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Synthesis of vinyl acetate monomer from synthesis gas

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Abstract

Previous attempts to synthesize vinyl acetate monomer (VAM) from synthesis gas involve routes that require a costly recycle of acetic acid through a carbonylation reactor. Two new routes to VAM from synthesis gas that avoid this acetic acid recycle have been investigated. One of these new routes synthesizes VAM from acetic acid via the intermediacy of ketene. Ketene is hydrogenated to acetaldehyde, and the acetaldehyde is reacted directly with ketene to produce VAM. The second route synthesizes VAM from the carbonylation of dimethyl ether to acetic anhydride followed by reaction of the acetic anhydride with acetaldehyde in a reactive distillation column to produce VAM and acetic acid. The co-produced acetic acid is hydrogenated to form the acetaldehyde required in the reactive distillation.

Keywords: Vinyl acetate; Ketene; Hydrogenation; Acetaldehyde; Reactive distillation

1. Introduction

The objective of this project was to develop a commercially viable process for the generation of vinyl acetate monomer (VAM) based entirely upon syngas. A VAM process based entirely on syngas is of interest because of lower raw material costs compared to the current ethylene oxidative acetoxylation route. Previous attempts at this objective have typically involved schemes similar to the one shown below.

$$2CO + 4H_2 \rightarrow 2MeOH \quad (1)$$

$$2MeOH + 2HOAc \rightarrow 2MeOAc + 2H_2O \quad (2)$$

$$MeOAc + CO + H_2 \rightarrow HAc + HOAc \quad (3)$$

$$MeOAc + CO \rightarrow Ac_2O \quad (4)$$

$$Ac_2O + HAc \rightleftarrows EDA \quad (5)$$

$$EDA \rightleftarrows VAM + HOAc \quad (6)$$

where MeOH=methanol, HOAc=acetic acid, MeOAc=methyl acetate, HAc=acetaldehyde, Ac_2O= acetic anhydride and EDA=ethylidene diacetate (1,1-diacetoxyethane).

These efforts have failed to generate a commercially viable process to date. One of the key reasons for this failure is the very large quantities of recycled acetic acid (and consequently large commercial facilities) inherent in the earlier proposed processes. Therefore, in our work, we sought syngas-based processes for the production of VAM that avoid the costly recycle of acetic acid to a carbonylation reactor. Although many approaches are possible, most were eliminated on thermodynamic grounds or upon the basis of the number of steps involved. Of those process candidates remaining, each contained an endothermic hydrogenation of acetic acid to acetaldehyde (7). If this conversion could be accomplished, the problem of acetic acid recycle to the carbonylation reactor could be resolved.

$$HOAc + H_2 \rightarrow HAc + H_2O \quad (7)$$

One approach to accomplishing this goal was to first convert the acetic acid to ketene and then to

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$$HOAc \rightarrow H_2C{=}C{=}O + H_2O \quad (8)$$

$$H_2C{=}C{=}O + H_2 \rightarrow HAc \quad (9)$$

$$HAc + H_2C{=}C{=}O \rightarrow VAM. \quad (10)$$

Scheme 1.

subsequently hydrogenate the ketene to acetaldehyde under mild conditions. The potential reactivity of ketene also prompted us to investigate the reaction of acetaldehyde with ketene to produce VAM directly. This series of reactions, which is shown in Scheme 1, represented one of two key focus routes for our studies.

The second key route we examined for the generation of VAM engendered a different approach to obtaining acetaldehyde. In the second route, dimethyl ether (Me_2O) is carbonylated to form acetic anhydride which is subsequently reacted with acetaldehyde in a reactive distillation column to produce VAM and acetic acid. To avoid recycling acetic acid through a carbonylation unit, the acetic acid is hydrogenated to provide the acetaldehyde needed in the reactive distillation. This series of reactions is shown in Scheme 2.

The last reaction (7), the hydrogenation of acetic acid to acetaldehyde, is endothermic but might be envisioned as theoretically proceeding directly or by the ketene route shown previously.

Here we provide an overview of initial results from our investigations of four new technologies required to realize the preferred routes described in Schemes 1 and 2: hydrogenation of ketene to acetaldehyde, production of VAM from ketene and acetaldehyde, direct hydrogenation of acetic acid to acetaldehyde, and the production of VAM from reactive distillation of acetic anhydride and acetaldehyde.

