

DIRECT AND SELECTIVE PRODUCTION OF ACETALDEHYDE FROM
ACETIC ACID UTILIZING A SUPPORTED METAL CATALYST

5 Claim for Priority

 This application is based upon United States Patent Application Serial No. 12/221,135, filed July 31, 2008, of the same title, the priority of which is hereby claimed and the disclosure of which is incorporated herein by reference.

10 Field of the Invention

 The present invention relates generally to a process for the production of acetaldehyde from acetic acid. More specifically, the present invention relates to a process including hydrogenating acetic acid utilizing a supported metal catalyst, such as, for example, iron, platinum or ruthenium supported on a suitable catalyst support optionally including one or more additional hydrogenating metals to form
15 acetaldehyde with high selectivity.

Background

 There is a long felt need for an economically viable process to convert
20 acetic acid to acetaldehyde. Acetaldehyde is an important commodity feedstock for a variety of industrial products. For instance, acetaldehyde can readily be hydrogenated to ethanol, which in itself has wide variety of industrial applications including its wide utility as a gasoline additive. Acetaldehyde can also be converted to ethyl acetate by the Tischenko reaction or reacted with other
25 compounds to form other products. Currently acetaldehyde is produced by the oxidation of ethylene, the Wacker oxidation of ethylene. Fluctuating natural gas and crude oil prices contribute to fluctuations in the cost of conventionally produced, petroleum or natural gas-sourced acetaldehyde, making the need for alternative sources of acetaldehyde all the greater when oil prices rise. Thus it is
30 of interest to develop commercially viable routes to selectively hydrogenate acetic acid to acetaldehyde.

The catalytic hydrogenation of aromatic carboxylic acids to produce aromatic aldehydes has been reported in the literature. For instance, United States Patent No. 4,613,700 to *Maki et al.* discloses that aromatic aldehydes can be
5 formed from aromatic carboxylic acids using a catalyst comprising zirconium oxide containing as an essential component at least one element selected from the group consisting of chromium, manganese, iron, cobalt, zinc, bismuth, lead rhenium and the elements of Group III in periods 3 to 6 of the periodic table. However, no examples of catalytic hydrogenation of aliphatic carboxylic acids
10 such as acetic acid are provided in this disclosure.

United States Patent No. 5,306,845 to *Yokohama et al.* discloses a method of producing an aldehyde, which comprises hydrogenating a carboxylic acid or its alkyl ester with molecular hydrogen in the presence of a catalyst containing
15 chromium oxide of high purity having a specific surface area of at least 10 m²/g and a total content of sodium, potassium, magnesium and calcium of not more than 0.4 weight percent. It is further reported therein that the hydrogenation reaction is conducted while maintaining the carboxylic acid or its alkyl ester at a concentration of not more than 10 volume percent. Additionally, the only
20 example reported therein is hydrogenation of stearic acid to stearyl aldehyde. Most importantly, the selectivity to aldehyde drops significantly even if the total content of sodium, potassium, magnesium and calcium increases from about 0.3 weight percent to about 0.46 weight percent, thus rendering the process not suitable for a commercial operation.

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United States Patent No. 5,476,827 to *Ferrero et al.* describes a process for the preparation of aldehydes by catalytic hydrogenation of carboxylic acids, esters or anhydrides utilizing a bimetallic ruthenium/tin catalyst. The preferred carboxylic acids are the α - β -unsaturated carboxylic acids with an aromatic back
30 bone or aromatic carboxylic acids. No examples of aliphatic carboxylic acids including acetic acid are provided.

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United States Patent No. 6,121,498 to *Tustin et al.* discloses a method for
5 producing acetaldehyde from acetic acid. In this process, acetic acid is
hydrogenated with hydrogen at an elevated temperature in the presence of an iron
oxide catalyst containing between 2.5 and 90 weight percent palladium. However,
the optimal condition reported therein is comprised of an iron oxide catalyst
containing at least about 20 weight percent palladium, which affords about 80
10 percent selectivity to acetaldehyde with about 50 percent conversion of acetic
acid. Additionally, significant amounts of by-products including methane, ethane,
ethylene, ethanol and acetone are formed.

From the foregoing it is apparent that existing processes do not have the
15 requisite catalysts to selectively convert acetic acid to acetaldehyde or existing art
employs catalysts, which are either expensive and/or non-selective for the
formation of acetaldehyde and produces undesirable by-products.

Summary of the Invention

20 Surprisingly, it has now been unexpectedly found that acetaldehyde can be
made on an industrial scale directly from acetic acid with very high selectivity and
yield. More particularly, this invention provides a process for the selective
formation of acetaldehyde from acetic acid comprising: hydrogenating acetic acid
in the presence of hydrogen over a hydrogenating catalyst comprising at least one
25 metal selected from the group consisting of iron, copper, gold, platinum,
palladium and ruthenium supported on a suitable catalyst support. Optionally, the
catalyst is further comprised of one or more metal catalysts selected from the
group consisting of tin, aluminum, potassium, cobalt, molybdenum, tungsten and
vanadium. More specifically, the catalyst suitable for the process of this invention
30 is typically comprised of supported ruthenium alone or in combination with tin or
iron; a supported iron alone or in combination with platinum or cobalt; or a

palladium/gold (Pd/Au) or palladium/copper (Pd/Cu), which can further comprise potassium acetate. Also suitable catalysts are a combination of palladium/iron (Pd/Fe), iron/cobalt (Fe/Co), copper/molybdenum (Cu/Mo) or copper/aluminum. Suitable catalyst supports include without any limitation, silica, alumina, calcium
5 silicate, carbon, zirconia, zirconia-silica, titania, titania-silica, iron oxide and zeolite catalysts such as for example H-ZSM-5. Silica and iron oxide are particularly preferred catalyst supports in the process of this invention.

Detailed Description of the Invention

10 The invention is described in detail below with reference to numerous embodiments for purposes of exemplification and illustration only. Modifications to particular embodiments within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to those of skill in the art.

