat slower than those in benzene and THF solvents (entries 1 and 2 vs entry 3), a drastic increase in the reaction rate was observed when a small amount of benzene or THF was added as a cosolvent into scCO$_2$ (entries 1 and 2 vs entries 4 and 5). It should be noted that the reaction in the scCO$_2$−THF system proceeded 1.5- and 2-fold faster than those in pure benzene and THF solvents and that in pure scCO$_2$ medium, respectively. The former results clearly indicated that performing the *meso*Al$_2$O$_3$/SO$_4^{2-}$-III-catalyzed reaction in scCO$_2$ offers distinct improvement in the catalysis as well as green-chemical benefits in using nonpoisonous inorganic medium. The higher diffusivity and lower viscosity of the scCO$_2$−THF medium than liquid benzene and THF along with high dissolving power for **1a** and **1b** are likely to bring about the remarkable rate enhancement.

The fact that THF was the best cosolvent was somewhat surprising to us, because we had observed noticeable inhibition effects with THF solvent in comparison with benzene solvent upon the Tishchenko reaction catalyzed by γ-alumina (ALO-4).[3d] Since promoting the Tishchenko reaction requires Lewis acid sites such as surface metal cations as well as strong base sites, Lewis basic molecules such as THF are considered to retard the reaction through the adsorption onto Lewis acid sites. Tanabe and Saito also reported the poisoning effect with Lewis basic pyridine on the Tishchenko reaction of benzaldehyde over CaO.[3a] It can be speculated that THF added into scCO$_2$ predominantly reacts with CO$_2$ to give a Lewis acid−base complex, and thus the tight adsorption of THF onto the Lewis acid sites (Al^{3+}) on *meso*Al$_2$O$_3$/SO$_4^{2-}$-III could be suppressed. In addition, the presence of THF cosolvent in scCO$_2$ medium could improve the solubilizing power of scCO$_2$ toward **1a** and
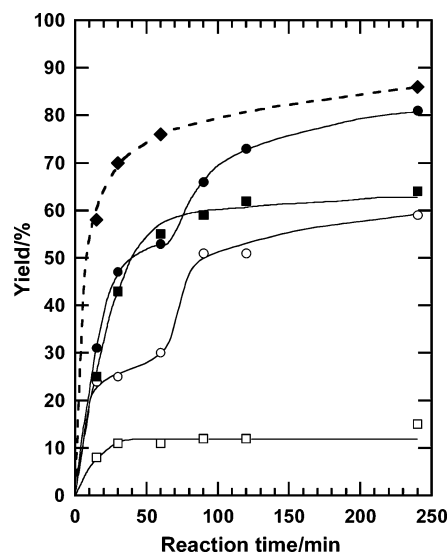

Figure 1. Variation of the yield of phthalide (**1b**) as a function of reaction time. Reaction conditions are as follows: reactor, a 10-mL stainless steel autoclave; catalyst (activated at 773 K for 2 h under vacuum (10^{-4} Torr)), 50 mg; phthalaldehyde (**1a**), 1.00 mmol; scCO$_2$, 8.0 ± 0.2 MPa; reaction temperature, 313 K; cosolvent, 0.1 mL (□) ALO-4, (■) ALO-2, (○) *meso*Al$_2$O$_3$(#2), (●) *meso*Al$_2$O$_3$/SO$_4^{2-}$-III, and (◆) *meso*Al$_2$O$_3$/SO$_4^{2-}$-III in scCO$_2$−THF medium.

1b. The **1a**-, **1b**-, and CO$_2$-philic natures of THF might lead to the formation of **1a**−THF−CO$_2$ and **1b**−THF−CO$_2$ clusters in the reactor, which should enhance the mass transfer of **1a** and **1b** inside the mesopores. It also should be noted that THF solvent does not essentially cause the rate retardation of the reaction catalyzed by *meso*Al$_2$O$_3$/SO$_4^{2-}$-III (entries 1 and 2 in Table 2). This implies that THF molecules would not interact with Al^{3+} sites on *meso*Al$_2$O$_3$/SO$_4^{2-}$-III more strongly than with those on ALO-4, so that **1a** would be able to replace the THF on the Lewis acid site smoothly, thereby initiating the reaction.

In contrast to the favorable effects of benzene and THF, the addition of a protic cosolvent such as acetic acid (CH$_3$CO$_2$*H*) and methanol (CH$_3$O*H*) gave remarkably negative effects on the reaction rates (entries 6 and 7). *The poisoning by a very weak acid, methanol (pK$_a$ = 15.5), clearly demonstrated that the Tishchenko reaction in scCO$_2$ was promoted by so strong base sites on mesoAl$_2$O$_3$/SO$_4^{2-}$-III as to be able to abstract a proton from methanol.* It can be estimated that the strength of the base sites on the alumina active for the Tishchenko reaction should be stronger than H_- = 15.5, where H_- is "acidity function" proposed by Paul and Long.[2,11]

Kinetic Study. Figure 1 shows changes in the yield of **1b** with reaction time over four alumina catalysts. The pure γ-alumina catalyst, ALO-4, exhibited the slowest reaction rate, and the reaction stopped after 30 min. By contrast, ALO-2 containing a few weight percent of SO$_4^{2-}$ ions that act as a "surface basicity controller" showed much higher activity and a longer lifetime of the catalysis compared with ALO-4. It was noted that the lifetime as well as the catalytic activity of *meso*Al$_2$O$_3$/SO$_4^{2-}$-III was the highest among the catalysts tested.

