

Formation of citraconic anhydride via condensation of dialkyl succinates and formaldehyde

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Abstract

The formation of citraconic anhydride (CAN) from the condensation of succinic acid and its derivatives with formaldehyde over oxide catalysts is described. Alumina and aluminum phosphate are active catalysts that give selectivity to citraconic anhydride as high as 75% in an integral fixed bed reactor. Weakly acidic sites on the catalyst surface, particularly Lewis acid sites, are responsible for activating the desired reaction pathway. Strongly acidic sites lead to cracking and coking, while basic sites facilitate the Cannizzaro reaction of formaldehyde to carbon dioxide and methanol. Catalyst deactivation via coking occurs over the course of reaction, but activity is easily restored by regeneration in air at elevated temperatures. The reaction system under investigation is part of an overall process to produce itaconic acid from renewable resource-based succinic acid. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The production of succinic acid (1,4-butanedioic acid) as a renewable resource-based feedstock is gaining momentum with new innovations in fermentation and process technology [1–5]. Recent advances in fermentation [6], based on genetic modifications of the microorganism, have led to yields of succinic acid as high as 1.1 kg succinic acid/kg glucose (with CO₂ incorporation) and have nearly eliminated acetic acid as a co-product. A significant decrease in the cost of producing succinic acid is expected as the manufactur-

ing technology matures. Succinic acid can also be obtained in large amounts as a by-product of adipic acid production [7]. This growing availability of succinic acid, coupled with the reactivity of its two carboxylic acid and two active methylene groups, has led us to examine it as a reactant for biomass-based chemicals production.

Succinic acid and its derivatives undergo many chemical transformations to specialty chemicals and commodities. One important reaction unique to diesters of succinic acid is condensation with aldehydes and ketones, known as the Stobbe condensation [8]. First reported in 1893 [9], the reaction takes place in alcohol solution in the presence of a strong base (alkoxide or sodium hydride) to give the half-ester of the corresponding substituted itaconate as a product.

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The classic Stobbe condensation does not occur to any practically useful extent when formaldehyde (methanal) is used as the aldehyde. However, the vapor-phase catalytic (heterogeneous) condensation reaction of succinic acid derivatives with formaldehyde does take place to give citraconic anhydride (3-methyl-2,5-furandione) (CAN). There are no reports in the open literature of citraconic anhydride formation via this route, but the patent literature describes two previous studies [10–13], with transient yields as high as 70% of theoretical claimed [10]. The motivation for CAN formation is to produce itaconic acid (2-methylene-1,4-butanedioic acid) via hydrolysis of CAN to citraconic acid (2-methyl-2-butenedioic acid) and isomerization to itaconic acid. Itaconic acid is a valuable monomer in the formulation of polymers because of its unique chemical properties, which derive primarily from the conjugation of one of its two carboxylic acid groups with the alkene function [14]. The molecule is thus a carboxylated analogue of the important monomer methacrylic acid, and as such, it is able to take part in addition polymerization, giving polymers with many free carboxylic acid groups that confer advantageous wettability and ion exchange properties.

Itaconic acid is currently produced commercially (8×10^6 kg per year) by the fermentation of glucose using *Aspergillus terreus* [14]. This fungal fermentation is carried out in batch processes requiring dilute solutions (~ 10 wt.% glucose as a feed) and 8–10 days per batch. Itaconic acid yields are on the order of 50–60% of theoretical; this process results in an itaconic acid price of \sim US \$ 2/lb and is not expected to lead to commodity-scale production in the foreseeable future.

In this paper, we examine a variety of potential catalyst materials for the formation of CAN via the vapor-phase reaction of succinic acid derivatives (succinates) with formaldehyde. The primary focus is to quantify the acid–base properties of the catalysts and correlate them with the yield of CAN and the conversion of dimethyl succinate (DMS), with the goal of identifying catalyst materials possessing a suitable composition of acidic and basic sites favorable for CAN formation. Optimization of the reaction and further conversion of citraconate to itaconic acid will be discussed in forthcoming publications.

2. Experimental

2.1. Feed materials

Two succinate esters were used as feedstocks in these investigations. Dimethyl succinate (DMS) (Aldrich Chemical Co., 98%) was used in most reactions. Diethyl succinate (DES) (Aldrich, 99%) was used in initial experiments, but led to complications in analysis because of transesterification to ethyl methyl succinate in the presence of methanol formed from formaldehyde in the reaction. Formaldehyde was used in one of two forms: 1,3,5-trioxane (TO) (Aldrich, 98%), the anhydrous trimer, and formalin (JT Baker), a commercially available source containing 37 wt.% formaldehyde and 10 wt.% methanol in aqueous solution. Citraconic anhydride (Aldrich, 99%) was used for calibration and control experiments.

2.2. Catalyst materials

A number of metal oxides were obtained from commercial sources or prepared in the laboratory and evaluated as catalysts for the condensation reaction. Purchased materials include aluminas (Saint-Gobain Norpro, described below), controlled pore silicas (CPG Inc.), and zeolite 13X (Aldrich). Alumina, aluminum phosphate, mixed MgO/Al_2O_3 , and iron oxides were prepared in the laboratory. Metal salts, acid, or base were impregnated onto some of these materials in an attempt to improve catalyst performance. Preparation procedures are given in the following sections.