15 Unless more specifically defined below, terminology as used herein is given its ordinary meaning.

Typically, the catalyst metal loadings are expressed as weight percent of a catalyst metal based on the total dry weight of the metal and catalyst support.
20 Thus, for example, one (1) weight percent of metal on a support means that one gram of pure metal is present in 100 grams of supported metal catalyst, i.e., the combined weight of support (99 grams) and the metal (1 gram).

“Conversion” is expressed as a mole percentage based on acetic acid in the
25 feed. The conversion of acetic acid (AcOH) is calculated from gas chromatography (GC) data using the following equation:

$$\text{AcOH conversion (\%)} = 100 * \frac{\text{mmol AcOH in (feed stream)} - \text{mmol AcOH out (GC)}}{\text{mmol AcOH in (feed stream)}}$$

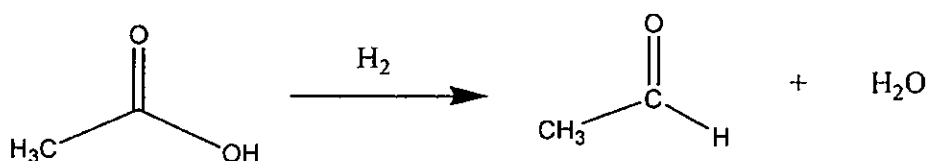
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“Selectivity” is expressed as a mole percent based on converted acetic acid. For example, if the conversion is 50 mole % and 50 mole % of the converted acetic acid is converted to acetaldehyde (AcH), we refer to the acetaldehyde selectivity as 50%. Selectivity is calculated from gas chromatography (GC) data using the following equation:

$$\text{Selectivity to AcH (\%)} = 100 * \frac{\text{mmol AcH out (GC)}}{\frac{\text{Total mmol C out (GC)}}{2} - \text{mmol AcOH out (GC)}}$$

wherein “Total mmol C out (GC)” refers to total mmols of carbon from all of the products analyzed by gas chromatograph.

The reaction proceeds in accordance with the following chemical equation:



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In accordance with the invention, conversion of acetic acid to acetaldehyde can be carried out in a variety of configurations, such as for example in a single reaction zone which may be a layered fixed bed, if so desired. An adiabatic reactor could be used, or a shell and tube reactor provided with a heat transfer medium could be used. The fixed bed can comprise a mixture of different catalyst particles or catalyst particles which include multiple catalysts as further described herein. The fixed bed may also include a layer of particulate material making up a mixing zone for the reactants. A reaction mixture including acetic acid, hydrogen and optionally an inert carrier gas is fed to the bed as a stream under pressure to the mixing zone. The stream is subsequently supplied (by way of pressure drop)

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to the reaction zone or layer. Reaction zone comprises a catalytic composition including a suitable hydrogenating catalyst where acetic acid is hydrogenated to produce acetaldehyde. Any suitable particle size may be used depending upon the type of reactor, throughput requirements and so forth.

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Although various metal supported hydrogenating catalysts known to one skilled in the art can be employed in hydrogenating acetic acid to form acetaldehyde in the process of this invention it is preferred that the hydrogenating catalyst employed contains at least one or more metals selected from the group consisting of iron, copper, gold, platinum, palladium and ruthenium supported on a suitable catalyst support. Optionally, a second or third metal can be selected from the group consisting of tin, aluminum, potassium, cobalt, molybdenum, tungsten and vanadium. Preferably, the catalyst suitable for the process of this invention is comprised of ruthenium alone, supported on a suitable support such as iron oxide or silica or a combination of ruthenium and tin or ruthenium and iron supported on a suitable catalyst support. Similarly, the preferred hydrogenation catalyst is iron alone supported on a suitable support such as silica or a combination of iron and platinum or a combination of iron and cobalt supported on a suitable catalyst support such as silica. Similarly, other catalysts suitable in the process of this invention include supported palladium alone or a combination of palladium/gold (Pd/Au) or palladium/copper (Pd/Cu), which can further comprise potassium acetate. Also suitable catalysts are a combination of palladium/iron (Pd/Fe), iron/cobalt (Fe/Co), copper/molybdenum (Cu/Mo) or copper/aluminum.

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Typically, when bimetallic catalysts are employed it is preferred that a suitable weight ratio of a combination of metals on a suitable support can be used as a hydrogenating catalyst. Thus, for example, a combination of ruthenium and iron (Ru/Fe), ruthenium and tin (Ru/Sn), palladium/copper (Pd/Cu), palladium/iron (Pd/Fe) in the weight ratio of about 0.1 – 1 are particularly preferred. More preferably, a weight ratio of Ru/Fe or Ru/Sn or Pd/Cu or Pd/Fe is

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about 0.2 -0.5 and most preferably the weight ratio of Ru/Fe or Ru/Sn or Pd/Cu or Pd/Fe is about 0.2. Similar weight ratios can be employed for a catalyst combination of platinum and iron Pt/Fe, i.e., a weight ratio of 0.1-1, preferably 0.2-0.5 and most preferably 0.2. When a combination of cobalt and iron (Co/Fe) or copper/molybdenum (Cu/Mo) or copper/aluminum (Cu/Al) supported on a suitable catalyst support is employed, the preferred weight ratio of Co/Fe or Cu/Mo or Cu/Al is in the range of 1 to 5. For instance, a combination of 17.4 weight percent of cobalt and 4.8 weight percent of iron supported on silica is commercially available. Similarly, a copper-aluminum catalyst is sold under the name of T-4489 by Sud Chemie.

When ruthenium alone or palladium alone or iron alone is used as the metal catalyst on a suitable support any loading level of ruthenium, palladium or iron can be employed so as to affect the selective hydrogenation of acetic acid to acetaldehyde. Typically, however, the ruthenium or palladium loading level can range from 0.5 weight percent to about 20 weight percent, preferably 1 weight percent to about 10 weight percent and most preferably 1 weight percent to about 5 weight percent. Generally when a noble metal such as ruthenium or palladium alone are employed in the process of this invention, 0.5 to 1 weight percent of catalyst metal may be sufficient to obtain the optimum catalytic benefit. Preferred catalyst supports for ruthenium or palladium are iron oxide or silica. Similarly, when iron alone is used as the metal catalyst, the loading level of iron can range from 1 weight percent to about 20 weight percent, preferably 2 weight percent to about 10 weight percent and most preferably 3 weight percent to about 8 weight percent. Preferred catalyst support for iron is silica.