The deactivation in catalysis of ALO-4 in a short period was only observed in the reaction operated in scCO$_2$, while the same reaction in benzene solvent proceeded until **1a** was completely consumed.[3d] The deactivation mechanism will be discussed in detail in the section on Mechanistic Consideration.

Another interesting feature of the Tishchenko reaction catalyzed by *meso*Al$_2$O$_3$/SO$_4^{2-}$-III and *meso*Al$_2$O$_3$(#2) is a two-stepwise increment in the yield of **1b** in Figure 1. Considering that the relatively low solubility of **1a** in scCO$_2$ at 313 K and
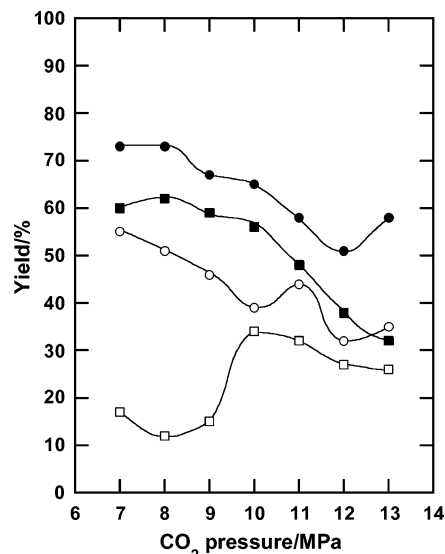
Figure 2. Variation of the yield of phthalide (**1b**) as a function of CO_2 pressure. Reaction conditions are as follows: reactor, a 10-mL stainless steel autoclave; catalyst (activated at 773 K for 2 h under vacuum (10^{-4} Torr)), 50 mg; phthalaldehyde (**1a**), 1.00 mmol; reaction temperature, 313 K; reaction time, 2 h; (□) ALO-4, (■) ALO-2, (○) *meso*Al_2O_3(#2), and (●) *meso*Al_2O_3/SO_4^{2-}-III.

8 MPa is responsible for the poor contact between **1a** and the alumina surface, we assume that the reaction on the mesoporous alumina proceeds in the following way: at the early stage within 30 min, the reaction is promoted mainly on the external surface of the mesoporous alumina. After the external active base sites are deactivated in 30 to 60 min, **1a** is gradually delivered into the cavity and the reactant can be contacted with the base sites on the internal alumina surface until the active base sites are fully deactivated. In Figure 1 is also shown the excellent acceleration effect of THF as cosolvent on the reaction with *meso*Al_2O_3/SO_4^{2-}-III. The addition of a slight amount of THF brought about a monotonic increase in the yield of **1b** instead of a stepwise one. This drastic change in the yield can be interpreted as follows: the concentration of **1a** in the vicinity of active base sites on the external surface and those inside the pores would always be almost equal owing to the high diffusivity and high solubilizing power of the scCO$_2$−THF medium for **1a**. In other words, the stepwise increment in the yield of **1b** would be attributed to the low solubility of **1a** in pure scCO$_2$.

Effect of CO$_2$ Pressure. Generally, the solubilizing power of a substance increases with an increase in its density.[1] Thus if the poor solubility of **1a** in scCO$_2$ retards the reaction, an increase in CO$_2$ density should enhance the reaction rate.

As is obvious from Figure 2, however, increasing the CO$_2$ density through an increase in the CO$_2$ pressure gradually decreased the activities of the catalysts, although some exceptional results were also observed. For instance, changing the CO$_2$ pressure from 9 to 10 MPa in the ALO-4-catalyzed reaction led to a remarkable increase in the yield of **1b**. It is well-known that the CO$_2$ density at 313 K greatly leaps from 493 kg m^{-3} at 9.0 MPa to 633 kg m^{-3} at 10.0 MPa.[12] Therefore, the improvement of the solubility of **1a** might account for the large increase in the yield in the CO$_2$ pressure range. In fact, using an autoclave with sapphire windows we observed that 1.00 mmol of **1a** completely dissolved in scCO$_2$ at 10.0 ± 0.2 MPa, but that a few oily drops of **1a** remained on the wall of the vessel at 9.0 ± 0.2 MPa. However, as we obtained a general tendency that the yields of **1b** roughly decreased with increasing

the CO$_2$ density on the other alumina catalysts, we can simply conclude that a dilution effect on **1a** with an increased amount of CO$_2$ mainly should be responsible for the reduction of the yield.