2.2.1. Aluminas

Several commercial aluminas (Norpro) designated SA3132, SA3177, SA6173, and SA6175 were obtained for use as catalysts. The SA6173 and SA6175 are γ -aluminas, SA3177 is classified as a transition-phase alumina, and SA3132 is a silica-alumina. Their compositions are given in Table 1; no impurities other than SiO_2 and Fe_2O_3 are present in detectable quantities. These materials were ground and sieved to $-30 + 60$ mesh and calcined in air for 6 h at $500^\circ C$ before loading into the reactor.

2.2.2. Aluminum phosphate

Aluminum phosphate with an atom fraction $P/(Al + P) = 0.44$ ($P/Al = 0.8$), hereafter

Table 1
Composition of Norpro aluminas (wt.%)

Alumina	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
SA3132	82	18	<0.1
SA3177	>98	<2	<0.1
SA6173	>99.85	<0.15	<0.1
SA6175	99.7–99.9	0.1–0.2	<0.1

referred to as AP-44, was prepared from Al(NO₃)₃ and (NH₄)₂HPO₄ by the method of Rebenstorf et al. [15]. These precursors were first mixed into water and were acidified with nitric acid. The hydrogel was formed by adding 30% ammonia solution to achieve a pH of 5.0. The residue was filtered and washed with deionized water, dried at 120°C overnight and then calcined at 400°C for 3 h.

2.2.3. Mixed MgO/Al₂O₃

Mixed Mg/Al oxides were prepared from gels produced by mixing two solutions (A and B) according to the procedure described by Corma et al. [16]. Solution A was prepared by mixing Mg(NO₃)₂ and Al(NO₃)₃ to a concentration (Al + Mg) of 1.5 M for Mg atom fractions of 0.005 (hereafter denoted AM-0.5), 0.04 (AM-04), 0.06 (AM-06), 0.12 (AM-12), 0.25 (AM-25), 0.36 (AM-36), and 0.75 (AM-75). Solution B was composed of either 1.0 M Na₂CO₃ with NaOH added to obtain a pH of 13 (for Mg atom fractions of 0.25–0.75), or of 30 wt.% NH₃ solution (for Mg atom fractions 0.005–0.12). Solution B was added slowly to solution A under vigorous stirring for a period of 2–3 h, during which time a white precipitate formed. The gel precipitate was aged overnight, filtered, washed thoroughly, and calcined at 450°C to get a Mg/Al mixed oxide of the stated ratio. A sample of pure alumina (denoted alumina in-house) was also prepared using this method, starting with Al(NO₃)₃.

2.2.4. Iron oxide

To obtain 15 g of Fe₂O₃, 50 g of FeCl₃ was dissolved in 350 ml of water and a 30% ammonia solution was added to attain a pH of 8.0. The residue was washed with deionized water, dried at 100°C overnight, and calcined at 500°C for 6 h.

Table 2
Salts, acid, and base addition to oxide supports

Species added	Oxide catalyst	Loading (mmol/g)
Ce ₂ (SO ₄) ₃	Zeolite 13X	0.5
NdCl ₃ + LaCl ₃	Zeolite 13X	2.0 (Combined)
Ce ₂ (SO ₄) ₃	SA3132 alumina	0.5
Li ₂ CO ₃	SA3132 alumina	0.5
KH ₂ PO ₄	SA3132 alumina	2.0
KOH	SA3177 alumina	0.3
KH ₂ PO ₄	SA3177 alumina	0.015
H ₂ SO ₄	SA3177 alumina	0.15

2.2.5. Supported catalysts

The salts, acid, and base added to several of the above oxide catalysts are listed in Table 2. The incipient wetness method was used to load metal salts KH₂PO₄, Ce₂(SO₄)₃, Li₂CO₃, K₂CO₃ as well as KOH and H₂SO₄ by introducing to the oxide a solution of the desired quantity of salt, acid, or base in an amount just sufficient to fill the pores and wet the outside of the particle. The wetted oxide was dried slowly to distribute the salt through the pore volume, and then calcined in a furnace at 500°C for 4–5 h. Zeolite 13X was partially ion exchanged with a mixed LaCl₃/NdCl₃ solution (0.20 M LaCl₃ and 0.21 M NdCl₃ in solution, 3.5 ml solution/g zeolite 13X) to reproduce materials reported as active for CAN formation in the patent literature [11–13].

2.3. Apparatus and experimental conditions

A fixed bed reactor system was designed and constructed to operate continuously at temperatures of 300–500°C and pressures up to 3.3 MPa. A schematic of the experimental reactor setup is depicted in Fig. 1. An Autoclave Engineers cone closure tubing reactor (Part# CC.985SS20) of 316 stainless steel is used as the reactor vessel. The length, o.d., and i.d. of the reactor vessel are 102, 19.1 and 11.1 mm, respectively. The nominal capacity of the reactor is 10 ml. A medium quartz frit fitted in a 5 mm long and 10 mm o.d. quartz tube is used to hold the catalyst in the reactor. A stainless steel screen is wrapped over the tube to secure it at the bottom of the reactor. This holds the solid catalyst yet allows the liquid and vapor phases to flow through and also enables the catalyst to be loaded and unloaded easily. The reactor is heated by clamshell heaters controlled by an Omega series