When bimetallic catalysts employed are two noble metals such as palladium and gold then the metal loading of each of the noble metal loading is in the range of from about 0.5 weight percent to about 20 weight percent, preferably 1 weight percent to about 10 weight percent and most preferably 1 weight percent to about 5 weight percent. However, as already noted above, low loadings of

about 0.5 weight percent or 1 weight percent of each of the noble metals, such as palladium or gold brings about optimum catalytic effect in the process of this invention.

5 Various catalyst supports known in the art can be used to support the catalysts of this invention. Examples of such supports include without any limitation, zeolite, such as H-ZSM-5, iron oxide, silica, alumina, titania, zirconia, magnesium oxide, calcium silicate, carbon, graphite and a mixture thereof. Preferred supports are silica and iron oxide. More preferably silica is used as a
10 catalyst support in the process of this invention. It is also important to note that the higher the purity of silica, the better it is as a support. Various forms of commercially available silica supports can be used in this invention including high surface area silica (HSA silica) as well as low surface area silica (LSA silica).

15 In another aspect of the process of this invention, any of known zeolite catalysts can also be employed as a catalyst support. While any zeolite having a pore diameter of at least about 0.6 nm can be used, preferably employed among such zeolites are the catalyst supports selected from the group consisting of mordenites, ZSM-5, a zeolite X and a zeolite Y.

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The preparation of large-pore mordenites is described, for example, in United States Patent No. 4,018,514 and in Mol. Sieves Pap. Conf., 1967, 78, Soc. Chem. Ind. London, by D. DOMINE and J. QUOBEX.

25 Zeolite X is described, for example, in United States Patent No. 2,882,244 and zeolite Y in United States Patent No. 3,130,007.

Various zeolites and zeolite-type materials are known in the art for the catalysis of chemical reactions. For example, United States Patent No. 3,702,886,
30 *of Argauer*, discloses a class of synthetic zeolites, characterized as "Zeolite ZSM-

5", which are effective for the catalysis of various hydrocarbon conversion processes.

The zeolites suitable for the procedure of the invention can be in the basic form, in the partially or totally acidified form, or in the partially dealuminated form.

Preferably, the zeolite catalyst support in the process of the present invention are in the protic form, characterized as "H-ZSM-5" or "H-mordenite" zeolites, which are prepared from a corresponding "ZSM-5" zeolite or "mordenite" zeolite by replacing most, and generally at least about 80% of the cations of the latter zeolite with hydrogen ions using techniques well-known in the art. These zeolite catalysts are essentially crystalline aluminosilicates or in the neutral form, a combination of silica and alumina in a well defined crystalline structure. In a particularly preferred class of zeolite catalysts for purposes of the present invention, the molar ratio of SiO_2 to Al_2O_3 in these zeolites is within the ratio of about 10 to 60.

In another aspect of this invention, ruthenium is supported on either silica or iron oxide. A combination of ruthenium and tin, iron alone or a combination of platinum and iron, iron and cobalt, iron and ruthenium, and platinum and tin are supported on a high purity, low surface area silica or high purity, high surface area silica using the procedures well known in the art or the procedures further described herein. Other preferred catalyst supports for platinum or ruthenium based metal catalysts are titania and zirconia.

As noted above, the loading levels of a combination of two metal catalysts are generally referenced with the content of main catalyst metal and the weight ratio of the combination. For instance, the weight ratio of Ru/Sn, Ru/Fe, Pt/Sn or Pt/Fe is in the range of about 0.1 to 2. Thus, when the weight ratio of Ru/Sn, Ru/Fe or Pt/Fe is 0.1, the amount of ruthenium or platinum can be 0.1 or 1 weight

percent and thus 1 or 10 weight percent of tin or iron is present on the catalyst support. Preferably, the weight ratio of Ru/Sn, Ru/Fe, Pt/Sn or Pt/Fe is about 0.5, and thus the amount of ruthenium or platinum on the catalyst support can be either 0.5 or 1 weight percent and that of tin or iron is either one or two weight percent.

5 More preferably, the weight ratio of Ru/Sn, Ru/Fe, Pt/Sn or Pt/Fe is one or 0.2. Thus the amount of ruthenium or platinum on a support is 0.5, one or two weight percent and that of tin or iron is also 0.5, one or two weight percent when the weight ratio is one. Similarly, when a weight ratio of Ru/Sn, Ru/Fe or Pt/Fe is 0.2, the amount of ruthenium or platinum on the support can be 0.5 or one weight

10 percent and of tin or iron is either 2.5 or five weight percent.

The amount of third metal loading if present on a support is not very critical in this invention and can vary in the range of about 0.1 weight percent to about 10 weight percent. A metal loading of about 1 weight percent to about 6

15 weight percent based on the weight of the support is particularly preferred.

The metal impregnation can be carried out using any of the known methods in the art. Typically, before impregnation the supports are dried at 120°C and shaped to particles having size distribution in the range of about 0.2 to 0.4

20 mm. Optionally, the supports may be pressed, crushed and sieved to a desired size distribution. Any of the known methods to shape the support materials into desired size distribution can be employed.

For supports having low surface area, such as, for example, alpha-alumina,

25 the metal solutions are added in excess until complete wetness or excess liquid impregnation so as to obtain desirable metal loadings.

As noted above, the hydrogenation catalysts used in the process of this invention are generally bimetallic containing platinum/iron, ruthenium/tin,

30 ruthenium/iron, iron/cobalt and so on. Generally, without intending to be bound by any theory, it is believed that one metal acts as a promoter metal and another

metal is the main metal. For instance, in the instant process of the invention, of the above noted combinations respectively, platinum, ruthenium, and iron are considered as main metals for preparing hydrogenation catalysts of this invention. The other metals, tin with ruthenium and iron with cobalt, platinum or ruthenium
5 are considered to be the promoter metals depending upon various reaction parameters including, but not limited to catalyst support employed, reaction temperature and pressure, etc. The catalysts may include other promoter metals, such as tungsten, vanadium, molybdenum, chromium or zinc.

