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Ketonization of acetic acid on titania-functionalized silica monoliths

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Abstract

Titania-functionalized monolith catalysts operated at short contact times are highly selective for the formation of ketones from carboxylic acids. The selectivity of ketonization of acetic acid to form acetone over such catalysts varies little as the conversion is varied from 3 to 100%. These results demonstrate that ketonization is not a sequential reaction proceeding via a gaseous ketene product. The selectivity for ketene versus ketone formation is determined by the intrinsic chemistry of the catalyst, and cannot be manipulated by contact time or conversion variations.

Keywords: Acetic acid ketonization; Acetone; TiO_2 catalyst; Monolith catalyst; Short contact time

1. Introduction

The menu of possible reactions for adsorbed acetic acid on metal oxides has been well documented [1]. For instance, decarboxylation produces CO_2, dehydration yields ketene, reduction produces acetaldehyde, and ketonization leads to the production of acetone. The selectivity of these reaction channels depends strongly on the nature of the metal oxide surface [1,2].

The decarboxylation and the dehydration reactions represent unimolecular reaction channels involving bond-scission processes of individual acetate intermediates on the surface. The availability of oxygen from the metal oxide lattice influences the selectivity of these unimolecular reactions: in general, the less reducible the oxide, the higher the dehydration selectivity [1,3]. Libby et al. [4] proposed additional site requirements for the dehydration of carboxylic acids to form the corresponding ketenes. The most important of these was that the catalyst should expose cations with single coordination vacancies to facilitate the formation and unimolecular reaction of surface carboxylates. It was demonstrated that C_2 to C_5 carboxylic acids could be catalytically dehydrated to the corresponding ketenes over a packed bed of high-surface-area SiO_2 above 700 K [4,5]. However, the selectivity for ketene synthesis from carboxylic acids appears to be limited by series reactions in which the desired product (ketene) reacts to form other products [6,7].

Recently, monolith catalysts have received special attention for their potential in maximizing selectivities in exothermic series and series-parallel reaction systems; such applications take advantage of the mass transfer and heat transfer characteristics of monoliths, and the opportunity they provide to optimize the contact time from the millisecond range upward [8–13]. We have previously demonstrated that short contact times lead to excellent yields for ketene formation by unimolecular dehydration reaction of carboxylic acids on functionalized silica monoliths, by limiting ketene loss. Ketene selectivities from acetic acid increased from < 40 to $> 90\%$ when the silica powder catalyst was replaced by a functionalized silica monolith operated at short contact times [6,7]. Moreover, in the short contact time mode, ketene selectivities were nearly constant for acetic acid conversions from 10 to 90% [6,7]. These results are illustrative of the use of short-contact-time catalytic reactors to minimize sequential reactions, even for highly reactive products and/or severe conditions. Commercial processes that exploit short contact times to maximize product yield include methanol oxidation to formaldehyde with unsupported silver catalysts, and ammonia oxidation for nitric acid production with Pt–Rh gauzes [14]. The present work is aimed in part at demonstrating the use of short-contact-time catalyst/reactor configurations for mechanistic studies, again taking advantage of the ability to minimize sequential reactions of intermediate products.

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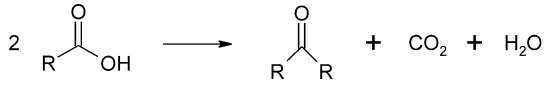
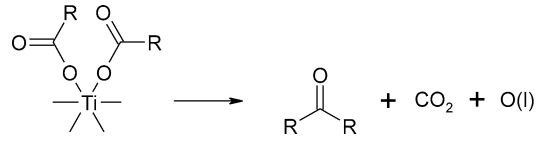
Ketonization represents an alternative selective reaction channel to ketene formation in the conversion of carboxylic acids over metal oxide catalysts. Ketonization is a bimolecular reaction in which two molecules of a carboxylic acid with n carbon atoms are coupled to produce the symmetric ketone (with $2n-1$ carbon atoms), liberating CO_2 during the process [1,2,15].