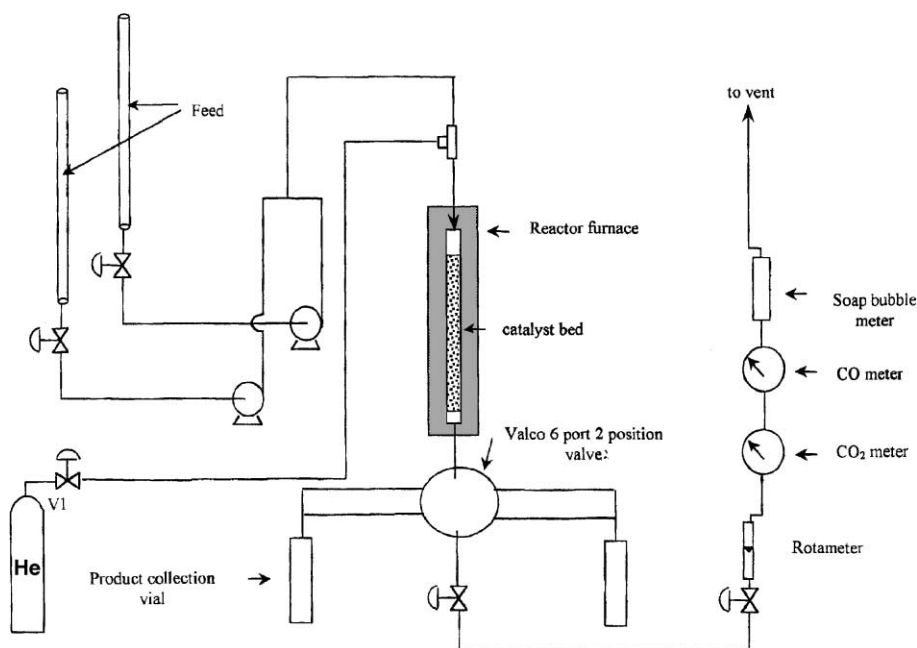


Fig. 1. Schematic diagram of reactor system.

CN-2010 programmable temperature controller with the control thermocouple reading the temperature of the external reactor surface.

The feed is introduced into the reactor using Bio-Rad Soft-Start HPLC Pumps. A 1/16 in. stainless steel tubing is used from the pump outlet to the reactor inlet. The choice of feed species dictates the feed configuration of the system used, and so the liquid feed system is designed accordingly. If TO is used as the formaldehyde source, then DMS and TO are combined to form a single, homogeneous phase and only a single pump is used. (The solubility of TO in DES and DMS is approximately 1 mol TO/mol ester at 25°C, so as long as the TO:DMS feed ratio is below one the feed is homogeneous.) For DMS/formalin feeds, two HPLC pumps are used to deliver the feeds separately to the reactor. All feeds are preheated by heating the 60 cm of feed tubing just before the reactor inlet to 250°C using 0.5 in. heating tape. Helium is used as a carrier gas in most experiments to aid in vaporization of feed and to sweep the vaporized feed into the reactor. A 1/8 in. stainless steel tube from the helium cylinder to the top of the reactor is also heated to 250°C using heating tape.

Reactor effluent exits the reactor via a heat-traced tube and enters a six port Valco valve; this valve directs products to one of two product collection traps consisting of 25 ml stainless steel sample cylinders immersed in water. The six-port valve and reactor outlet tube are maintained at 200°C to keep the products in the vapor phase above the trap. The temperature of product traps was varied with the feed used for the reaction: ice water was used as a coolant if the feed was DMS and formalin, in order to collect methanol and formaldehyde, and warm water was used for DMS/TO feeds to prevent solidification of unreacted TO. Most experiments were carried out for 5 h at steady state, with samples taken in 30 min intervals. The reaction conditions are presented in Table 3; the liquid flow rate reported is the sum of the flow rates from each pump when two pumps are used.

2.4. Product analysis

2.4.1. Chromatography

High-performance liquid chromatography (HPLC) and gas chromatography (GC) were used to identify

Table 3

Base-case reaction conditions	
Reaction temperature (°C)	380
Reactor pressure (MPa)	0.5
Feed line pre-heat temperature (°C)	250
Succinate to formaldehyde molar ratio	1:2
Liquid feed flow rate (ml/min)	0.15
Carrier gas flow rate (ml (STP)/min)	27
WHSV (kg succinate/kg catalyst/h)	0.90

and separate the reaction products. For HPLC, a Bio-Rad HPX-87H organic acid Aminex ion exchange resin column (300 mm × 7.8 mm i.d.) was used with UV and RI detectors in series for product quantification with oxalic acid as an internal standard. A solution of 20% acetonitrile in 5 mM sulfuric acid was taken as the mobile phase; raw product samples were diluted 20-fold with mobile phase and then injected. The HPLC column temperature was kept at 40°C using a column heater to achieve better resolution than at room temperature. GC analysis was performed using an intermediate capillary column (SPB1, Supelco) of 0.53 mm i.d. and 30 m length. The column was installed in a Varian 3300 GC with a flame ionization detector (FID) and helium (30 ml/min) as a carrier gas. Methyl lactate was used as an internal standard. Product identification was conducted by matching residence times in GC and HPLC, and by GC coupled with mass spectrometry (GC–MS) in a separate instrument. Outlet gases from the reactor were analyzed directly using CO and CO₂ meters (Riken Inc.).

2.4.2. Product hydrolysis

Complete analysis of the raw reactor effluent was difficult to carry out, because 20% of the total citraconates formed were present as monomethyl or dimethyl esters and these esters co-elute with their analog succinates. To accurately measure product yields and selectivities, it was necessary to hydrolyze the reaction product mixture to recover all citraconate and succinate species as free acid. This hydrolysis was accomplished by adding dilute sulfuric acid to the product solution and then refluxing for 2–3 h. Since hydrolysis was time consuming, it was only performed extensively for product samples from selected experiments. Results that follow are noted as being either hydrolyzed or unhydrolyzed,

with total citraconate yield or citraconic anhydride yield, respectively, used as a measure of catalyst performance.