2. Experimental

2.1. Ketene hydrogenation

The apparatus for the hydrogenation of ketene has been described in detail previously [1]. The following is a condensed description of the actual apparatus and method used. Fig. 1 is a schematic overview of the apparatus. Metered gas flows were provided by Tylan Model FC-260 mass flow controllers. Typically, ketene was generated by the pyrolysis of acetic anhydride as described by Fisher et al. [2]. The ketene was condensed at −78°C in a trap, and the pyrolysis process was terminated. The ketene was distilled and condensed in a trap/vaporizer assembly held at −78°C. A series of stopcocks (SC1 through SC5 in Fig. 1) were used to direct the vapor streams to the reactor and various scrubbers. The ketene (1 mmol/min) was transpired in metered nitrogen (88 standard cubic centimeters per minute, SCCM) from the trap/vaporizer held at −78°C at 1 bar pressure. Hydrogen (44.8 SCCM) and helium (50 SCCM) were metered and mixed with the nitrogen/ketene mixture, and the combined stream was fed to the reactor. The glass reactor consisted of a 53 cm×25 mm OD tube fitted with a permanent thermowell extending from the base of the reactor. The central portion of the reactor was constructed with a condenser jacket, which in turn was enclosed in a vacuum jacket to prevent heat loss. The reactor was heated to 97°C with steam. The heated portion of the reactor contained the catalyst powder (1 g) diluted with 8×16 mesh quartz chips. The reactor effluent was fed to a scrubber containing methanol (100 ml). Any unreacted ketene was converted to methyl acetate in the methanol scrubber, and acetaldehyde existed as free acetaldehyde and acetaldehyde dimethyl acetal. Products contained in the methanol scrubber solution were analyzed by gas chromatography using a Hewlett-Packard Model 5890 gas chromatograph fitted with a 30 m×0.25 mm FFAP capillary column (0.25 μm film thickness) pro-

$$Me_2O + 2CO \rightarrow Ac_2O \quad (11)$$

$$Ac_2O + HAc \rightarrow VAM + HOAc \quad (12)$$

$$HOAc + H_2 \rightarrow HAc + H_2O \quad (7)$$

Scheme 2.

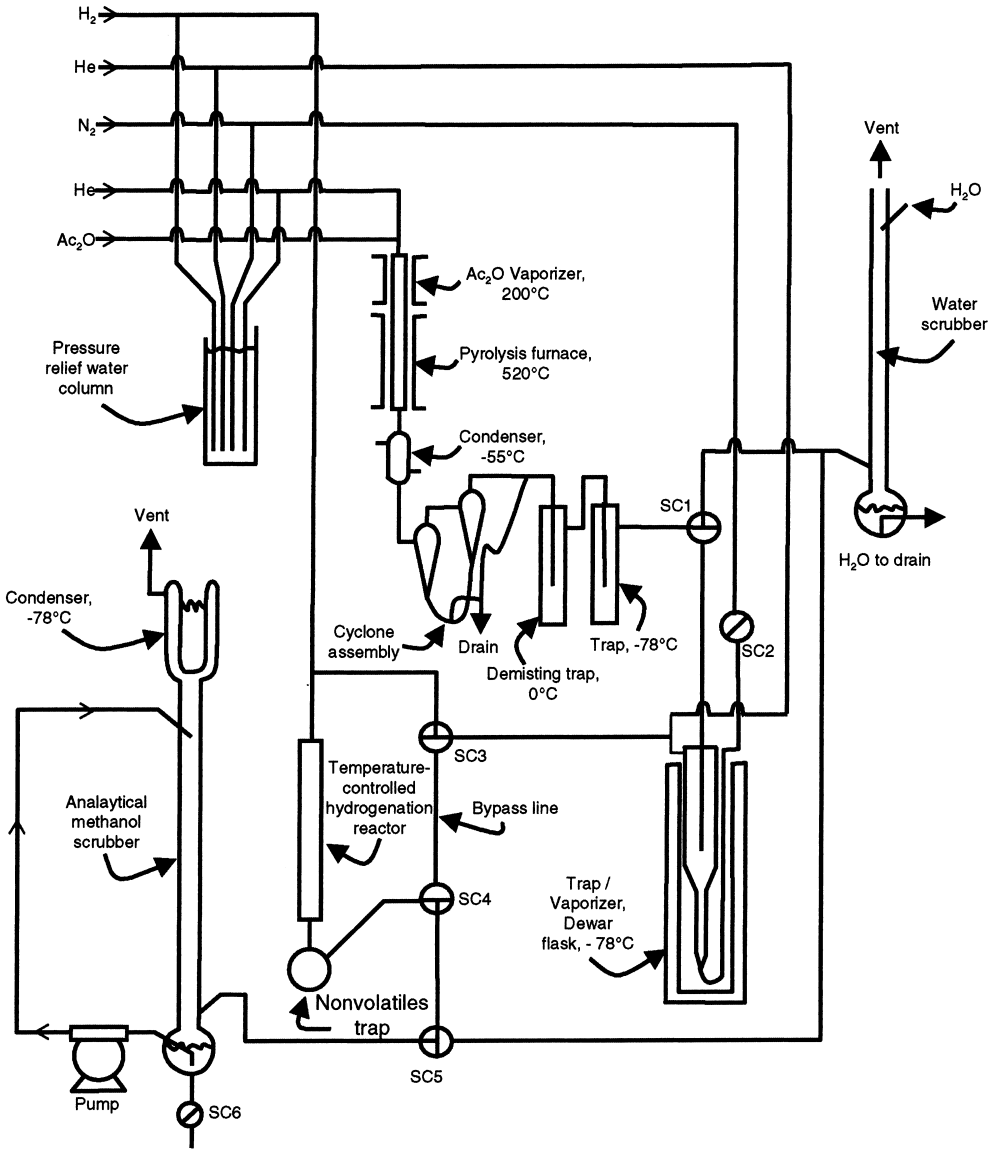

Fig. 1. Ketene generator and hydrogenation reactor.