10 The bimetallic catalysts are generally impregnated in two steps. Each impregnation step is followed by drying and calcination. The bimetallic catalysts may also be prepared by co-impregnation. In most cases, the impregnation may be carried out using metal nitrate solutions. However, various other soluble salts which upon calcinations release metal ions, can also be used. Examples of other
15 suitable metal salts for impregnation include metal oxalate, metal hydroxide, metal oxide, metal acetate, ammonium metal oxide, such as ammonium heptamolybdate hexahydrate, metal acids, such as perhenic acid solution, and the like.

20 Thus in one embodiment of this invention, there is provided a hydrogenation catalyst wherein the catalyst support is silica or iron oxide with ruthenium alone as the hydrogenation catalyst. In this aspect of the invention the metal loading of ruthenium can range from one (1) weight percent to about twenty (20) weight percent, preferably one to ten weight percent and most preferably one
25 to five weight percent.

In another embodiment of this invention, there is provided a hydrogenation catalyst wherein the catalyst support is silica with iron alone as the hydrogenation catalyst. In this aspect of the invention the metal loading of iron can range from
30 one (1) weight percent to about twenty (20) weight percent, preferably two to ten weight percent and most preferably three to eight weight percent of iron.

In another embodiment of this invention, there is provided a bimetallic loading of ruthenium and tin or platinum and tin. In this aspect of the invention, the loading of ruthenium or platinum is about 0.5 weight percent to about 2 weight percent and the loading of tin is about 2.5 weight percent to about 10 weight percent. Specifically, ruthenium/tin or platinum/tin loading levels of 1/1, 1/5, 0.5/5, and 0.5/2.5 weight percent on silica can be used.

In another embodiment of this invention, there is further provided a hydrogenation catalyst wherein the catalyst support is high purity, low surface area silica with a bimetallic loading of platinum and iron or ruthenium and iron. In this aspect of the invention, the loading of platinum or ruthenium is about 0.5 weight percent to about 2 weight percent and the loading of iron is about 4 weight percent to about 10 weight percent. Specifically, platinum/iron or ruthenium/iron loading levels of 1/1, 1/5, 0.5/5, and 0.5/2.5 weight percent on high purity, low surface area silica can be used. Other preferred supports in this aspect of the invention include H-ZSM-5, graphitized carbon, zirconia, titania, iron oxide, silica-alumina and calcium silicate.

In another embodiment of this invention, there is further provided a hydrogenation catalyst wherein the bimetallic catalyst is cobalt and iron supported on silica. In this aspect of the invention, the loading level of cobalt is about 12 weight percent to about 22 weight percent and of iron is from about 3 to 8 weight percent. Specifically, cobalt loading level of 17.4 weight percent and iron loading level of 4.8 weight percent supported on silica is commercially available.

In general, by the practice of this invention, acetic acid can selectively be converted to acetaldehyde at very high rates. The selectivity to acetaldehyde in general is very high and may be at least 60 percent. Under preferred reaction conditions, acetic acid is converted to acetaldehyde at a selectivity of at least 70

percent or more preferably at a selectivity of over 80 percent such as at least 90 percent.

The conversion of acetic acid using the catalysts of this invention is at
5 least 10% and can be up to 40% with selectivity to acetaldehyde at least 60%, preferably 70% and most preferably 80%.

Generally, the active catalysts of the invention are the single metal or the bimetallic catalysts as described herein. More specifically, a bimetallic catalyst
10 containing ruthenium and tin, ruthenium and iron, platinum and tin, platinum and iron, and cobalt and iron supported on silica with a ruthenium or platinum loadings of 0.5 to 1 weight percent and tin and iron loadings of 5 weight percent and cobalt loading of about 18 weight percent are preferred. In accordance with the practice of this invention, acetic acid can be converted using this catalyst at
15 conversions of around 40% with acetaldehyde selectivity of at least 60%, more preferably selectivity to acetaldehyde of at least 80% can be achieved.

Similar conversions and selectivities are achieved using zirconia, graphite or titania as a support and with similar loadings of ruthenium, platinum, tin, iron
20 and cobalt as described above. Other promoter metals can also be used in conjunction with ruthenium or platinum as noted above.

In another aspect of this invention it is also possible to obtain high levels of conversions in the order of at least 25% and high selectivity to acetaldehyde of
25 at least about 80% using ruthenium or iron loading of one weight percent to about five weight percent on silica or iron oxide as catalyst supports. In this aspect of the invention, other preferred catalyst supports include graphitized carbon, titania, zirconia, silica-alumina and calcium silicate.

In another aspect of the process of this invention, the hydrogenation is carried out at a pressure just sufficient to overcome the pressure drop across the catalytic bed.

5 The reaction may be carried out in the vapor or liquid state under a wide variety of conditions. Preferably, the reaction is carried out in the vapor phase. Reaction temperatures may be employed, for example in the range of about 250°C to about 350°C, preferably about 290°C to about 310°C. The pressure is generally uncritical to the reaction and subatmospheric, atmospheric or superatmospheric
10 pressures may be employed. In most cases, however, the pressure of the reaction will be in the range of about 5 to 30 atmospheres absolute, most preferably the pressure of reaction zone is in the range of about 8 to 20 atmospheres absolute.

 Although the reaction consumes a mole of hydrogen per mole of acetic
15 acid to produce a mole of acetaldehyde, the actual molar ratio of acetic acid to hydrogen in the feed stream may be varied between wide limits, e.g. from about 100:1 to 1:100. It is preferred however, that such ratio be in the range of about 1:20 to 1:2. More preferably, the molar ratio of acetic acid to hydrogen is about 1:5.