Variation in Reactants. Table 3 shows the results of the Tishchenko reactions of various aromatic 1,2-dicarbaldehydes (0.10 mmol) to the corresponding lactones with *meso*Al_2O_3/SO_4^{2-}-III (5 mg) in scCO$_2$ (353 K, 10.0 ± 0.2 MPa) for 2 or 24 h. Under this condition, the conversion of **1a** into **1b** was very rapid, and **1b** was formed in 86% yield in a short period of 2 h (entry 1).

Although the reaction of 2,3-naphthalenedicarbaldehyde (**2a**) was sluggish compared with that of **1a**, the corresponding lactone (**2b**) was obtained in 31% yield in 24 h (entry 2). The reaction of **2a** also proceeded much slower than that of **1a** in benzene solvent when γ-alumina (ALO-4) was used as a catalyst.[3d] The adsorption of **2a** on the alumina surface is a prerequisite process for the initiation of the reaction. The low reactivity is ascribed to the steric hindrance of a large naphthalene ring of the adsorbed species as well as the less CO$_2$-philic and less soluble nature of the naphthalene derivative.[13] The yield, however, could be raised to 60% by using THF (0.1 mL) as a cosolvent (entry 2) with the improvement of the mass transfer of **2a** and **2b** in the mesoporous network through the enhancement of the solubility of them.

The reaction of 4,5-dimethylbenzene-1,2-dicarbaldehyde (**3a**) progressed much faster than that of **2a**, but slower than that of **1a** (entry 3). This reactivity order suggests that the reaction rate was influenced mainly by the steric bulkiness of a reactant dialdehyde.
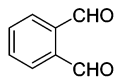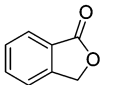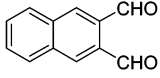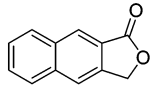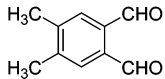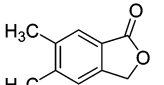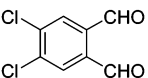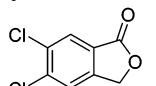
The present catalytic system was also successfully applicable to the chlorine-containing aromatic 1,2-dicarbaldehyde, **4a** (entry 4). The production of 4,5-dichlorophthalide (**4b**) even in a moderate yield was attractive, because **4b** has been employed as a precursor for the synthesis of pharmaceutically promising compounds.[9d,14] The result that the reaction of **4a** was much slower than that of **1a** might come from the Lewis acid−base interactions between the Lewis acid sites (Al^{3+}) and the two chlorine atoms of **4a**. Such interactions should prevent **4a** from being adsorbed in the appropriate arrangement for the reaction to take place. In addition, the highly volatile nature of **4a** would cause poor contact of **4a** with the solid catalyst that mainly stayed around the bottom of the autoclave. **4a** sublimes at 303−313 K at 760 Torr.[7]

The ^{1}H NMR spectra of the THF-extracted crude material in entries 1−4 included those of products **1b**−**4b** and reactants **1a**−**4a** exclusively.

Surface Basicity Measurement by Infrared Spectroscopy of Adsorbed Pyrrole. The noticeable difference in the catalytic activity for the Tishchenko reaction in scCO$_2$ between conventional γ-alumina (ALO-4) and *meso*Al_2O_3/SO_4^{2-} indicates that *meso*Al_2O_3/SO_4^{2-} possessed a less CO$_2$-philic surface with strongly basic sites: the SO_4^{2-} ions incorporated into the mesoporous alumina framework should render the surface less CO$_2$-philic by electron-withdrawing inductive effects of SO_4^{2-} ions upon lowering the average base strength of the oxide ions.[2a,10] In addition, considering that pure *meso*Al_2O_3 also exhibited a much higher activity than conventional γ-alumina (ALO-4), the mesoporous structure itself is associated with some reduction in the average base strength of oxide ions.

To compare the surface basicity between conventional γ-alumina (ALO-4) and *meso*Al_2O_3/SO_4^{2-}, we employed infrared spectroscopy using pyrrole as a probe molecule.[15] For less basic oxides such as zeolites, their base strength can be

Strong Base Catalysis of *meso*Al$_2$O$_3$/SO$_4^{2-}$ in scCO$_2$

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TABLE 3: Intramolecular Tishchenko Reaction of Various Aromatic 1,2-Dicarbaldehydes to Phthalides with *meso*Al$_2$O$_3$/SO$_4^{2-}$-III in Supercritical Carbon Dioxide[a]

entry	reactant		product		reaction time/h	yield (%)[b]
1	(2-CHO benzaldehyde)	**1a**	(phthalide)	**1b**	2	86
2	(naphthalene-2,3-dicarbaldehyde)	**2a**	(naphtho phthalide)	**2b**	24	31 (60[c])
3	(4,5-dimethyl benzene dicarbaldehyde)	**3a**	(dimethyl phthalide)	**3b**	2	60
4	(4,5-dichloro benzene dicarbaldehyde)	**4a**	(dichloro phthalide)	**4b**	24	40