grammed at 35°C for 7 min, 15°C/min to 220°C and holding at 220°C for 2 min using a flame ionization detector held at 280°C (injector temperature=240°C). Mixtures were prepared for gas chromatographic analysis by adding 5 ml of a tetrahydrofuran solution containing 2% decane internal standard to an accurately weighed 1 g sample of the methanol scrubber solution.

2.2. Reaction of ketene with acetaldehyde

The apparatus for the reaction of ketene with acetaldehyde has been described in detail previously [3]. The following is a condensed description of the actual apparatus and method used. Fig. 2 provides a schematic description of the reactor and recovery system. The ketene generation and delivery system is

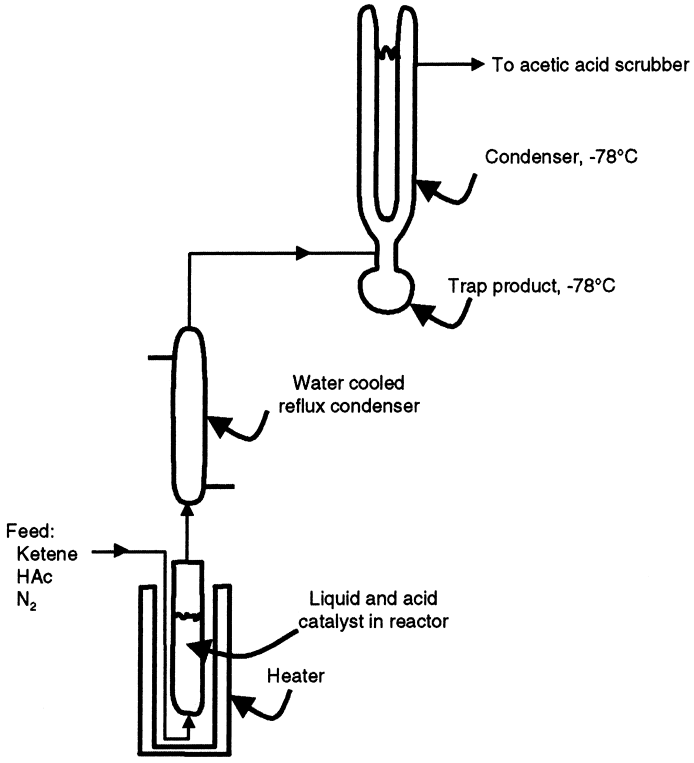

Fig. 2. Reactor and recovery system for the reaction of ketene with acetaldehyde.

essentially the same as described above for the ketene hydrogenation with the ketene being transpired from a trap at −78°C in nitrogen. Acetaldehyde was also transpired in nitrogen from a trap held at −20°C. In a typical experiment the separate streams were mixed to provide a ketene (0.7 mmol/min), acetaldehyde (1.0 mmol/min), nitrogen (206 SCCM) mixture. The mixed gas stream was then fed to the reactor. Most of the experiments were performed using a 36 mm OD and 175 mm high gas stripped reactor typically held at 150°C. The reactant gas stream entered the base of the reactor which typically contained acetic anhydride (65.8 g, 0.645 mol), *p*-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and *tert*-butylhydroquinone (TBHQ, 140 mg, 0.84 mmol). The gaseous reactor effluent was passed through a trap held at −78°C containing TBHQ (about 40 mg) and then to a scrubber containing acetic acid (about 60 ml) and TBHQ (about 40 mg). Reactions were normally run for several hours each day and run for 4–5 days. The trap product and scrubber solution were weighed and analyzed each day, and the reactor heel was analyzed after the termination of the experiment. Products obtained from the trap, acetic acid scrubber solution and reactor heel were analyzed by gas chromatography using Hewlett-Packard Model 5890 gas chromatographs using flame ionization detectors. Vinyl acetate, acetaldehyde and acetic acid were analyzed using a 25 m × 0.53 mm FFAP capillary column (1.0 micron film thickness) programmed at 40°C for 5 min, 15°C/min to 235°C and holding at 235°C for 1.67 min. Acetic anhydride and ethylidene diacetate were analyzed using a 30 m × 0.53 mm DB-5 capillary column (1.5 micron film thickness) programmed at 40°C for 8 min, 7°C/min to 200°C with a 0 min holding time at 200°C. Mixtures were prepared for gas chromatographic analysis by adding 5 ml of a tetrahydrofuran solution containing 2% decane internal standard to an accurately weighed 1 g sample of the reaction product.