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 The raw materials used in connection with the process of this invention may be derived from any suitable source including natural gas, petroleum, coal, biomass and so forth. It is well known to produce acetic acid through methanol carbonylation, acetaldehyde oxidation, ethylene oxidation, oxidative fermentation,
25 and anaerobic fermentation and so forth. As petroleum and natural gas have become more expensive, methods for producing acetic acid and intermediates such as methanol and carbon monoxide from alternate carbon sources have drawn more interest. Of particular interest is the production of acetic acid from synthesis gas (syngas) that may be derived from any suitable carbon source. United States
30 Patent No. 6,232,352 to *Vidalin*, the disclosure of which is incorporated herein by reference, for example, teaches a method of retrofitting a methanol plant for the

manufacture of acetic acid. By retrofitting a methanol plant the large capital costs associated with CO generation for a new acetic acid plant are significantly reduced or largely eliminated. All or part of the syngas is diverted from the methanol synthesis loop and supplied to a separator unit to recover CO and
5 hydrogen, which are then used to produce acetic acid. In addition to acetic acid, the process can also be used to make hydrogen which is utilized in connection with this invention.

United States Patent No. RE 35,377 *Steinberg et al.*, also incorporated
10 herein by reference, provides a method for the production of methanol by conversion of carbonaceous materials such as oil, coal, natural gas and biomass materials. The process includes hydrogasification of solid and/or liquid carbonaceous materials to obtain a process gas which is steam pyrolyzed with additional natural gas to form synthesis gas. The syngas is converted to methanol
15 which may be carbonylated to acetic acid. The method likewise produces hydrogen which may be used in connection with this invention as noted above. *See also*, United States Patent No. 5,821,111 *Grady et al.*, which discloses a process for converting waste biomass through gasification into synthesis gas as well as United States Patent No. 6,685,754 *Kindig et al.*, the disclosures of which
20 are incorporated herein by reference.

The acetic acid may be vaporized at the reaction temperature, and then it can be fed along with hydrogen in undiluted state or diluted with a relatively inert carrier gas, such as nitrogen, argon, helium, carbon dioxide and the like.
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Alternatively, acetic acid in vapor form may be taken directly as crude product from the flash vessel of a methanol carbonylation unit of the class described in United States Patent No. 6,657,078 of *Scates et al.*, the disclosure of which is incorporated herein by reference. The crude vapor product may be fed
30 directly to the reaction zones of the present invention without the need for

condensing the acetic acid and light ends or removing water, saving overall processing costs.

Contact or residence time can also vary widely, depending upon such variables as amount of acetic acid, catalyst, reactor, temperature and pressure. Typical contact times range from a fraction of a second to more than several hours when a catalyst system other than a fixed bed is used, with preferred contact times, at least for vapor phase reactions, between about 0.5 and 100 seconds.

Typically, the catalyst is employed in a fixed bed reactor e.g. in the shape of an elongated pipe or tube where the reactants, typically in the vapor form, are passed over or through the catalyst. Other reactors, such as fluid or ebullient bed reactors, can be employed, if desired. In some instances, it is advantageous to use the hydrogenation catalysts in conjunction with an inert material to regulate the pressure drop, flow, heat balance or other process parameters in the catalyst bed including the contact time of the reactant compounds with the catalyst particles.

In one of the preferred embodiments there is also provided a process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature with a suitable hydrogenating catalyst containing about 0.5 weight percent to about 1 weight percent of platinum or ruthenium and about 2.5 weight percent to about 5 weight percent of tin or iron on a suitable catalyst support. Preferred catalyst support in this embodiment of the invention is silica.

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In this embodiment of the process of this invention, the preferred hydrogenation catalyst contains about 0.5 weight percent or about one (1) weight percent platinum and about five (5) weight percent iron or tin; or about 0.5 weight percent or about one (1) weight percent ruthenium and about five (5) weight percent tin or iron. In this embodiment of the process of this invention, it is preferred that the hydrogenation catalysts are layered in a fixed bed and the

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reaction is carried out in the vapor phase using a feed stream of acetic acid and hydrogen in the molar range of about 1:20 to 1:5 and at a temperature in the range of about 290°C to 310°C and at a pressure of reaction zones in the range of about 8 to 20 atmospheres absolute, and the contact time of reactants is in the range of
5 about 0.5 and 100 seconds.

The following examples describe the procedures used for the preparing various catalysts employed in the examples which follow.

10 Example A

Preparation of 1 weight percent ruthenium on Iron Oxide

Powdered and meshed iron oxide (99 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven under nitrogen atmosphere overnight and then cooled to room temperature. To this was added a
15 solution of ruthenium nitrosyl nitrate (Heraeus) (3.14 g) in distilled water (32 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

20 Example B

Preparation of 3 weight percent ruthenium on Iron Oxide

The procedures of Example A were substantially repeated except for utilizing a solution of ruthenium nitrosyl nitrate (Heraeus) (9.42 g) in distilled water (96 ml) and 97 grams of iron oxide.

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Example C

Preparation of 5 weight percent Iron on High Purity, Low Surface Area Silica

Powdered and meshed high purity, low surface area silica (95 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven
30 under nitrogen atmosphere overnight and then cooled to room temperature. To this was added a solution of iron nitrate nonahydrate (Alfa Aesar) (36.2 g) in

distilled water (36 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

5 Example D

Preparation of 5 weight percent tin and 0.5 weight percent ruthenium on High Purity Low, Surface Area Silica

Powdered and meshed high purity, low surface area silica (94 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven
10 under nitrogen atmosphere overnight and then cooled to room temperature. To this was added a solution of tin oxalate (Alfa Aesar) (8.7 g) in dilute nitric acid (1N 45 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min). To this calcined and cooled material was added a
15 solution of ruthenium nitrosyl nitrate (Heraeus) (1.57 g) in distilled water (16 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

20 Example E

Preparation of 1 weight percent ruthenium and 5 weight percent iron on High Purity Low, Surface Area Silica

Powdered and meshed high purity low surface area silica (94 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven under
25 nitrogen atmosphere overnight and then cooled to room temperature. To this was added a solution of ruthenium nitrosyl nitrate (Heraeus) (3.14 g) in distilled water (32 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min). To this calcined and cooled material was added a solution of
30 iron nitrate nonahydrate (Alfa Aesar) (36.2 g) in distilled water (36 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours,