2.4.3. Product yield and selectivity calculations

Product yield is reported as a percentage of the theoretical yield based on succinate fed to the reactor; product selectivity is the percentage of succinate reacted that goes to the product. The CO₂ yields are also based on succinate in the feed, but are divided by two to account for the fact that each mole of succinate ester can give 2 mol of CO₂ upon cracking. The conversion of DMS is given by the ratio of moles of succinate reacted to moles of succinate fed to the reactor. Finally, a balance on total succinate (C₄) carbon is done for each sample as a measure of the quality of the experiment. Results are reported as the percentage of initial succinate carbon recovered in the product mixture.

2.5. Catalyst characterization

Properties of the catalysts obtained from commercial sources or prepared by the methods described earlier have been characterized for BET surface area, surface acidity and basicity, and strength of acidic sites. A Micromeritics Pulse Chemisorb 2700 was used to determine the BET surface area of solid materials used in experiments via nitrogen adsorption at 78 K.

Acid site concentration and strength on the catalyst surface were measured by temperature-programmed desorption (TPD) of ammonia using the Micromeritics Pulse Chemisorb 2700. Base site concentration was determined by TPD of CO₂ in the same instrument. For both of these analyses, 1 g of catalyst was placed in a sample tube and heated to 500°C for 3 h, then cooled to room temperature. The catalyst sample was exposed to flowing CO₂ or NH₃ for 1 h at 298 K, flushed with nitrogen until a stable baseline was achieved on the detector, and then heated under flowing nitrogen to 500°C at 20°C/min while monitoring the effluent gas composition.

Acid site strength and base site strength were further characterized by *n*-butyl amine adsorption and titration with Hammett indicators in dry benzene; results are reported as the range of the Hammett acidity function H_0 for each indicator.

3. Results and discussion

3.1. Catalyst properties

Table 4 shows the surface area, acid and base site concentrations, and acid strengths of the catalysts used in the study.

3.1.1. Acidic and basic site concentrations

Representative ammonia and carbon dioxide TPD profiles to characterize surface acid and base site concentrations are given in Figs. 2 and 3, respectively. As seen in Table 4, silica CPG-3000 has low surface area and does not adsorb detectable quantities of either CO₂ or NH₃. In contrast, CPG-75 displays significant surface acidity because of its high surface area. This acidity is Brønsted in nature as reported in the literature [17]. Aluminum phosphate (AP-44) and zeolite 13X have high concentrations of acidic sites, and do not adsorb CO₂. Alumina (SA3177) has both acidic and basic sites; the acid sites are understood to exhibit Lewis acidity [17]. The Mg/Al oxides also have significant acid and base site densities. There is relatively little dependence of acid and base site densities on Mg content of mixed oxides except at high Mg loadings (AM-36). This finding is consistent with that of Shen et al. [18], who have characterized the acidity and

basicity of mixed Mg/Al oxides using techniques similar to those we have used.

3.1.2. Acid strength by Hammett indicators

Acid strength is given as a range corresponding to the Hammett acidity function H_0 . As seen in Table 4, AlPO₄ and the zeolite were the most acidic catalysts, and the least acidic was Fe₂O₃.

3.2. Catalyst evaluation for CAN formation

Evaluation of catalyst materials was conducted at base-case conditions described in Table 3; results at other conditions are noted for each material investigated. Typically, reactions were conducted for 5 h and yields reported are the maximum achieved. Carbon balances typically range from 80 to 95% closure when catalyst coking was included. It is noteworthy that if the deficit in carbon recovery involves a loss of reactants or desired products, it results in lower calculated yields and selectivities. If all carbon were accounted for, the values of yield and selectivity reported would only increase.

3.2.1. Silicas

Control reaction with nonporous 1 mm glass (Pyrex) beads gave no CAN formation. However, 15%

Table 4
Catalyst properties

Catalyst	SA (m ² /g)	Acid strength (H_0)	Acid site density (mmol/g)	Basic site density (mmol/g)
Aluminum phosphate (AP-44)	137	−0.2 to −3.2	1.92	0
Zeolite 13X	455	−3.0 to −5.6	3.80	0
Silica (CPG Inc.)				
CPG-75	155	–	0.24	0
CPG-3000	7	–	0	0
Alumina (Norpro)				
SA3132	32	–	–	–
SA3177	107	+1.1 to −0.2	0.34	0.23
SA6175	236	−0.2 to −3.2	–	0.09
Alumina in-house	173	+1.1 to −0.2	1.14	0.15
Mixed Mg/Al oxides				
AM-0.5	163	+2.4 to −1.2	0.95	0.21
AM-04	174	+2.4 to −1.2	1.51	0.30
AM-06	176	+2.4 to −1.2	1.14	0.19
AM-12	171	+2.4 to −1.2	1.16	0.35
AM-36	175	+2.4 to −1.2	0.49	0.44
Iron oxide	–	>+4.8	–	–