The ketonization of carboxylic acids has been a well-known reaction in organic chemistry for more than a century. For example, classic chemistry textbooks report that either carboxylic acids in the presence of thorium oxide [15] or bulk carboxylate salts of divalent and higher-valent cations can be converted to symmetrical ketones by pyrolysis [16]. Thermodynamically, ketonization is more favorable than dehydration [2]. For instance, the dehydration of the acetic acid to produce ketene has an enthalpy of reaction of 31.6 kcal/(mol of acetic acid) whereas the ketonization of acetic acid to produce acetone has an enthalpy of reaction of only 4.4 kcal/(mol of acetic acid). It is therefore not surprising that the ketonization reaction is well known on polycrystalline oxide samples, and numerous oxides have been found to be active for this reaction. These include γ-Al_2O_3 [17], ThO_2 [18,19], UO_2 [18], MgO [20], Bi_2O_3 [17,21], Fe_3O_4 [22], Fe_2O_3 [22,23], TiO_2 [17,23–25], Cr_2O_3 [26], ZrO_2 [23,27], and PbO_2 [17]. Different mechanisms for the ketonization of carboxylic acids have been proposed and debated so far [2]:

1. An acid anhydride intermediate that loses CO_2 to produce the ketone [28,29]. This mechanism has been proposed to explain the production of cyclic ketones from dicarboxylic acids [2].
2. A β-keto acid intermediate formed from two monodentate carboxylates via α-hydrogen abstraction [30]. This mechanism does not explain the formation of ketones from acids that do not possess any α-hydrogen atoms [2].
3. A concerted mechanism involving two monodentate carboxylates [31]. It has been claimed that this mechanism is restricted to the ketonization of aromatic acids [2].
4. An intermediate formed from two adsorbed molecules of carboxylic acid [32]. Isotopic labeling studies showed that molecular acetic acid adsorbed on the surface is not directly involved in ketonization [2,24].
5. A ketene intermediate that reacts with a carboxylate to produce the ketone [17,23,25,33]. However, ketene intermediates have not been observed during XPS and mass spectrometry studies in the course of ketonization [2].
6. A bimolecular coupling of two carboxylates bound to the same cation [1,3,24,34].

According to Rajadurai [2], the bimolecular interaction between either two adsorbed acetate ions or one adsorbed acetate and one adsorbed acyl carbonium ion should be responsible for ketonization of acetic acid. However, it is difficult to distinguish between an acyl carbonium ion and a carboxylate because an acyl carbonium can be converted to a carboxylate by nucleophilic addition of lattice oxygen. In surface science experiments, the ketonization reaction was not reported before 1990. Only after this date have experiments on titania single-crystal surfaces provided clear insights on this classic reaction [1]. To date, carboxylate ketonization has been reported only on the TiO_2 (001)–{114} faceted surface [3,24,35], which is characterized by the presence of surface cations with two coordination vacancies. Its activity has been ascribed to these sites on which a pair of carboxylates bound to a common cation couple together [1]:



Recently Dooley and co-workers [36,37] reported extensive studies, including isotopic labeling experiments, of the cross-ketonization of acetic acid with decanoic acid and cyclopentane carboxylic acid on supported ceria catalysts. Their results provide strong support for a "ketene mechanism" of ketonization via a *surface* ketene intermediate. Although this mechanism is not inconsistent with the conclusion from surface science experiments that the reaction involves a complex in which both species to be coupled must be bound to a common cation, much remains to be determined about the structure of this complex and of the transition state for the ketonization reaction.

Given the observation that ketene is generated as a volatile product in temperature-programmed reaction of acetic acid on TiO_2 powders and single crystals, and that ketene can be produced with high yield with functionalized monolith catalysts operated at short contact times, one might also consider the possibility that ketonization is a sequential reaction involving an intermediate ketene product that is consumed by subsequent coupling. Therefore we investigated the reactions of acetic acid over titania-functionalized monoliths at short contact times. Titania-functionalized monoliths were chosen over bulk titania, as at high temperatures titania sinters easily and it is difficult to obtain titania through extrusion [38]. Previous results for the deposition of titania on silica gel by the hydrolysis of $TiCl_4$ showed that this is feasible because the growth proceeds through formation of TiO_x aggregates formed at silanol groups [38]. This work reports results for the steady-state reaction of acetic acid on a titania-functionalized silica monolith prepared by hydrolysis of titanium isopropoxide over a plain silica monolith. As will be shown, the ability to vary contact time and conversion over a wide range by this approach provides new tools for distinguishing between various proposed reaction mechanisms.