10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

Example F

5 Preparation of 5 weight percent iron and 1 weight percent platinum on High Purity, Low Surface Area Silica

 Powdered and meshed high purity, low surface area silica (94 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven under nitrogen atmosphere overnight and then cooled to room temperature. To
10 this was added a solution of iron nitrate nonahydrate (Alfa Aesar) (36.2 g) in distilled water (36 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min). To this calcined and cooled material was added a solution of platinum nitrate (Chempur) (1.64 g) in distilled water (16 ml).
15 The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

Example G

20 Preparation of 1 weight percent platinum and 5 weight percent tin on High Purity, Low Surface Area Silica

 Powdered and meshed high purity, low surface area silica (94 g) of uniform particle size distribution of about 0.2 mm was dried at 120°C in an oven under nitrogen atmosphere overnight and then cooled to room temperature. To
25 this was added a solution of platinum nitrate (Chempur) (1.64 g) in distilled water (16 ml) and a solution of tin oxalate (Alfa Aesar) (8.7 g) in dilute nitric acid (1N, 43.5 ml). The resulting slurry was dried in an oven gradually heated to 110°C (>2 hours, 10°C/min.). The impregnated catalyst mixture was then calcined at 500°C (6 hours, 1°C/min).

Example HPreparation of 1 weight percent palladium, 1 weight percent gold and 5 weight percent potassium acetate on High Purity, Low Surface Area Silica

The procedures of Example D were substantially repeated except for
5 utilizing a solution of palladium nitrate (Heraeus) (2.17 g) in distilled water (22 ml), a solution of gold(III) hydroxide (Alfa Aesar) (1.26 g) and potassium hydroxide (0.28 g) in distilled water (10 ml), a solution of potassium acetate (Sigma) (5 g) in distilled water (10 ml) and 93 grams of silica. The catalyst was sequentially impregnated first with palladium and then with gold and finally with
10 potassium acetate.

Example IPreparation of 1 weight percent palladium, 5 weight percent copper and 5 weight percent potassium acetate on High Purity, Low Surface Area Silica

15 The procedures of Example D were substantially repeated except for utilizing a solution of palladium nitrate (Heraeus) (2.17 g) in distilled water (22 ml), a solution of copper nitrate trihydrate (Alfa Aesar) (19 g) in distilled water (20 ml), a solution of potassium acetate (Sigma) (5 g) in distilled water (10 ml) and 89 grams of silica. The catalyst was sequentially impregnated first with
20 copper and then with palladium and finally with potassium acetate.

Example JPreparation of 1 weight percent palladium and 5 weight percent copper on Carbon

The procedures of Example D were substantially repeated except for
25 utilizing a solution of palladium nitrate (Heraeus) (2.17 g) in distilled water (22 ml), a solution of copper nitrate trihydrate (Alfa Aesar) (19 g) in distilled water (20 ml) and 94 grams of carbon. The catalyst was sequentially impregnated first with copper and then with palladium.

Example KPreparation of 1 weight percent palladium and 5 weight percent iron on High Purity, Low Surface Area Silica

The procedures of Example D were substantially repeated except for
5 utilizing a solution of palladium nitrate (Heraeus) (2.17 g) in distilled water (22 ml), a solution of iron nitrate nonahydrate (Alfa Aesar) (36.2 g) in distilled water (30 ml) and 94 grams of silica. The catalyst was sequentially impregnated first with iron and then with palladium.

10 Example LPreparation of 5 weight percent iron and 5 weight percent cobalt on High Purity, Low Surface Area Silica

The procedures of Example D were substantially repeated except for
utilizing a solution of iron nitrate nonahydrate (Alfa Aesar) (36.2 g) in distilled
15 water (30 ml), a solution of cobalt nitrate hexahydrate (24.7 g) in distilled water (25 ml) and 90 grams of silica. The catalyst was sequentially impregnated first with iron and then with cobalt.

Example M20 Preparation of 5 weight percent copper and 5 weight percent molybdenum on High Purity, Low Surface Area Silica

The procedures of Example D were substantially repeated except for
utilizing a solution of copper nitrate trihydrate (Alfa Aesar) (19 g) in distilled
water (20 ml), a solution of ammonium heptamolybdate hexahydrate (Sigma) (9.5
25 g) in distilled water (65 ml) and 90 grams of silica. The catalyst was sequentially impregnated first with copper and then with molybdenum.

Example NPreparation of 5 weight percent tin and 1 weight percent ruthenium on High Purity, Low Surface Area Silica

The procedures of Example D were substantially repeated except for
5 utilizing a solution of tin oxalate (Alfa Aesar) (8.7 g) in dilute nitric acid (1N, 43.5 ml), a solution of ruthenium nitrosyl nitrate (Heraeus) (3.14 g) in distilled water (32 ml) and 94 grams of silica. The catalyst was co-impregnated with tin and ruthenium.

10 Example OPreparation of 1 weight percent palladium on Iron Oxide

The procedures of Example D were substantially repeated except for
utilizing a solution of palladium nitrate (Heraeus) (2.17 g) in distilled water (22 ml) and 99 grams of iron oxide.

15

Gas Chromatographic (GC) analysis of the Products

The analysis of the products was carried out by online GC. A three
channel compact GC equipped with one flame ionization detector (FID) and 2
thermal conducting detectors (TCDs) was used to analyze the reactants and
20 products. The front channel was equipped with an FID and a CP-Sil 5 (20 m) + WaxFFap (5 m) column and was used to quantify:

Acetaldehyde
Ethanol
25 Acetone
Methyl acetate
Vinyl acetate
Ethyl acetate
Acetic acid
30 Ethylene glycol diacetate
Ethylene glycol

Ethylidene diacetate

Paraldehyde

The middle channel was equipped with a TCD and Porabond Q column
5 and was used to quantify:

CO₂

Ethylene

Ethane

10

The back channel was equipped with a TCD and Molsieve 5A column and
was used to quantify:

Helium

15

Hydrogen

Nitrogen

Methane

Carbon monoxide

20 Prior to reactions, the retention time of the different components was
determined by spiking with individual compounds and the GCs were calibrated
either with a calibration gas of known composition or with liquid solutions of
known compositions. This allowed the determination of the response factors for
the various components.