[a] Reaction conditions are as follows: reactor, a 10-mL stainless steel autoclave; catalyst (*meso*Al$_2$O$_3$/SO$_4^{2-}$-III activated at 773 K for 2 h under vacuum (10^{-4} Torr)), 5 mg; reactant, 0.10 mmol; CO$_2$ pressure, 10.0 ± 0.2 MPa; reaction temperature, 353 K. [b] Determined by ^{1}H NMR, using Ph$_3$CH as an internal standard. [c] Tetrahydrofuran (0.1 mL) was used as a cosolvent.

PY$^-$/M   PY$^-$---HO   PYH---O   PYH---OH   PYH---(HO)

more basic oxide
lower wavenumbers (ν_R(ring))
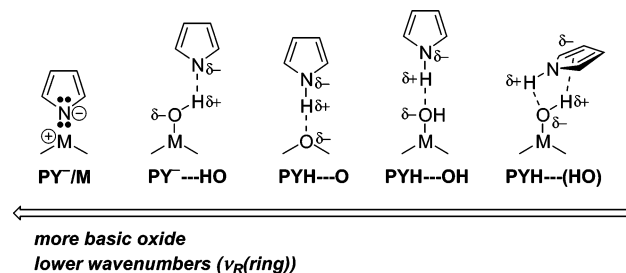
Figure 3. Various types of adsorbed species between metal oxide surface and a pyrrole molecule.[15c]

estimated by the shift of the NH stretching vibration (ν(NH)) band of the pyrrole hydrogen bonding with the base sites. This method, however, cannot be applied to such stronger basic oxides as alkaline earth oxides and alumina, because their base sites, O^{2-}, are so strong that they completely abstract an NH proton of a pyrrole to give a pyrrolate ion, C$_4$H$_4$N$^-$, and a surface OH group. In such cases, the empirical rule found out by Binet et al. on the shift of the ring-stretching (ν_R(ring)) bands of adsorbed pyrrole is instructive.[15c] According to this rule, the two ν_R(ring) bands of B$_{1,14}$ and B$_{1,15}$ for the pyrrolate ion coordinated on a Lewis acid site of a surface metal cation (designated as PY$^-$/M) appear at the lowest wavenumbers among the ν_R-(ring) bands of adsorbed pyrrole species shown in Figure 3. Thus, one can evaluate the number of strong base sites on a basic oxide by the intensity of the ν_R(ring) bands of PY$^-$/M.

Panels a and b in Figure 4 show the absorption bands due to ν_R(ring), B$_{1,14}$ of PY$^-$/M species and the bands due to the CH in-plane deformation, δ(CH), of adsorbed pyrrole, respectively. The strong absorptions at 1369 and 1373 cm^{-1} can be attributed to the ν_R(ring) of PY$^-$/M species on CaO and ALO-4, respectively,[15c] while no distinctive peak appears on *meso*Al$_2$O$_3$/SO$_4^{2-}$-III in the same range. The noticeable difference in the intensity reveals that the *average* base strength of O^{2-} ions of *meso*Al$_2$O$_3$/SO$_4^{2-}$-III is weaker than that of ALO-4, implying that not only the oxide framework arranged in the concave mesopores but the incorporated SO$_4^{2-}$ ions would cause some reduction in the surface basicity of *meso*Al$_2$O$_3$/SO$_4^{2-}$-III. Compared with the B$_{1,14}$ peaks, the corresponding B$_{1,15}$ peaks that would appear near 1450 cm^{-1} could not be clearly confirmed because of the confusion with other peaks. We thus
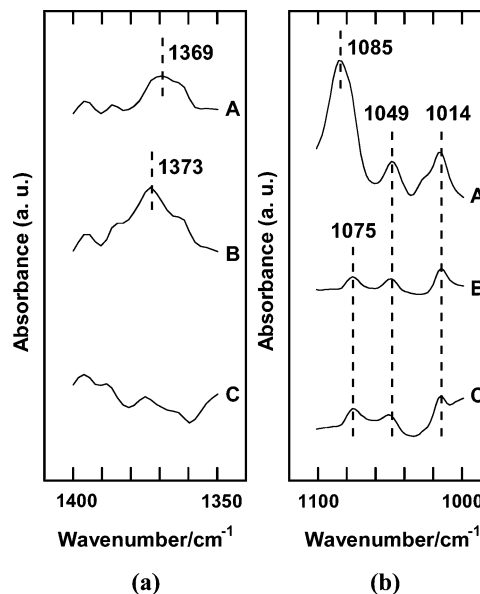
Figure 4. Infrared difference spectra between the catalysts before and after the adsorption of pyrrole: (a) ring-stretching of a pyrrole ring in pyrrolate ions, ν_R(ring); (b) CH in-plane deformation of pyrrole, δ-(CH). Spectra A, B, and C correspond to CaO, ALO-4, and *meso*Al$_2$O$_3$/SO$_4^{2-}$-III, respectively.

employed only the B$_{1,14}$ peaks for the discussion on the surface basicity.