2. Experimental

A reticulated foam silica monolith (Vesuvius Hi-Tech Ceramics, Inc) 20 mm in diameter × 10 mm in height and 45 pores per linear inch was used. Prior to the titania deposition, the silica monolith was placed in boiling distilled and deionized water for 8 h and dried in air at 393 K for 2 h. The clean monolith was immersed in a beaker containing 10 mL of titanium(IV) isopropoxide (Aldrich, 99.999%) and stirred. Then 2.0 mL of distilled and deionized water was added. Stirring was continued until the titanium(IV) isopropoxide reacted (the solution becomes a white suspension in less than 2 min), then the stirring was stopped and the monolith was left in the slurry for 3 h. The functionalized monolith was dried at 403 K for 5 h. Finally the monolith was pretreated in the reactor with 125 sccm of oxygen (grade 4) at 573 K for 12 h. Prior to experiments, the catalyst was inserted in the reactor and heated in flowing helium (125 sccm) at 573 K for 5 h.

The reactor was a quartz tube (length = 48 cm, internal diameter = 22 mm) in which the cylindrical foam monolith was placed using a small amount of quartz wool between the monolith and the quartz tube to hold it in place. Two MDC Kwik-Flange® disconnect adapters were located at the ends of the quartz tube to permit coupling of the quartz tube to the ¼-in. stainless-steel tubing. The reactor was placed in a cylindrical furnace (length of heating zone = 40 cm) where the temperature was controlled with a PID controller. The monolith was located 12 cm from the downstream end of the reactor. Temperature was measured with a type K thermocouple located at the downstream face of the monolith. All lines that carried reactants and products were constructed of 316 stainless steel and were heated by electrical heating tape to avoid carboxylic acid and water condensation. A schematic of the apparatus has been given previously [6].

High-purity He (grade 5) was used as a carrier gas. Gas flow was controlled by a mass flow controller (Brooks, 5850E). The carrier gas at atmospheric pressure passed through a glass bubbler containing the glacial acetic acid (Fisher). The temperature of the bubbler was controlled by an automatic water bath (RM 20, Lauda); the temperature of the bubbler was typically maintained at 298 K, achieving a vapor pressure of around 12 Torr. A quadrupole mass spectrometer (UTI 100C) with a differentially pumped UTI atmospheric pressure sampling module (APSM) was used to monitor product and feed compositions. The APSM consisted of a zone enclosed by two gold-plated orifice plates (orifice diameter 0.0457 mm) pumped to an intermediate pressure of around 10^{-2} Torr with a Welch Duo-Seal 1402 vacuum pump. The mass spectrometer was computer controlled and multiplexed to monitor different masses. The MS probe was kept at approximately 395 K with an external heating mantle. The base pressure in the probe was about 4×10^{-8} Torr and increased to approximately 8×10^{-7} Torr during sampling. A Bayard–Alpert-type ionization gauge tube driven by a Varian Model 843 vacuum ionization gauge controller measured the pressure at the mass spectrometer probe. An Edwards Diffstak Model 100-300M diffusion pump with Santovac 5 oil maintained the low pressure in the mass spectrometer probe and was backed by a roughing pump (Welch Model 1402).

The steady-state experiments were performed in three consecutive steps. Initially, helium bypassed the bubbler and reactor for at least 5 min and the mass spectrometer background signals were determined for all fragments. Next, helium was passed through the bubbler while bypassing the reactor; this permitted determination of the relative acid concentration in the feed as well as the reactant fragmentation pattern. For acetic acid, the vapor phase was saturated with the acid in approximately 10–15 min. Finally, the flow was directed through the reactor. Reactant signals and product signals were monitored continuously with the mass spectrometer. Steady state was typically reached in less than 10 min and the activity was monitored for 1–10 h.