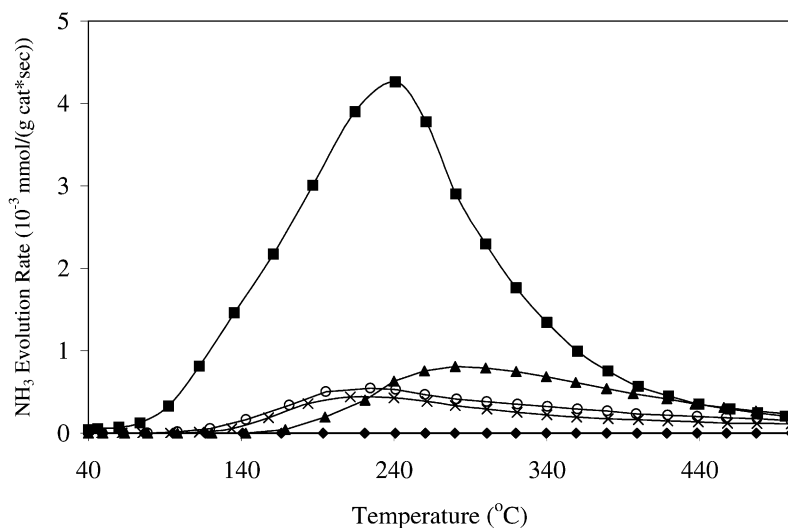


Fig. 2. NH_3 TPD profiles of catalysts: (○) SA3177 alumina; (■) AP-44 aluminum phosphate; (◆) CPG-3000 silica; (×) CPG-75 silica; (▲) AM-36 Mg/Al oxide.

conversion of DMS was observed with 7 and 5% yields of monomethyl succinate (MMS) and succinic acid, respectively, with DMS and formalin as the feed. A small amount of carbon dioxide (0.7% yield) was also obtained from the reaction over glass beads. No hydrolysis was seen when dry DMS was fed over glass beads, because of the absence of water

in the system, but when formalin (53 wt.% H_2O) was included, the water partially hydrolyzed the DMS, yielding some MMS and succinic acid.

Over CPG-75 and CPG-300 silicas, CAN yield did not exceed 1% under any conditions from 350 to 470°C. The conversion of DES was higher with high surface area CPG-75 than with CPG-3000, with

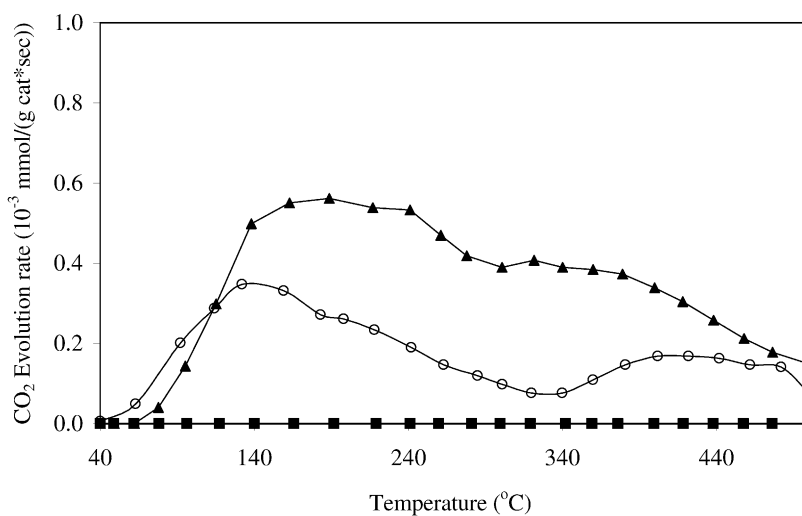


Fig. 3. CO_2 TPD profiles of catalysts: (○) SA3177 alumina; (■) AP-44 aluminum phosphate; (▲) AM-36 Mg/Al oxide.

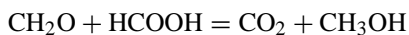
cracking and coking predominant. This is in agreement with the Brønsted acidity of the silica surface sites [17] and with our prior studies using this material [19].

3.2.2. Zeolites

The strongly acidic zeolite 13X in H form, impregnated with $\text{Ce}_2(\text{SO}_4)_3$ via incipient wetness, or ion-exchanged with a solution of NdCl_3 and LaCl_3 , were evaluated and found to primarily crack DMS to carbon dioxide and carbon monoxide. Their strongly acidic sites also led to coke formation; consequently, deactivation of the zeolite-based catalysts was much faster than with other catalysts. Only carbon dioxide, carbon monoxide, and water were observed as products in the first 60 min of the reaction of DMS and TO over zeolite 13X; beyond this time some CAN was formed, but activity rapidly decreased to a low level. A maximum CAN yield of 7% at 80% DMS conversion was obtained with $\text{Ce}_2(\text{SO}_4)_3$ on zeolite 13X at 380°C; other forms of the zeolite exhibited lower yields.

3.2.3. Iron oxide

Iron oxide was completely inactive for CAN formation. However, formaldehyde was partially converted into methanol and CO_2 via the base-catalyzed Cannizzaro reactions:



Conversion of DMS was low (<30%) over iron oxide catalyst, with MMS, succinic anhydride, and CO_2 as the main products of the reaction.

3.2.4. Aluminas

Alumina catalysts containing weak Lewis acid sites show significant promise for CAN formation and have been studied in detail. The yield of CAN and conversion of DMS over different alumina catalysts at base-case reaction conditions (Table 3) are depicted in Fig. 4a and b, respectively.