It should be noted that the addition of a small amount of methanol obstructed the catalysis of *meso*Al$_2$O$_3$/SO$_4^{2-}$-III (see, Table 2, entry 7). This clearly demonstrates that *on the surface of mesoAl$_2$O$_3$/SO$_4^{2-}$-III exist a small number of strong base sites* that can promote the Tishchenko reaction even in the acid medium of scCO$_2$. All the previous reports on the Tishchenko reaction have also demonstrated that the reaction requires strong base sites on a solid catalyst to proceed.[2,3]

Analysis of the Catalyst Structures. The repeated measurement by the infrared absorption method after combustion of sulfated alumina samples in an induction furnace showed a constant sulfur content: *meso*Al$_2$O$_3$/SO$_4^{2-}$-I (0.23 wt %), *meso*Al$_2$O$_3$/SO$_4^{2-}$-II (0.48 wt %), and *meso*Al$_2$O$_3$/SO$_4^{2-}$-III (1.30 wt %). This proves that these catalysts are made of aluminum oxides with SO$_4^{2-}$ ions *homogeneously dispersed* in their frameworks.
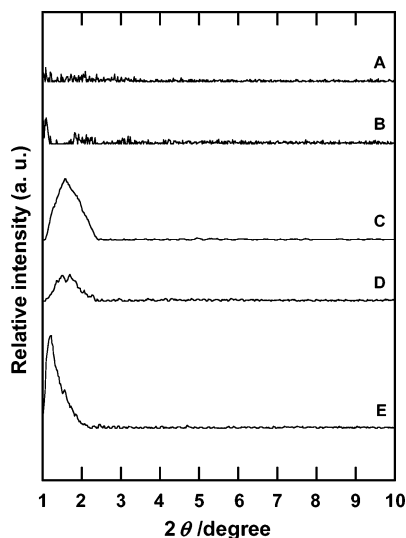
Figure 5. XRD spectra of ALO-4 (A), ALO-2 (B), *meso*Al$_2$O$_3$(#1) (C), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I (D), and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III (E) in the 2θ region of 1−10°.
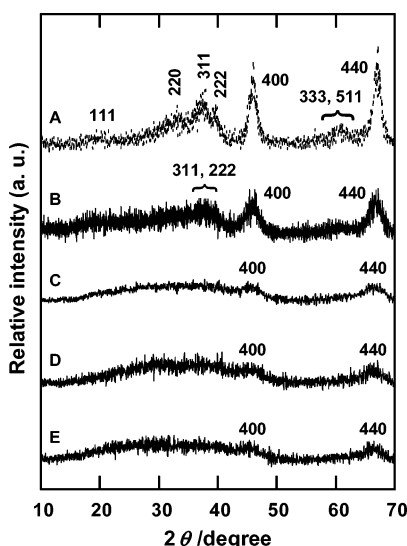
Figure 6. XRD spectra of ALO-4 (A), ALO-2 (B), *meso*Al$_2$O$_3$(#1) (C), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I (D), and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III (E) in the 2θ region of 10−70°.

X-ray diffraction analyses of ALO-2, ALO-4, *meso*Al$_2$O$_3$-(#1), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III were performed for elucidation of their porous and bulk structures, and the results are shown in Figures 5 and 6.

For ALO-2 and ALO-4 possessing irregular pores, no intense peak was observed in the low 2θ region of 1−10° (spectra A and B in Figure 5), while *meso*Al$_2$O$_3$(#1), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III exhibited an intense peak at 1−2° that is assignable to the mesoporous structure (spectra C, D, and E in Figure 5).[5] Davis et al. reported that the use of sodium dodecylbenzenesulfonate was not appropriate as an anionic surfactant for the synthesis of mesoporous alumina, because traces of sulfur components remained in the material even after calcination treatment and caused some collapse in the mesopore structure.[5] They showed that the partially collapsed mesostructure brought about a higher *d* spacing in XRD patterns, which is peculiar to the mesoporous materials with randomly ordered pores. The characteristic peak of *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III appeared at a higher *d* spacing than that of pure *meso*Al$_2$O$_3$(#1), indicating that the sulfur components in *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III were incorporated into the alumina framework to disturb the meso-