Deconvolution analysis of the overlapping mass spectrometer fragmentation patterns for the various reactants and products and the quantification of the products using sensitivity factors have been described previously [4]. The carbon balance was carried out by measuring the intensity decrease for the acid during the reaction step and comparing it with the sum of the product signals. The carbon content of the products computed in this fashion was within 10% of the carbon provided by the feed. Deviations reflect the accuracy limit of the computed mass spectrometer sensitivity factors.

3. Results

The main reaction of acetic acid on TiO_2-functionalized silica monoliths at temperatures between 533 and 680 K is ketonization. Fig. 1 illustrates an example of a steady-state experiment for the reaction of acetic acid at 633 K with a helium flow of 250 sccm. The uncorrected MS profiles in Fig. 1 are divided into three different regions corresponding to the experiment sequence given above. The signal for $m/q = 60$ was used to monitor the reactant signal. In the second region the reactant came to a steady-state concentration after approximately 10 min. During this time, the corresponding intensities of the mass/charge (m/q) ratios corresponding to the cracking pattern of acetic acid increased. In the third region, the reactant-helium flow was diverted to the reactor. As can be seen in the lowest trace of Fig. 1, the intensity of the acetic acid signal ($m/q = 60$) decreased substantially on contact with the TiO_2-functionalized silica monolith. There was a net increase in the signal for $m/q = 18$ (water), 44 (CO_2), and 58 (acetone). To correct the product signals for contributions from acetic acid cracking in the mass spectrometer, baseline corrections were made as described previously [4]. For all the experiments carried out with titania-functionalized silica monoliths, the selective dehydration to ketene as well as the production of volatile hydrocarbon products from the nonselective decarboxylation reaction appeared to be negligible. For example, the produc-

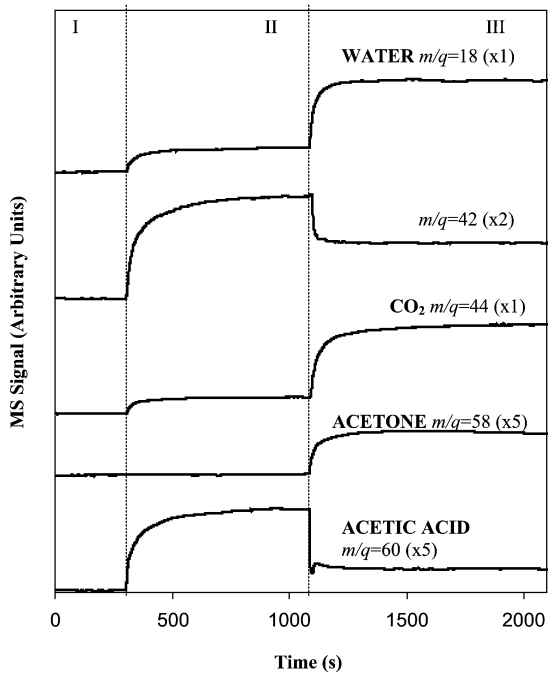


Fig. 1. Reaction of acetic acid on titania-functionalized silica monolith. Carrier flow rate = 250 sccm. Monolith temperature = 633 K. Region I shows the MS signals for the background. Region II shows the MS signals of the acetic acid. Region III shows the MS signals of the product stream. Partial pressure of acetic acid = 12 Torr.

tion of ketene was monitored using $m/q = 42$. In the third region, the intensity of the signal for $m/q = 42$ was fully accounted for by the contributions of acetic acid and acetone cracking. Likewise no evidence was seen for the production of possible higher-molecular-weight coupling products of ketene (e.g., acetic anhydride) or of acetone (e.g., mesityl oxide). However, it is important to note that carbon deposition on the titania-functionalized silica monolith was more apparent than in the case of ketene synthesis with silica-functionalized monoliths [6]. It was also observed that the catalyst activity decreased by about 15% after 8 h of steady-state operation, presumably due to carbon deposition. The accumulated carbon was removed by heating the catalyst in an oxygen flow at 703 K for 8 h. After this regeneration procedure, the catalyst performance was restored to its original level. In fact, all of the data reported in this study were obtained after cycles of reaction and regeneration.