25

Example 1

The catalyst utilized was 1 weight percent ruthenium on iron oxide
prepared in accordance with the procedure of Example A.

30 In a tubular reactor made of stainless steel, having an internal diameter of
30 mm and capable of being raised to a controlled temperature, there are arranged

50 ml of 1 weight percent ruthenium supported on iron oxide. The length of the catalyst bed after charging was approximately about 70 mm. Prior to the reaction the catalyst was reduced *in situ* by heating at a rate of 2°C/min to a final temperature of 400°C. Then, 5 mol% hydrogen in nitrogen was introduced to the catalyst chamber at a gas hourly space velocity (GHSV) of 7500 h⁻¹. After reduction, the catalyst was cooled to reaction temperature of 350°C by continuing the gas flow of 5 mol% hydrogen in nitrogen. Once the reaction temperature was stabilized at 350°C, the hydrogenation of acetic acid was begun as follows.

10 A feed liquid was comprised essentially of acetic acid. The reaction feed liquid was evaporated and charged to the reactor along with hydrogen and helium as a carrier gas with an average combined gas hourly space velocity (GHSV) of about 2500 hr⁻¹ at a temperature of about 350°C. The resulting feed stream contained a mole percent of acetic acid from about 4.4% to about 13.8% and the mole percent of hydrogen from about 14% to about 77%. A portion of the vapor effluent was passed through a gas chromatograph for analysis of the contents of the effluents. The selectivity to acetaldehyde was 60% at a conversion of acetic acid of 50%.

20 Example 2

The catalyst utilized was 5 weight percent iron on silica prepared in accordance with the procedure of Example C.

25 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 350°C. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 75% and acetaldehyde selectivity was 70%.

Example 3

The catalyst utilized was 0.5 weight percent ruthenium and 5 weight percent tin on silica prepared in accordance with the procedure of Example D.

5 The procedure as set forth in Example 1 is substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the
10 effluents. The acetic acid conversion was 4% and acetaldehyde selectivity was 91%. The other products formed were ethane (1%) and ethanol (8%).

Example 4

15 The catalyst utilized was 1 weight percent ruthenium and 5 weight percent iron on silica prepared in accordance with the procedure of Example E.

 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of
20 5) at a temperature of 300°C. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion is 35% and acetaldehyde selectivity is about 70%.

Example 5

25 The catalyst utilized was 1 weight percent platinum and 5 weight percent iron on High Purity, Low Surface Area Silica prepared in accordance with the procedure of Example F.

 The procedure as set forth in Example 1 was substantially repeated with an
30 average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of

5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 65% and acetaldehyde selectivity is 60%. The other products formed were carbon dioxide (6%) and ethyl acetate (9%).

Example 6

The catalyst utilized was 0.5 weight percent platinum and 5 weight percent tin on silica prepared in accordance with the procedure of Example G.

10

The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 85% and acetaldehyde selectivity was 65%. The other products formed were methane (4%) and ethyl acetate (9%).

15

Example 7

The catalyst utilized was a commercially available Co/Fe catalyst containing 17.4 weight percent cobalt and 4.8 weight percent iron on silica.

20

The procedure as set forth in Example 1 is substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen at a temperature of 350°C. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion is about 65% and acetaldehyde selectivity is 75%.

25

30

Example 8

The catalyst utilized was 1 weight percent palladium, 1 weight percent gold and 5 weight percent potassium acetate on silica prepared in accordance with the procedure of Example H.

5

The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 5% and acetaldehyde selectivity was 98.5%. The other products formed were ethane (1%) and ethanol (0.5%).

10

Example 9

The catalyst utilized was 1 weight percent palladium, 5 weight percent copper and 5 weight percent potassium acetate on silica prepared in accordance with the procedure of Example I.

15

The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 2% and acetaldehyde selectivity was 97.5%. The other product formed was ethane (2.5%).

20

25

Example 10

The catalyst utilized was 1 weight percent palladium and 5 weight percent copper on carbon prepared in accordance with the procedure of Example J.

5 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the
10 effluents. The acetic acid conversion was 1% and acetaldehyde selectivity was 97%. The other product formed was ethane (3%).

Example 11

15 The catalyst utilized was 1 weight percent palladium and 5 weight percent iron on silica prepared in accordance with the procedure of Example K.

 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of
20 5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 9% and acetaldehyde selectivity was 96%. The other products formed were ethane (0.6%) and ethanol (3.6%).

25 Example 12

 The catalyst utilized was 5 weight percent iron and 5 weight percent cobalt on silica prepared in accordance with the procedure of Example L.

30 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of

5) at a temperature of 250°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 11% and acetaldehyde selectivity was 95%. The other products formed were ethane (1%) and ethanol (4%).

5

Example 13

The catalyst utilized was 5 weight percent iron and 5 weight percent cobalt on silica prepared in accordance with the procedure of Example L.

10 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the
15 effluents. The acetic acid conversion was 75% and acetaldehyde selectivity was 70%. The other products formed were methane (4%) and carbon dioxide (3%).

Example 14

The catalyst utilized was 5 weight percent copper and 5 weight percent
20 molybdenum on silica prepared in accordance with the procedure of Example M.

The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of
25 5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 10% and acetaldehyde selectivity was 90%. The other products formed were ethane (1.5%) and acetone (6.6%).

Example 15

The catalyst utilized was 1 weight percent ruthenium and 5 weight percent tin on silica prepared in accordance with the procedure of Example N.

5 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of 5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the
10 effluents. The acetic acid conversion was 60% and acetaldehyde selectivity was 78%. The other products formed were methane (6%) and ethanol (12%).

Example 16

 The catalyst utilized was 1 weight percent palladium on iron oxide
15 prepared in accordance with the procedure of Example O.