2.3. Low pressure acetic acid hydrogenation

Iron oxide catalysts containing up to 10 wt.% Pd were prepared by impregnating Fe_2O_3 with an aqueous solution of palladium nitrate followed by drying on a steam bath and then calcination at 400°C for 4–5 h. Catalysts containing 10 wt.% or more Pd were prepared by drying aqueous solution containing ferric nitrate, palladium nitrate and citric acid on the steam bath to produce glassy solids which were then calcined at 400°C for 5 h. These same catalysts were also used in the high pressure hydrogenation experiments described in Section 2.4.

Metered gas flows were provided by Tylan Model FC-260 mass flow controllers. Acetic acid was fed by metering hydrogen or nitrogen through a temperature-controlled vaporizer containing the acetic acid. The temperature of the vaporizer was maintained by a circulating water/ethylene glycol bath. The reactor was constructed of a main section of 19.6 cm long by 8 mm OD borosilicate glass fused to a lower section consisting of 15.2 cm long by 7.5 mm OD −3 mm ID capillary tubing. Accurately weighed catalyst charges (typically 0.2 g) were loaded into the reactor by first inserting a glass or quartz wool plug from the top of the reactor into the top part of the capillary section and then placing the catalyst charge on top of the glass or quartz wool plug. A thermocouple was placed in the catalyst bed. The reactor was heated with a vertically-mounted single element electric furnace containing a 30.5 cm long heat zone. The apparatus allowed for additional hydrogen or inert gas to be metered into the vapor stream exiting the temperature-controlled vaporizer. The acetic acid partial pressure could be controlled by altering the temperature of the vaporizer or by adding hydrogen or inert gas to the vapor stream exiting the temperature-controlled vaporizer. The apparatus could also easily be configured to allow inert gas to be metered to the temperature-controlled vaporizer. This flexibility in setting the feed composition facilitated the study of the reaction kinetics. Normally catalysts were reduced in hydrogen (22.4 SCCM) overnight at 300°C before feeding the acetic acid and hydrogen mixture. When the reactor was idle between acetic acid hydrogenation experiments with the same catalyst charge, hydrogen flow (22.4 SCCM) was maintained at 300°C. Product analysis was performed by on-line gas chromatography utilizing a Hewlett-Packard Model 5790A gas chromatograph fitted with a 183 cm × 3.2 mm stainless steel column containing 80/120 Carbopack B/6.6% Carbowax® 20M programmed for 80°C for 0 min, 4°C/min to 150°C, and 150°C for 0 min using a flame ionization detector.

2.4. High pressure acetic acid hydrogenation

The reactor was constructed from a 30.5 cm length of Hastelloy C tubing having an outer diameter of 6.4 mm. All gas flow, pressure and temperature control devices were controlled by a Camile® Model 3300 process monitoring and control system interfaced with an IBM Model 750-P90 computer. Hydrogen flow was provided by a Brooks mass flow controller, and acetic acid was fed using dual ISCO high pressure syringe pumps. The device was fitted with a relief valve set for 34 atm. Pressure was controlled by a modified Research Control Valve with a pressure transducer located between the flow controller and the reactor. The product exiting the Research Control Valve was fed to a Valco Industries 6-port gas chromatographic sampling valve containing a 1 ml sample loop. Gas chromatograph and parameters were the same as in the low pressure hydrogenation experiments. The transfer lines, filter and Research Control Valve connecting the reactor to the gas chromatographic sampling valve were heated to 200°C by a temperature-controlled heating tape. The gas chromatographic sampling valve and the transfer line connecting it to the gas chromatograph were maintained at 150°C. The reactor tube was loaded to position the accurately weighed catalyst charge (typically 0.2 g) in the middle of the reactor. Quartz fines (2.5 cm layer), 12 × 20 mesh quartz chips (8.9 cm layer) and quartz or glass wool plugs were placed on both sides of the catalyst charge. The entire length of the reactor was heated with a temperature-controlled heating tape. The acetic acid was delivered to the reactor via a line passing concentrically through the reactor head and about 2.5 cm into the upper portion of the heated portion of the reactor. The hydrogen delivery line and the relief valve were also fitted to the reactor head. Thus the upper portion of the heated reactor acted as an acetic acid vaporization and vapor mixing zone. Catalysts were reduced in hydrogen (25 SCCM) at

1.68 atm absolute at 300°C in the reactor over night or longer before feeding hydrogen and acetic acid. Reactions were started by setting the hydrogen and acetic acid feeds to the desired rates at the 1.68 atm absolute setting and then setting the pressure to the desired amount. When the reactor was idle between acetic acid hydrogenation experiments with the same catalyst charge, hydrogen flow (22.4 SCCM) at 1.68 atm absolute was maintained at 300°C.