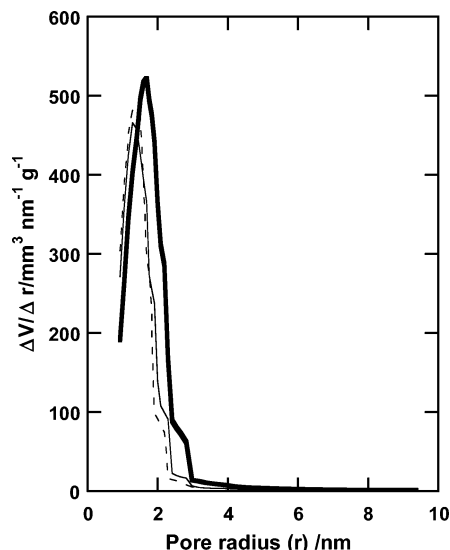**Figure 7.** Pore-size distribution curves calculated by Dollimore−Heal theory.[8b] Solid line, *meso*Al$_2$O$_3$(#1); dashed line, *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I; bold line, *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III.

structure. Although the similar shift to a higher *d* spacing was not observed with *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, the intensity of the peak was weak and the peak was split compared with *meso*Al$_2$O$_3$-(#1), indicative of the partial collapse of mesoporous structure by the bulk sulfur components.

The XRD patterns reflecting the bulk structures appeared in the higher 2θ region of 10−70° (Figure 6). The peaks attributed to the cubic spinel structure (400 and 440) were confirmed with ALO-2 and ALO-4, indicating that the two aluminas are composed of γ- and η-alumina (spectra A and B).[16] It should be noted that *meso*Al$_2$O$_3$(#1), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III also exhibited the 400 and 440 peaks (spectra C, D, and E), although their intensities are quite low. It can be speculated that *meso*Al$_2$O$_3$(#1), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III possess the cubic spinel structures considerably distorted by the formation of regularly mesoporous frameworks.

The mesoporous structures were also characterized by the N$_2$ adsorption−desorption measurement employing the Dollimore−Heal (DH) theory,[8b] and the pore-size distribution curves are given in Figure 7 for *meso*Al$_2$O$_3$(#1), *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III. Although the pore-size distribution of *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III was somewhat broader than those of *meso*Al$_2$O$_3$(#1) and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I, the presence of sulfur components hardly affected the pore-size distribution.

To further confirm whether the SO$_4{}^{2-}$ ions in *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-I and *meso*Al$_2$O$_3$/SO$_4{}^{2-}$-III exist in the alumina frameworks or on the surface, we measured the infrared spectra of these catalysts that had been pressurized into thin disks and activated at 773 K for 2 h under vacuum (10^{-4} Torr). Considering that no distinctive absorption band due to the covalent S=O bonds of SO$_4{}^{2-}$ species on the surface[2a,10,17] was observed (not shown here), we can deduce that the SO$_4{}^{2-}$ ions are not on the surface but are incorporated into the alumina framework, leading to weakening characteristic S=O stretching vibration. It has been well accepted that *surface* SO$_4{}^{2-}$ species with S=O bonds possessing high double bond character remarkably increase the surface acidity of metal oxides and in some cases convert the oxides into solid superacids, while *bulk* SO$_4{}^{2-}$ ions with partial double bond character hardly influence the surface acidity.[2a,17] For instance, Bedilo and Klabunde reported that surface SO$_4{}^{2-}$ species on ZrO$_2$ remarkably increase the surface acidity of ZrO$_2$ and make the oxide into a solid
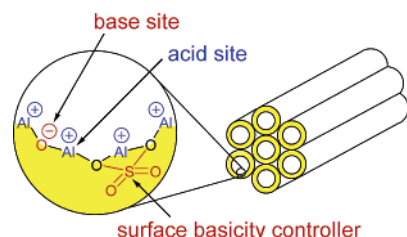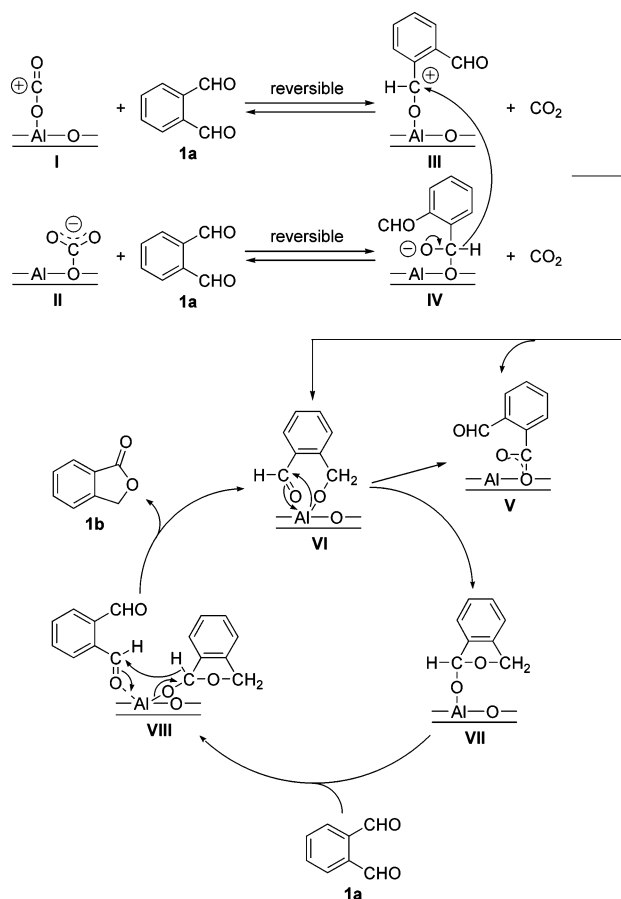
Figure 8. Proposed framework structure of *meso*Al$_2$O$_3$/SO$_4^{2-}$.