Fig. 2 shows acetic acid conversion on a titania-functionalized silica monolith as a function of temperature and helium flow rate. For a carrier gas flow rate of 125 sccm, the conversion was negligible below 533 K but approached 100% at 680 K. Increasing the helium flow rate caused the conversion–temperature profile to shift to higher temperatures, as expected. Fig. 3 illustrates acetone carbon selectivity as a function of helium flow rate and temperature. Acetone carbon selectivity is the number of moles of carbon contained in the acetone produced, divided by the number of moles of carbon in the acetic acid consumed, as calculated from the corrected mass spectrometer signals for these two compounds. Although Fig. 3 shows a small net increase in the acetone selectivity in the temperature range 533 to 630 K, there are several important issues to note. First, acetone carbon selectivity is not enhanced by using shorter contact times. Further, considering the accuracy limit of the computed mass spectrometer sensitivities, we can say that acetone carbon selectivity remains practically constant for the different helium flow rates and temperatures. For example, for the results in Figs. 2 and 3 at 533 K, representing acid conversions of 3 to 5%, an absolute error of 0.2% in the measured conversions (i.e., a relative error of ∼5%) would be sufficient to produce the observed deviation from the ideal maximum acetone carbon selectivity (75%). Within this level of uncertainty the acetone carbon selectivity for all results shown in Fig. 3 is at the maximum value that can be obtained if only ketonization occurs.

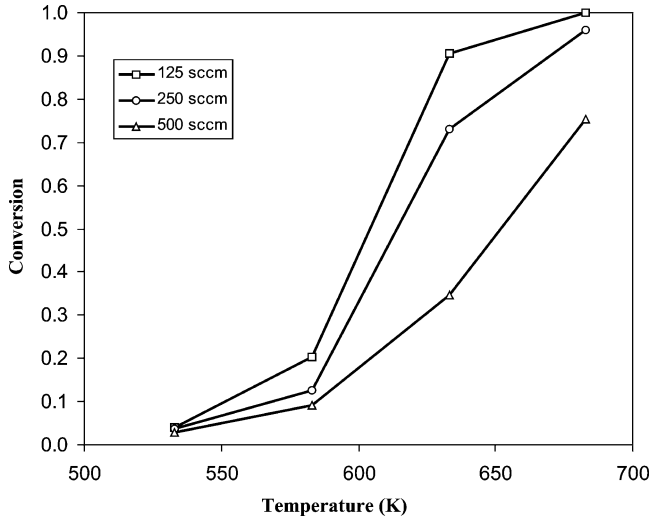


Fig. 2. Acetic acid conversion as a function of helium flow rate and temperature on a titania-functionalized silica monolith.

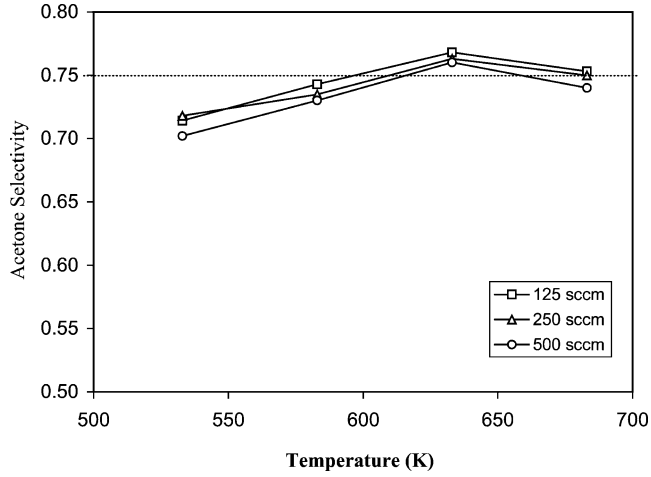


Fig. 3. Acetone carbon selectivity for the reaction of acetic acid on a TiO_2-functionalized silica monolith as a function of temperature and helium flow rate.