Intermediate surface area aluminas (100–150 m^2/g) gave the best activity for CAN formation. Norpro SA3177 gave 21% yield of CAN before hydrolysis and 35% yield of all citraconates after hydrolysis at 48% conversion of DMS, for a selectivity of 70%

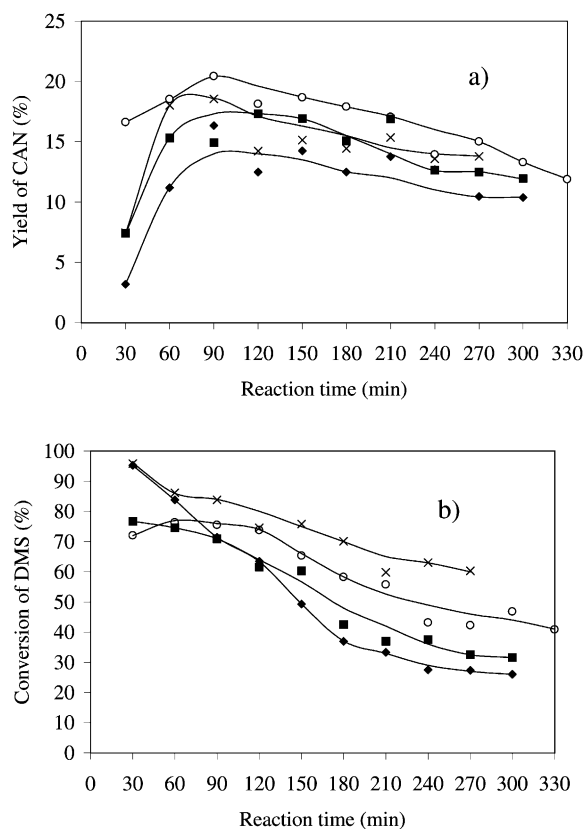


Fig. 4. (a) Yield of CAN and (b) conversion of DMS over different catalysts at base-case conditions (feed: DMS + TO, unhydrolyzed products): (○) SA3177 alumina; (×) alumina in-house; (◆) SA6175 alumina; (■) AP-44 aluminum phosphate.

at base-case conditions. Similarly, in-house prepared alumina gave 19% yield of CAN (before hydrolysis) at 56% conversion of DMS. As seen in Fig. 4a, the yield of CAN was low initially but reached a maximum and then slowly declined after 120 min. The formation of substantial quantities of carbon dioxide and carbon monoxide was also seen initially, an indication of succinate cracking, but the quantity of gas formation declines to a very low level after the first hour of reaction.

Table 5 gives yield and conversion data for a DMS/formalin feed over SA3177 alumina at base-case conditions both before and after hydrolysis of product samples. Yields of CAN are approximately 1.25 times higher with formalin (Table 5) as a feed than with trioxane (Fig. 4a), and the decline in yield is

Table 5
Comparison of results before and after hydrolysis of product stream^a

Reaction time (min)	Citraconate yield (%)		Succinate conversion (%)		Selectivity to citraconates ^b (%)
	Before hydrolysis	After hydrolysis	Before hydrolysis	After hydrolysis	
60	26	26	42	55	48
90	26	29	45	42	70
180	23	26	37	46	57
240	20	25	30	42	60

^a SA3177 alumina catalyst; DMS/formalin feed; base-case reaction conditions.

^b Post-hydrolysis.

slower with time-on-stream. Hydrolysis leads to the recovery of up to five additional percentage points of citraconic acid from the monomethyl and dimethyl citraconate formed in the condensation reaction.

High surface area SA6175 alumina gave maximum CAN yields of 16–19% from DMS and TO, similar to those of the intermediate surface area SA3177 alumina. However, SA6175 alumina gave a higher initial conversion of DMS accompanied by greater carbon dioxide and carbon monoxide formation than did SA3177, indicative of cracking over the more highly acidic SA6175. Over time, carbon monoxide and carbon dioxide production declined to smaller values, suggesting that these strongly acidic sites were deactivated by coking. This was verified by greater weight gain of SA6175 than SA3177 as measured after reaction. The initial low selectivity for CAN on these higher surface area materials, along with extensive DMS loss via cracking, thus makes the high surface area alumina less desirable as a catalyst than its lower surface area counterpart.

Low surface area SA3132 alumina (not shown) had the lowest activity of the aluminas evaluated, giving a CAN yield of 6% at base-case conditions. Addition of Ce₂(SO₄)₃ to SA3132 only increased CAN yield to a maximum of 8% with 52% DMS conversion at 410°C. Addition of basic salts such Li₂CO₃ or KH₂PO₄ essentially eliminated activity for CAN formation. This further indicates that acidic sites are linked to CAN formation, because addition of basic salts neutralizes acid sites on the alumina surface.

3.2.5. Aluminum phosphate

A maximum CAN yield of 18% at 60% conversion of DMS was observed over AP-44 aluminum phosphate at base-case conditions. The yields of CAN and

conversion of DMS are included in Fig. 4a and b, respectively. Results with AP-44 follow those for aluminas: high activity in the beginning of the run resulted in high conversion of DMS with cracking to form carbon monoxide and carbon dioxide; later the CAN yield (Fig. 4a) and DMS conversion (Fig. 4b) stabilized. Significantly less carbon dioxide formation was observed over AP-44 relative to SA3177 alumina, because the absence of basic sites prevented the Cannizzaro reaction from taking place.

3.3. Further evaluation of alumina-based catalysts

The intermediate surface area aluminas were thus identified as attractive catalysts and are further investigated here. Norpro SA3177 was used in most experiments for convenience; the alumina prepared in-house gave similar results but required a lengthy preparation process.