2.5. Vinyl acetate by reactive distillation

The reactive distillation apparatus has been described in detail previously [4]. The following is a condensed description of the actual apparatus and method used. The reactive distillation system used comprised a single column containing a reaction zone and a distillation zone. The reaction zone utilized 31 Oldershaw® trays, each being 19 mm in diameter by 32 mm high and having a 13 mm weir height. The distillation zone, which was mounted atop the reaction zone, consisted of 28 cm of stainless steel Goodloe® packing and 25 mm of copper Goodloe® packing in a 25 mm diameter column. A solenoid-actuated, liquid dividing takeoff head equipped with condenser and jacketed receiver was used to control reflux ratios and remove distillate. A circulating cooling bath was used to maintain the condenser and distillate receiver at 0–5°C. One feed port, which was used to feed acetic anhydride and benzenesulfonic acid catalyst, was positioned at the top Oldershaw® tray and another feed port, which was used to feed acetaldehyde, was positioned in the base. Sample ports were located in the base, at the 15th plate of the Oldershaw® column, and in the distillate receiver. Samples were analyzed by gas/liquid chromatography. The glass column, receiver, takeoff head, and base pot were designed to operate at pressures up to two atmospheres absolute.

3. Results and discussion

3.1. Ketene hydrogenation

The reaction of hydrogen with ketene to produce acetaldehyde is exothermic by about 17 kcal/mol at 100°C [5]. There are no references in the literature describing the hydrogenation of ketene to acetaldehyde in a continuous fashion. Ketene is known to react with hydrogen atoms to produce mainly methane and carbon monoxide [6]. The interaction of ketene with metal surfaces (Ru and Pt) has been studied by White and co-workers [7–11] using spectroscopic techniques. Although adsorbed acetaldehyde can be observed in some cases, it either decomposes or polymerizes on the catalyst. No free acetaldehyde is produced. The desorbed products from these reactions are generally methane or higher hydrocarbons and carbon monoxide. Ponec and co-workers [12,13] describe a high temperature (350°C) hydrogenation of acetic acid over reduced iron oxide catalysts. Ketene was identified as a byproduct and possible intermediate.

A number of ketene–metal complexes have been described in the literature. A ruthenium based ketene complex that does not react with hydrogen has been reported [14]. Miyashita et al. [15] describe a platinum based ketene complex that produces a mixture of acetaldehyde, ethanol and hydrocarbons when treated with hydrogen. A ketene–osmium cluster complex decomposes in the presence of hydrogen to form several other osmium clusters, acetic acid and acetaldehyde [16]. None of these metal complex materials are catalytic in their reaction with hydrogen, and none of the complexes other than the case described by Miyashita et al. were prepared from ketene. We have discovered that ketene is readily hydrogenated to acetaldehyde under very mild conditions.

Typical reaction conditions for the hydrogenation of ketene were ketene:hydrogen:helium+nitrogen molar ratio=1:2:6.2 at 1 atm at 97–100°C and GSHV=18 600 h^{-1}. Of all the transition metals surveyed, palladium is by far the most efficient catalyst for this reaction. A low surface area (0.13 m^2/g) Pd sponge catalyst provided acetaldehyde at 1200 g/(l h) at 20% ketene conversion at 90–100% selectivity. Other products are methane, CO, ethyl acetate and oils. A high surface area (1259 m^2/g) 5% Pd on carbon provided acetaldehyde at 700 g/(l h) at 92% ketene conversion at 75% selectivity. These catalysts deactivate 20–30% during the first day of operation. The Pd sponge catalyst can be regenerated by maintaining the hydrogen overnight flow in the absence of ketene at normal reaction temperature. The supported catalyst is not totally regenerated by this treatment. The fouling rate increases as the partial pressure of

ketene increases, and the presence of the diluent gases appears to moderate the fouling rate. The fouling is likely to be related to the facile dimerization and subsequent reactions that are well known for ketene.

A preliminary kinetic study performed at low ketene conversion revealed the reaction to be approximately 0.6 order in hydrogen, 0.3 order in ketene and had an activation energy=8 kcal/mol. The low reaction order in ketene is consistent with it being strongly adsorbed on the catalyst surface. This is consistent with the bonding mode presented in the literature for ketene on other metals [7–11]. Carbon monoxide is normally present in industrial ketene streams at a level of about 1% and is a moderate poison for the reaction. However, the reaction will operate at about 50% efficiency when the feed contains 2.5% CO.