4. Discussion

The TiO_2-functionalized silica monolith is an active catalyst for the ketonization reaction of acetic acid within the temperature range 533–680 K. As we have shown previously [6], at temperatures near 680 K, silica-functionalized monoliths are very selective for the production of ketene. However, we did not observe any significant production of ketene on the TiO_2-functionalized silica monolith below 700 K. These results therefore demonstrate that the titania surface is responsible for the high selectivity toward the ketonization reaction of acetic acid. These observations support previous results on polycrystalline TiO_2 [16,23,25] and on faceted $TiO_2(001)$–{114} single-crystal surfaces [24,35]. This surface promotes the formation of ketones with $2n-1$ carbon atoms from carboxylates with n carbons by coupling a pair of ligands bound to the same surface Ti^{4+} cation [1]. These results lead to the conclusion that the preparation technique used in this study produces a significant population of four-coordinate surface cations.

In contrast to the results for ketene production on silica monoliths, the selectivity of the bimolecular ketonization reaction on the titania-functionalized monolith is not affected by using short contact times, as shown in Fig. 3. The value of acetone carbon selectivity of approximately 75%, as well as the acetone molar selectivity, agrees with the theoretical values given by the stoichiometry of the ketonization reaction. The results also show that the decarboxylation reaction does not occur to a substantial extent on this catalyst, and that using different contact times does not change the CO_2 selectivity.

Some authors have proposed that the formation of ketones on oxides is a sequential reaction going through a "ketene intermediate" [17,23,25,33,36,37]. This mechanism has also been proposed for the formation of acetone by the reaction of acetic acid on alkali-exchanged faujasites [39]. Grootendorst et al. [33] reported that the partial pressure of ketene started to drop as soon the concentration of acetone started to increase. Therefore they proposed this mechanism to support their results, assuming that ketene and acetone come from the same "ketene intermediate" adsorbed on the surface [33]. While the results of our present and previous studies [6,24] do not preclude an adsorbed ketene intermediate in ketonization, they clearly rule out the participation of a gas-phase ketene product in ketone formation. In the gas phase it is well known that ketene reacts with acetic acid to form acetic anhydride. We have previously shown that this secondary reaction of ketene is negligible for a selective ketene catalyst (a silica-functionalized monolith) operated at short contact times across a wide range of acid conversions. If sequential reactions of a reactive ketene product were significant, then the ketene selectivity should depend on conversion. Likewise, the present work demonstrates that a high, conversion-invariant selectivity for acetic acid ketonization can be achieved with a titania-functionalized monolith catalyst. Again, if the reaction were sequential, one would expect to observe significant selectivities to ketene at low conversion given our previous demonstration of the ability to preserve ketene products in short-contact-time operation. Taken together, these short-contact-time studies demonstrate that the formation of ketene and formation of ketone *products* from carboxylic acids are *parallel* processes. This conclusion is entirely consistent with previous surface science studies [24,35], which have shown the formation of both ketene and acetone from adsorbed acetates on TiO_2 surfaces. These two pathways may also have in common a surface ketene intermediate as well, but direct spectroscopic evidence for this intermediate is lacking to date. While one cannot state definitively at present whether the *surface reactions* leading to ketones or ketenes are strictly parallel or are series-parallel, the structure of the reaction network with respect to fluid-phase reactants and products is clear: ketenes and ketones are produced in parallel. Hickman and Schmidt [8] have shown that for parallel reaction systems, the reaction order with respect to the common species (in this case acetic acid) will determine the nature and magnitude of the effect of using short contact times. For the case of both reactions having the same order, the selectivity is determined only by the rate constants; contact time will influence only the conversion. The results of this investigation indicate that the acetone selectivity for the reaction of acetic acid on a titania-functionalized silica monolith is consistent with this description of the reaction network and kinetics.

5. Conclusions

The TiO_2-functionalized silica monoliths prepared from hydrolysis of titanium(IV) isopropoxide on plain silica monoliths are highly selective for the production of acetone from acetic acid at temperatures between 533 and 680 K. In this temperature range only two reactions are observed: ketonization and coke formation. The use of shorter contact times does not improve the acetone selectivity from the bimolecular coupling of acetic acid on TiO_2. The formation of acetone on TiO_2 is not a sequential reaction going through an intermediate ketene product. In short, variation of contact time cannot alter the intrinsic chemistry of the catalytic material.

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