3.3.1. Base addition to alumina

We attempted to neutralize the strongly acidic sites on SA3177 alumina (and thus reduce cracking to CO₂) by loading 0.3 mmol KOH/g and then calcining at 500°C. This loading is nearly sufficient to deactivate all acidic sites, present at a concentration of 0.34 mmol/g (as measured by NH₃ adsorption), on the alumina surface. The results in Table 6 show that only a 2% yield of CAN was achieved for KOH on SA3177. The base-treated alumina greatly reduced DMS conversion and increased formation of methanol and CO₂, the products of the Cannizzaro reaction. Thus, we were successful at reducing DMS cracking; unfortunately, the absence of citraconate formation over base-loaded alumina indicates that base deactivates the sites responsible for

Table 6
Effect of base addition to SA3177 alumina^a

Reaction time (min)	Yield of CAN (%)		Conversion of DMS (%)		Yield of MMS (%)		Yield of CO ₂ (%)		Yield of methanol (%)	
	KOH/SA3177	SA3177	KOH/SA3177	SA3177	KOH/SA3177	SA3177	KOH/SA3177	SA3177	KOH/SA3177	SA3177
30	1	17	65	92	9	19	48	37	111	36
60	2	22	33	76	10	23	24	30	67	39
90	2	19	25	75	6	21	24	20	60	40
120	2	19	17	73	4	19	9	15	46	45
150	1	19	14	67	5	23	7	13	64	45

^a DMS/TO feed, unhydrolyzed results.

citraconic anhydride formation as well as those for cracking.

In an attempt to more selectively reduce cracking without eliminating CAN formation, we added a smaller quantity of base as KH₂PO₄ at a loading of 0.015 mmol/g SA3177 alumina. This loading is about 8% of the total acid site density. Conversion of DMS (with TO) over this material was not much different than over SA3177 alone, but the yield of CAN was 3–4% points higher than the yield over SA3177 alone. Further, the extent of cracking was reduced as a result of adding base in small quantities. Thus, it appears that addition of small quantities of base is effective in increasing selectivity toward the condensation reaction, by inhibiting to some extent cracking reactions at strongly acidic sites.

3.3.2. Acid addition to alumina

Addition of H₂SO₄ to alumina was done to minimize the based-catalyzed Cannizzaro reaction, which consumes a significant part of the formaldehyde fed to the reactor. Again, we were successful in inhibiting the undesired side reaction: the conversion of formaldehyde over acid-treated SA3177 was only 25% as compared to 80% with untreated SA3177. Low conversion of formaldehyde was also evident from the lower yield of methanol. Unfortunately, the acid-treated SA3177 was not active for CAN formation, with less than 5% CAN yield and a maximum DMS conversion less than 50%. The yield of succinic acid was abnormally high because hydrolysis of DMS was facilitated by the acid present on the catalyst surface. It is not understood why acid addition essentially eliminated CAN formation; it is possible that sulfuric acid physically blocks access to the alumina sites or in some way alters the

alumina surface. It is also possible that basic sites play a role in the condensation reaction, but such a suggestion is speculative at this point.

3.3.3. Mg/Al mixed oxides

These materials serve as a further probe of the relative acidity/basicity of the catalyst. Yields of CAN and conversions of DMS at base conditions over different Mg/Al oxides are given and compared with SA3177 in Fig. 5a and b, respectively. As the Mg content of the catalyst increases, the conversion of DMS and the CAN yield decline. The catalysts AM-25, AM-36, and AM-75 (not reported in Fig. 5) showed essentially no activity for CAN formation. The yields of succinic acid and MMS also decrease as Mg content increases, because the basic catalyst does not catalyze DMS hydrolysis. In contrast, yields of CO₂ and methanol were higher at high Mg content because the Cannizzaro reaction is enhanced. Catalyst coking over the mixed Mg/Al oxides was greater than on SA3177 alumina. From these results and those on iron oxide, we conclude that predominantly basic catalysts such as AM-36 and AM-75 are not suitable for the conversion, both because they do not catalyze the formation of CAN and because formaldehyde is rapidly consumed via the Cannizzaro reaction.

3.3.4. Catalyst deactivation and regeneration

The full time sequence of catalyst deactivation with time-on-stream for SA3177 alumina with TO and DMS as feed materials is shown in Fig. 6 at base-case conditions. It is clear that conversion of succinate and yield of citraconate substantially decay over the 17 h run, but selectivity to CAN remains consistently high at 70–80% beyond the first hour of reaction.

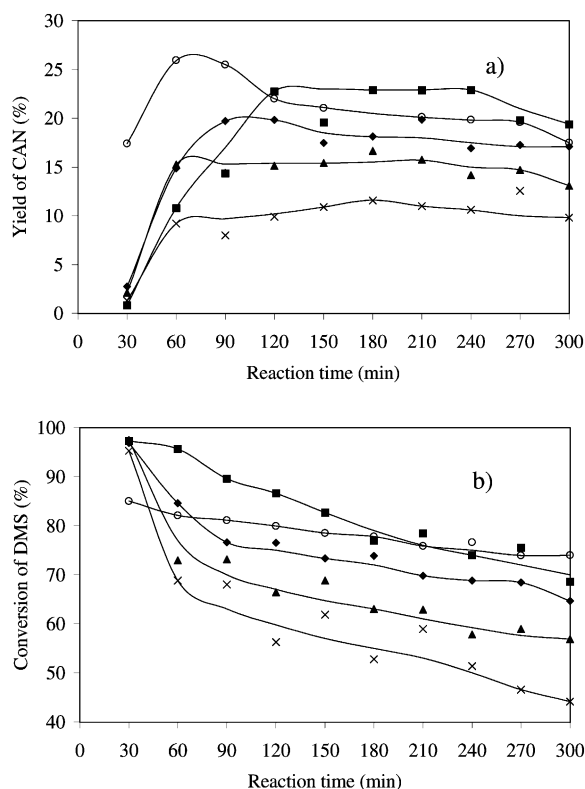


Fig. 5. (a) Yield of CAN and (b) conversion of DMS over Mg/Al oxide catalysts with different Mg atom fractions (feed: DMS + formalin, unhydrolyzed products): (○) SA3177 alumina (0.0 Mg); (■) AM-0.5; (◆) AM-04; (▲) AM-06; (×) AM-12.