3.2. Reaction of ketene with acetaldehyde

This reaction is performed by contacting ketene and acetaldehyde in the presence of a Bronsted acid. Arenesulfonic acids are excellent catalysts. Reaction temperature is preferably in the range between 120 and 160°C. The reaction is preferably performed in the presence of a solvent, although it has been shown to work in the vapor phase using polymeric sulfonic acid catalysts. Typical results are shown in Table 1. Acetic anhydride or 1-methyl-2-pyrrolidinone (NMP) are excellent solvents for the reaction. Excellent results were obtained using a gas stripped reactor containing acetic anhydride and *p*-toluenesulfonic acid through which the ketene, acetaldehyde and diluent nitrogen were sparged at 150°C. Reactions generally were performed for 5–6 h per day for 1–5 days. All reactions require a period to come to steady state as indicated in Table 1. In the case of *p*-toluenesulfonic acid in Ac_2O, during the first day of operation 1.1 wt.% acetic acid was condensed from the reactor effluent in the −78°C cold trap (most of the remaining material in the trap was vinyl acetate). No acetic acid was found in the trap during the following three days of reaction. This initial acetic acid is likely due to the reaction of the catalyst's water of hydration with acetic anhydride or ketene and may also arise from trace amounts acetic acid in the starting acetic anhydride. Strong acids, such as sulfuric acid, cause excessive tar formation under similar reaction conditions and lower VAM yields, and higher amounts of acetic acid are produced (21.4 wt.% isolated from the −78°C cold trap). Weak acids, such as methanesulfonic acid, provide lower tar formation rates and lower VAM yields compared to *p*-toluenesulfonic acid.

Eqs. (5), (6) and (13) may be relevant in the formation of VAM from acetaldehyde and ketene in the acetic anhydride solvent

$$H_2C{=}C{=}O + HOAc \rightarrow Ac_2O \quad (13)$$

While the equilibria of reactions (5) and (6) favor EDA, the reaction of ketene with acetic acid is essentially irreversible and drives the overall reaction to completion. Consistent with this notion is the observation that the reactor heel from the above-described reaction with *p*-toluenesulfonic acid catalyst contained EDA (39.2 wt.%) along with acetic anhydride (47.7 wt.%), acetic acid (1.1 wt.%), acetaldehyde (0.3 wt.%) and VAM (1.7 wt.%). The observation that a day is needed before optimum VAM yields are achieved is consistent with the time required for the level of EDA to reach steady state. The cracking of EDA in the presence of ketene has been reported by Denis and Perron [17]. Hull describes a process where a low yield of VAM (23% from ketene) along with methyl propenyl ketone is obtained by bubbling

Table 1
Daily yield of VAM from ketene and acetaldehyde[a]

Catalyst system	Percentage of VAM yield from ketene				
	Day 1	Day 2	Day 3	Day 4	Day 5
p-Toluenesulfonic acid in Ac_2O	42	78	78	81	–
Sulfuric acid in Ac_2O	12	–	–	–	–
Methanesulfonic acid in Ac_2O	23	32	25	–	–
p-Toluenesulfonic acid in NMP	59	76	77	71	68

[a] Conditions: ketene (0.7 mmol/min), acetaldehyde (1.0 mol/min) and nitrogen (9.2 mmol/min) sparged through a solution of solvent (645 mmol Ac_2O or 638 mmol NMP), acid catalyst (30.6 mmol) and TBHQ (0.84 mmol) for several hours each day at 150°C.

ketene into acetaldehyde–sulfuric acid at −15°C followed by distillation [18]. The nature of the intermediates in the Hull process are unknown, and generally the reaction of ketene with aldehydes at low temperature in the presence of acids produces β-butyrolactone rather than VAM [19,20]. If the Hull reactant mixture contained water, then EDA would form under the reaction conditions and crack upon distillation. However, EDA may not always be a required intermediate in all ketene–acetaldehyde reactions. When NMP was the solvent with the same catalyst, the reactor heel after five days of operation only contained 1.1% EDA. The low level of EDA could indicate that a low steady state level is required in NMP, or it could indicate that ketene and acetaldehyde react directly in this solvent.

3.3. Direct hydrogenation of acetic acid to acetaldehyde

The key barriers to the hydrogenation of acetic acid to acetaldehyde are that the reaction:

1. is thermodynamically unfavorable ($\Delta G_{300^\circ C}$= 2.51 kcal/mol),
2. must compete with a parallel (and thermodynamically favorable) dimerization reaction of acetic acid to acetone (with co-production of water and carbon dioxide),
3. is subject to a subsequent (also thermodynamically favorable) hydrogenation of acetaldehyde to ethanol, and
4. needs to be performed in a manner allowing a practical means to actually recover the volatile acetaldehyde from the product.

Initial studies concentrated on addressing items (1)–(3) to optimize the chemistry and perform kinetic evaluations. Once these were done, efforts turned to item (4). The catalysts for acetic acid hydrogenation consist of an essential component, Fe_2O_3, (A) and a promoting component, Pd (B). Ponec and co-workers [12,13,21–24] have described similar catalysts based on Fe_2O_3 and an optional second component, preferably Pt. A series of catalysts was prepared and evaluated where the amounts of components A and B were varied. Catalysts studied contained in wt.%: 100A–0B, 97.5A–2.5B, 95A–5B, 90A–10B, 80A–20B, 60A–40B, 20A–80B and 0A–100B. Most of the initial studies were performed with the 97.5A–2.5B catalyst with hydrogen/acetic acid=37/1 (90 SCCM) at 1 bar pressure at 300°C at GHSV=71 000 h^{-1}. This catalyst produced acetaldehyde at a rate of 312 g/(l h) at 25% acetic acid conversion with 88% selectivity to acetaldehyde with the other products being ethanol (6%), acetone (2%), methane (3%), and C_2 hydrocarbons (<1%). Catalytic performance remained reasonably steady over 200 h.