 The procedure as set forth in Example 1 was substantially repeated with an average combined gas hourly space velocity (GHSV) of 10,000 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of
20 5) at a temperature of 350°C and at a pressure of 15 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 66% and acetaldehyde selectivity was 59%. The other products formed were carbon dioxide (4%) and ethanol (18%).

25 Example 17

 The catalyst utilized was commercially available copper-aluminum catalyst sold under the name of T-4489 from Sud Chemie.

 The procedure as set forth in Example 1 was substantially repeated with an
30 average combined gas hourly space velocity (GHSV) of 2,500 hr⁻¹ of the feed stream of the vaporized acetic acid and hydrogen (H₂ to acetic acid mole ratio of

5) at a temperature of 350°C and at a pressure of 1 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents. The acetic acid conversion was 88% and acetaldehyde selectivity was 51%. The other products formed were carbon dioxide (5%) and ethanol (16%).

5

Comparative Examples 1A – 4A

These examples illustrate the reaction of acetic acid and hydrogen over a variety of catalysts wherein either no acetaldehyde was formed and/or very low selectivity to acetaldehyde was observed at low conversions of acetic acid.

10

In all of these examples, the procedure as set forth in Example 1 was substantially followed with the exception of using different catalysts as listed in Table 1. The reaction temperature and selectivity to acetaldehyde and other products are also tabulated in Table 1.

15

Table 1. Acetic Acid Conversion and Selectivities for Comparative Examples

Example	Catalyst	Acetaldehyde selectivity (%)	Acetic acid conversion (%)	Other products
1A	5 wt% Cu/ Fe ₂ O ₃	31	100	ethylene-16%, ethane-15%, ethyl acetate-4%, CO ₂ -5%
2A	5 wt % Co/ H- ZSM-5	44	3	ethylene-28%, ethane-28%
3A	5 wt% Co 5 Wt% Ru/SiO ₂	78	4	ethylene-14%, ethane-8%
4A	5 wt % Co/ Carbon	0	2	Ethylene – 12% acetone-8%, methane-47%, ethane-5%

While the invention has been illustrated in connection with particular
20 examples, modifications to these examples within the spirit and scope of the

invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is
5 deemed unnecessary.

WHAT IS CLAIMED IS:

1. A process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature with a hydrogenating catalyst carried on a support, said hydrogenating catalyst comprising cobalt and a second metal selected from the group consisting of iron, molybdenum, aluminum, and combinations thereof.
2. The process according to claim 1, wherein the support is selected from the group consisting of silica, titania, alumina, zirconia, calcium silicate, titania-silica, zirconia-silica and combinations thereof.
3. The process according to claim 1, wherein the hydrogenating catalyst contains a combination of cobalt and iron, and wherein the loading level of cobalt is about 8 weight percent to about 20 weight percent and the loading level of iron is about 3 weight percent to 10 weight percent.
4. The process according to claim 1, wherein the hydrogenation to acetaldehyde is carried out in the vapor phase and at a temperature in the range of about 250°C to 350°C.
5. The process according to claim 1, wherein the selectivity to acetaldehyde based on acetic acid consumed is at least 60 percent.
6. The process according to claim 1, wherein the pressure of the reaction zone is about 1 atmosphere absolute.
7. A process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature of from 290°C to 350°C with a hydrogenating catalyst carried on a support, said hydrogenating catalyst comprising platinum and tin.
8. The process according to claim 7, wherein the support is selected from the group consisting of

silica, titania, alumina, zirconia, calcium silicate, titania-silica, zirconia-silica and combinations thereof.

9. The process according to claim 7, wherein the loading level of platinum is about 0.5 weight percent to about 20 weight percent.

10. The process according to claim 7, wherein the selectivity to acetaldehyde based on acetic acid consumed is at least 60 percent.

11. The process according to claim 7, wherein the pressure of the reaction zone is about 1 atmosphere absolute.

12. A process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature with a hydrogenating catalyst consisting of 0.5 to 1.0 wt % of ruthenium carried on a support selected from the group consisting of iron oxide or silica.

13. The process according to claim 12, wherein the selectivity to acetaldehyde based on acetic acid consumed is at least 60 percent.

14. A process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature with a hydrogenating catalyst comprising iron carried on a support, and optionally a second metal selected from the group consisting of tin, aluminum, potassium, molybdenum, tungsten, platinum, ruthenium and vanadium.

15. The process according to claim 14, wherein the support is selected from the group consisting of silica, titania, alumina, zirconia, calcium silicate, titania-silica, zirconia-silica and combinations thereof.

16. The process according to claim 14, wherein the loading level of iron is about 0.5 weight

percent to about 20 weight percent.

17. The process according to claim 14, wherein the hydrogenation to acetaldehyde is carried out in the vapor phase and at a temperature in the range of about 250°C to 350°C.

18. The process according to claim 14, wherein the selectivity to acetaldehyde based on acetic acid consumed is at least 60 percent.

19. The process according to claim 14, wherein the pressure of the reaction zone is about 1 atmosphere absolute.

20. A process for selective and direct formation of acetaldehyde from acetic acid comprising: contacting a feed stream containing acetic acid and hydrogen at an elevated temperature with a hydrogenating catalyst comprising palladium and potassium acetate carried on a support, and optionally a third metal selected from the group consisting of iron, copper, gold, platinum, and ruthenium.

21. The process according to claim 20, wherein the support is selected from the group consisting of silica, titania, alumina, zirconia, calcium silicate, titania-silica, zirconia-silica and combinations thereof.

22. The process according to claim 20, wherein the loading level of palladium is about 0.5 weight percent to about 20 weight percent.

23. The process according to claim 20, wherein the hydrogenation to acetaldehyde is carried out in the vapor phase and at a temperature in the range of about 250°C to 350°C.

24. The process according to claim 20, wherein the selectivity to acetaldehyde based on acetic acid consumed is at least 60 percent.

25. The process according to claim 20, wherein the pressure of the reaction zone is about 1 atmosphere absolute.