SCHEME 2: Proposed Mechanism for the Intramolecular Tishchenko Reaction of Phthalaldehyde (1a) to Phthalide (1b) in ScCO$_2$

superacid, while SO$_4^{2-}$ ions inside the ZrO$_2$ framework scarcely raise the surface acidity of ZrO$_2$.[6]

We suppose that the SO$_4^{2-}$ ions in *meso*Al$_2$O$_3$/SO$_4^{2-}$-I and *meso*Al$_2$O$_3$/SO$_4^{2-}$-III slightly suppress the surface basicity of the mesoporous aluminas.

On the basis of the above XRD, pore-size distribution, and IR data, we imagine the surface structures of *meso*Al$_2$O$_3$/SO$_4^{2-}$-I and -III as depicted in Figure 8.

Mechanistic Consideration. It has been established by previous studies with IR, XPS, and UPS techniques that the Cannizzaro-type disproportionation of nonenolizable aldehydes such as benzaldehyde and formaldehyde takes place over basic metal oxides such as MgO and alumina.[18,19] We have also proved through an IR study[3d] that the adsorption of **1a** onto an acid site (Al^{3+}) and a base site (O^{2-}) on γ-alumina produces Cannizzaro-type products, i.e., a reduced product, *o*-AlOCH$_2$C$_6$H$_4$-CHO (**VI**) and an oxidized product, *o*-AlOCOC$_6$H$_4$CHO (**V**), where Al is a surface aluminum cation in Scheme 2.

Figure 9 shows the infrared spectrum of **1a** adsorbed on *meso*Al$_2$O$_3$/SO$_4^{2-}$-III. The strong absorption band at 3005 cm^{-1}

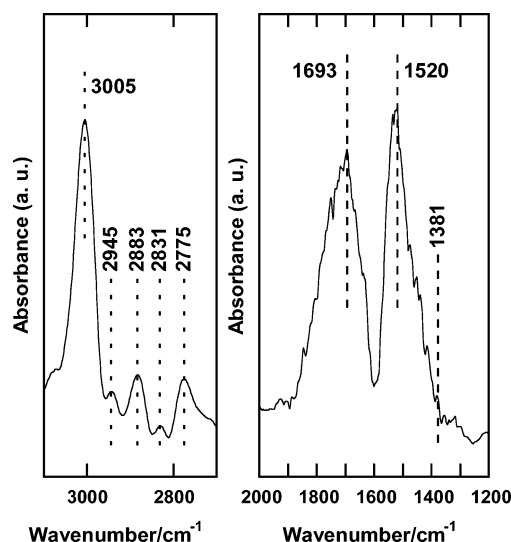**Figure 9.** Infrared difference spectra of *meso*Al$_2$O$_3$/SO$_4^{2-}$-III between before and after the adsoprtion of phthalaldehyde (**1a**).

can be assigned to the aryl-H stretching vibration of the adsorbed species involving **V** and **VI** in Scheme 2. The bands at 2831 cm^{-1} and 2775 cm^{-1} and the band at 1693 cm^{-1} are assignable to the C-H and C=O stretching vibration of the aldehyde groups of **V** and **VI**, respectively. The bands at 2945 and 2883 cm^{-1} should be due to the C-H stretching vibration of the -CH$_2$- group of **VI**, while the band at 1381 cm^{-1} may be attributed to the vibration of the -CH$_2$-O- moiety.[3d,19a] The band at 1520 cm^{-1} and its shoulder part around 1450 cm^{-1} are assignable to the asymmetric and symmetric stretching vibration of a carboxylate group of **V**.

Intermediate **VI** is playing a key role as an active species in the catalytic Tishchenko reaction of phthalaldehyde as described previously (Scheme 2).[3d] In scCO$_2$ medium, the interaction of dense CO$_2$ molecules with the alumina surface should also affect the catalysis. Apparently the prompt deactivation of a catalyst observed especially for more basic ALO-3 and -4 is caused by the strong adsorption of an acidic CO$_2$ molecule onto an active base site of O^{2-}. For the Tishchenko reaction to take place, tight adsorption of CO$_2$ on alumina surface must be avoided and the adsorbate-exchange reaction of **II** to **IV** on the base site must proceed smoothly. This prospect has been realized on ALO-2 and *meso*Al$_2$O$_3$/SO$_4^{2-}$-III, whose average surface basicities were weakened by the contained SO$_4^{2-}$ ions for ALO-2 and by both SO$_4^{2-}$ and the mesoporous structure for *meso*Al$_2$O$_3$/SO$_4^{2-}$-III.