Since the selectivity of this catalyst was excellent and its activity fairly stable, it was decided to perform a kinetic study at low and medium conversions so we could later optimize reaction conditions. These studies were complicated somewhat by the observation that, under some conditions, the catalyst becomes oxidized. This condition favors acetone formation. The results of the kinetic studies are summarized:

1. Activation energy data (kcal/mol)
   - acetaldehyde=16;
   - acetone=32 (reduced catalyst), 9 (oxidized catalyst);
   - ethanol=29.
2. Hydrogen reaction order
   - acetaldehyde=0.98 (reduced catalyst), 0.79 (oxidized catalyst);
   - acetone=−0.08 (reduced catalyst), −0.32 (oxidized catalyst);
   - ethanol=1.76 (reduced catalyst), 1.40 (oxidized catalyst).
3. Acetic acid reaction order
   - all products: non-linear behavior (Fig. 3 illustrates the case of acetaldehyde).

The observation that the rate increases and then decreases with increasing acetic acid partial pressure as illustrated in Fig. 3 is consistent with acetic acid being strongly adsorbed on the catalyst. The activation energy study was very useful in revealing the need to keep the catalyst reduced to minimize acetone formation and in selecting the temperature for optimum selectivity.

The next step in the development was determining which conditions allowed the amount of hydrogen to be lowered while maintaining the catalyst in the reduced state. Optimum performance using a 5:1 ratio of hydrogen and acetic acid was found with the 90A–10B catalyst. This material produced acetaldehyde at a rate of 278 g/(l h) at 48% acetic acid conversion, and the following selectivities were observed: acetaldehyde=89%, acetone=4%, ethanol=5%,

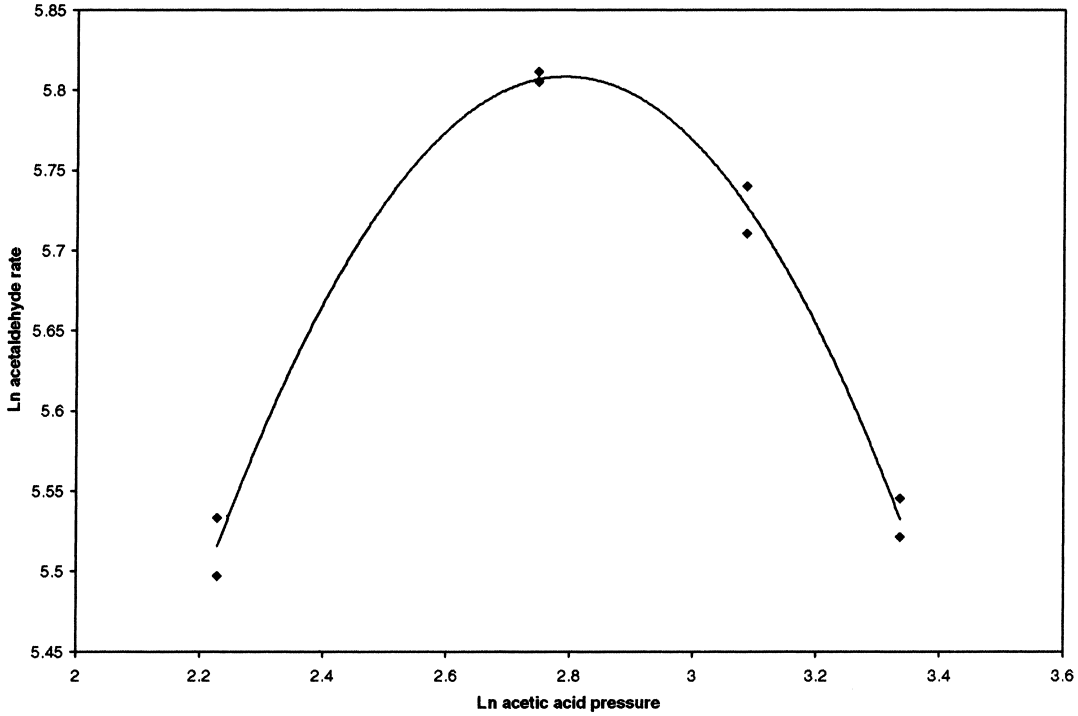

Fig. 3. Profile of the natural logarithms of the g/(l h) acetaldehyde production as a function of mm Hg acetic acid partial pressure using the 2.5 wt.% Pd/Fe_2O_3 catalyst at 300°C.

methane+C_2 hydrocarbon=2%. In his earlier studies, Ponec indicated that the addition of greater than 1.25 at.% of the promoting metal has a detrimental effect on selectivity [24]. However, Ponec used a 50:1 ratio of hydrogen and acetic acid. Apparently, when less hydrogen is used, more of the promoting reducing metal is desirable.