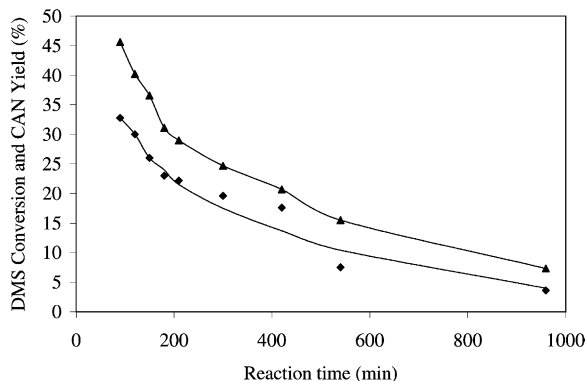


Fig. 6. Yield of citraconates and conversion of succinates over SA3177 alumina in extended-length experiment at base-case conditions (DMS/TO feed, hydrolyzed products): (◆) yield of citraconates; (▲) conversion of succinates.

The decline in catalyst activity is attributed to coking of the alumina. In early stages of the reaction, DMS conversion and production of carbon dioxide and carbon monoxide are very high, indicating that cracking reactions predominate. Catalyst weight gain measured for experiments of different time lengths shows that, for a typical 5 g catalyst charge, a gain of 1.5 g is observed after 5 h, with 1.0 g of the coke deposited after only 1 h of reaction. Thus, coking occurs rapidly early in the reaction and then slows considerably, as evidenced by reduced carbon monoxide and carbon dioxide production later in the reaction. The strongly acidic sites responsible for cracking are thus selectively deactivated by coke deposition early in the reaction. At the same time, the CAN yield slowly increases during the first hour of reaction, as more DMS becomes available for the desired reaction as coking slows. Beyond this time, access to the catalyst surface is progressively restricted by additional coke deposition; the constant selectivity over the later stages of reaction indicates that this limitation is a result of physical pore blocking. Control experiments show that coking of the alumina occurs from formaldehyde, DMS, and CAN.

Catalyst deactivation was much slower with formalin as the formaldehyde source than when trioxane was used; hence DMS conversion and CAN yield decreased very little over time. The quantity of coke deposited on the catalyst was also lower with formalin: 0.9 g over 5 h versus 1.5 g after 5 h with trioxane. We attribute this behavior to the presence of water, which reacts with the deposited coke and thus cleans the catalyst during reaction. The water may also suppress the coking reaction entirely; in early stages of reaction relatively little carbon dioxide and carbon monoxide were observed with DMS/formalin feed relative to reactions with DMS/TO feedstock. Interestingly, the BET surface area of SA3177 alumina increased as the reaction progresses and coke was deposited, presumably because the coke formed during reaction is a porous material of high surface area.

The regeneration of the alumina catalysts for CAN formation has been demonstrated. When the coked alumina was calcined in air at 500°C for 5 h to remove carbon, its surface area returned to that of the fresh material. Analogous calcination of used catalyst in air (500°C, 1 h) in the reactor proper recovered the full catalytic activity as shown in Table 7. (These

Table 7
Comparison of fresh and regenerated SA3177 alumina catalyst^a

Reaction time (min)	Yield of CAN (%)		Yield of CO ₂ (%)		Conversion of DMS (%)	
	Fresh	Regenerated	Fresh	Regenerated	Fresh	Regenerated
30	8	8	11	12	77	74
60	12	13	5	5	57	62
90	11	11	8	8	59	63
120	12	11	4	3	54	60
150	10	9	6	6	58	59
180	9	10	3	2	55	53
210	12	10	5	5	47	50

^a DMS/formalin feed; DMS:formaldehyde = 2:1, otherwise base-case conditions.

reactions were performed at base-case conditions except that formaldehyde was the limiting reactant, with a succinate:formaldehyde ratio of 2:1 instead of 1:2 as in the base-case.) This is an important result regarding the commercial feasibility of this process, as it is clear the alumina catalyst can be easily and rapidly regenerated even if deactivation occurs after only a few hours on-stream.

4. Conclusions

The acid–base properties of the oxide catalysts studied here play an important role in the formation of citraconates from DMS. Norpro SA3177 alumina, alumina in-house, and aluminum phosphate, catalysts with Lewis acid character, showed significant activity for the formation of citraconates from succinates. A maximum (post-hydrolysis) citraconate yield of 35% at 48% DMS conversion over SA3177 was observed at the base-case conditions, giving a selectivity of 73%. In contrast, materials with Brønsted acidity (zeolite 13X, silica CPG-75) were active only for cracking dialkyl succinate into carbon dioxide and carbon monoxide, and the extent of coke formation is related to the acidity of the material. Catalysts that are basic in nature (Mg/Al mixed oxides and iron oxide) gave little CAN but instead catalyzed the Cannizzaro reaction of formaldehyde to methanol and carbon dioxide. Similarly, no CAN was produced from alumina loaded with base, because the weakly acidic sites were neutralized and thus inactive for CAN formation.

Deactivation of the alumina catalyst occurred over time as a result of coke formation, more slowly with

formalin as the formaldehyde source than with trioxane because of water content. However, the alumina catalyst was regenerated in air upon deactivation and the original catalyst activity restored.

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