As described above, the deactivation of a catalyst in the Tishchenko reaction is likely to depend on the relative stability between adsorbed species of **II** and **IV** in Scheme 2. Over the more basic alumina, stronger adsorption of CO$_2$ at a base site is realized and the state of **II** is more stabilized with the base site occupied. In contrast, on less basic and more acidic *meso*Al$_2$O$_3$/SO$_4^{2-}$-III due to the electron-withdrawing effect of SO$_4^{2-}$ ions, an adsorbed CO$_2$ molecule should be less stabilized and a strong acid site of an adjacent Al cation tends to coordinate with an oxygen atom of the adsorbed CO$_2$ to displace the CO$_2$ molecule from the base site to the aluminum cation as shown in Scheme 3. Therefore, the base site is regenerated. Such a dynamic migration of CO$_2$ on an oxide surface has been observed even over a strong solid base, CaO, whose acid strength is far lower than that of alumina.[20] Moreover, Parkyns confirmed the formation of **X** on γ-alumina in which only an oxygen atom of CO$_2$ participates in the coordination based on the bands at 1820 and 1780 cm^{-1} with infrared spectroscopy.[21]

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SCHEME 3: A Migration of Adsorbed CO_2 from a Strong Base Site (O^{2-}) to an Adjacent Strong Acid Site (Al^{3+}) through an Adsorbate-Exchange Reaction
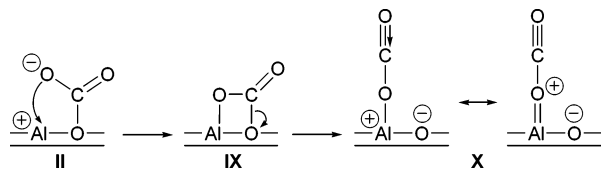
In addition to the CO_2 adsorption on the active base sites, another cause should be taken into account to explain why the conversion of **1a** to **1b** was incomplete and why the two-stepwise increment was observed in the yield of **1b** in the *meso*Al_2O_3(#2)- and *meso*Al_2O_3/SO_4^{2-}-III-catalyzed reactions in Figure 1 (see, Kinetic Study). It can be speculated that a catalytically active species of **VI** would be oxidized to an inactive species of **V** along with the conversion of **VI** to **VII** as shown in Scheme 2. In fact, Knözinger et al.,[22] Tanabe and Saito,[3a] and we[3d] have previously observed by infrared spectroscopy that the oxidation of surface alkoxide species to the corresponding carboxylate takes place smoothly over alumina. Tanabe and Saito concluded that this oxidation, i.e., the oxidation of aluminum benzylate to aluminum benzoate, is responsible for the low activity of alumina catalyst for the *intermolecular* Tishchenko reaction of benzaldehyde.[3a]

Conclusions

It was demonstrated for the first time that $scCO_2$, an ideal reaction medium in view of *green chemistry*, can be applied to solid strong base-catalyzed reactions. The mesoporous alumina with SO_4^{2-} incorporated in the alumina framework (*meso*Al_2O_3/SO_4^{2-}) exhibited highly effective strong base catalysis for the Tishchenko reaction in $scCO_2$. Especially, when $scCO_2$ was used together with a small amount of THF as a cosolvent, remarkable acceleration in the reaction rate was achieved; the reaction in the $scCO_2$−THF medium proceeded 1.5-fold faster than those in conventional organic solvents such as benzene and THF.

The high activity of *meso*Al_2O_3/SO_4^{2-}-III for the Tishchenko reaction in $scCO_2$ medium is attributed to the following three key factors: (i) aluminum atoms intrinsically do not form stable carbonate salts; (ii) SO_4^{2-} ions incorporated in the alumina framework and the specific mesoporous structure of *meso*Al_2O_3/SO_4^{2-}-III decrease the *average* surface basicity to a certain extent, but there exists a small number of strong base sites on its surface that can abstract a proton from a very weak Brönsted acid of methanol and promote the Tishchenko reaction in $scCO_2$; and (iii) a Lewis acid site (Al^{3+}) adjacent to an active strong base site (O^{2-}) enhances the adsorbate-exchange reaction between CO_2 and a reactant aldehyde on the base site: the Al^{3+} site is coordinated with an oxygen atom of CO_2 adsorbed on the base site as shown in **IX** in Scheme 3, and the resulting coordination state of **IX** becomes unstable to give **X** with a *free* base site.

The following two roles of THF as cosolvent are considered for the improvement in the reaction rate: (i) enhancement of the mass transfer of the reactant and the product into mesopores by improving their solubilities in $scCO_2$, and (ii) prevention of strong CO_2 adsorption onto an active base site by the formation of THF−CO_2 interaction (Lewis base and acid interaction).

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