Although excellent selectivity to acetaldehyde at good acetic acid conversion can be obtained at 1 bar pressure, recovery of the acetaldehyde from this dilute stream is not practical at low pressure. Thus attention focused on operating at elevated pressure where acetaldehyde recovery might be feasible. Ethyl acetate (EtOAc) becomes a significant product at elevated pressure. Although the 90A–10B catalyst initially performed very well at 5:1 ratio of hydrogen and HOAc at 18 atm and 300°C, its activity and selectivity declined with total time on stream (TTOS). These results are summarized in Table 2. An increase in the acetone selectivity suggested that the catalyst became oxidized with time on stream.

Table 2
Effect of time on stream on the performances of 10 and 40 wt.% Pd/Fe_2O_3 at 250 psig and 5:1 ratio of hydrogen and acetic acid[a]

	Pd (wt.%)			
	10	10	40	40
TTOS[b] (min)	1739	2089	534	2318
HOAc Conv. (%)	22	10	42	38
Hac g/(l h)	3350	970	2125	2175
HAc sel.[c] (%)	77.9	62.7	77.1	77.0
Acetone sel. (%)	1.5	4.6	1.3	1.5
EtOH sel. (%)	15.0	16.2	15.9	15.2
EtOAc sel. (%)	4.6	15.5	5.6	6.3
CH_4 sel. (%)	0.7	0.7	<0.1	<0.1
C_2 H. C. sel.[d] (%)	0.2	0.1	<0.1	<0.1

[a] Conditions: GHSV=12 200 h^{-1}, 300°C.
[b] TTOS=total time on stream under hydrogen and acetic acid feed.
[c] Selectivities are normalized.
[d] C_2 hydrocarbons=ethylene+ethane.

Significantly higher levels of palladium were required to maintain activity and selectivity. The 60A–40B catalyst proved to provide the optimal performance under the conditions of high pressure and low hydrogen/HOAc ratios. The performance of this catalyst is also summarized in Table 2. The highest acetaldehyde selectivity (86.4%) observed at 18 atm occurred with the 60A–40B catalyst when the hydrogen/acetic acid was 7:1.

3.4. Reactive distillation of acetic anhydride with acetaldehyde

The production of VAM from acetic anhydride and acetaldehyde involves the two equilibria mentioned previously in Eqs. (5) and (6). Both of these equilibria favor EDA. When EDA is heated in the presence of an acid catalyst, it will produce acetic anhydride, acetaldehyde, VAM and acetic acid as volatile products even though the desired products are only acetic acid and VAM. Previous routes to VAM utilizing EDA cracking crack the EDA in the presence of excess acetic anhydride to drive the equilibrium towards VAM and acetic acid, but these processes require several distillation columns to capture acetaldehyde and other components for recycle [25]. The process of reactive distillation overcomes many of these limitations by feeding recycled catalyst solution and acetic anhydride to the middle of a distillation column while feeding acetaldehyde to the base of the column. Any acetaldehyde that rises up the column encounters a stream that is increasingly rich in acetic anhydride thus continuously pushing the equilibrium toward VAM and acetic acid which are collected from the top of the column.

In a typical experiment acetic anhydride (250 g) containing 0.1 wt.% benzenesulfonic acid was charged initially to the base of the apparatus described in Section 2 and warmed to a gentle reflux. The acetaldehyde feed was started and gradually increased to 12 ml/h and allowed to reach steady state over 14.2 h. Upon reaching steady state, feed rates were fixed at 9 ml/h for acetic anhydride containing 1 wt.% benzenesulfonic acid and 12 ml/h for acetaldehyde for the remainder of the experiment. This provides an acetaldehyde:acetic anhydride mole ratio of 2.3:1. An additional 18.4 h of operation at these conditions produced an average of 8.9 g/h vinyl acetate, 3.7 g/h acetaldehyde, and 1.18 g/h acetic acid in the overhead takeoff, which was operated to remove the distillation fraction boiling below or at 65°C.

4. Conclusion

Four new technologies for the production of VAM have been explored with the intent of eliminating the recycle of acetic acid to a carbonylation reactor: the hydrogenation of ketene to acetaldehyde, VAM from ketene and acetaldehyde, direct hydrogenation of acetic acid to acetaldehyde and VAM from reactive distillation of acetic anhydride and acetaldehyde. When combined with established processes for the conversion of synthesis gas to acetic acid or acetic anhydride, these new technologies represent potentially viable routes to the generation of VAM from synthesis gas.

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