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Synthesis of methacrylic acid by aldol condensation of propionic acid with formaldehyde over acid–base bifunctional catalysts

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Abstract

A variety of catalysts consisting of MgO, SiO_2, Al_2O_3 and ZrO_2, with and without added cesium, were evaluated in the aldol condensation of propionic acid with formaldehyde to produce methacrylic acid. Reactions were performed in a fixed-bed reactor operating at atmospheric pressure and 598 K. Stepwise TPD of pre-adsorbed NH_3 and CO_2 was used to estimate the number and strength of surface acid and base sites, respectively. Both a strong solid base such as MgO and a non-basic solid such as SiO_2 were ineffective at catalyzing the aldol condensation reaction. However, Cs-loaded silica and alumina exhibited moderate activity and high selectivity for the reaction. Results from reactivity measurements and surface characterization suggest that both acid and base sites are needed to catalyze the reaction, and the observed rates over the bifunctional ZrO_2 catalyst support this hypothesis. A reversible inhibition of the rate by added water was observed over Cs–SiO_2 and is attributed to migration and agglomeration of the cesium on the support in the presence of water.

Keywords: Aldol; Condensation; Silica; Alumina; Zirconia; Cesium

1. Introduction

Methacrylic acid and it ester product methyl methacrylate (MMA) are widely used industrial monomers. Most of the MAA and MMA are produced by the traditional acetone cyanohydrin (ACH) process [1,2]. In this route, acetone and hydrogen cyanide react to form cyanohydrin, which is subsequently converted to methacrylamide sulfate by reaction with sulfuric acid. The methacrylamide sulfate is either hydrolyzed to MAA and ammonium sulfate or converted to a mixture of MAA and MMA in a combined hydrolysis-esterification step with methanol [1,2]. Unfortunately, the ACH route to MAA and MMA utilizes corrosive, concentrated H_2SO_4 and highly toxic HCN that are difficult to handle. The process also generates large quantities of ammonium bisulfate as a byproduct, which is processed as low value fertilizer or decomposed thermally to recover H_2SO_4.

Due to the drawbacks of the ACH process, researchers have pursued more environmentally friendly processes. For example, an improved ACH process was developed by Mitsubishi Gas Chemicals to eliminate the use of H_2SO_4 [3]. The new route uses α-hydroxy isobutylamide as a starting material and the HCN required for the process is generated *in situ*, thus reducing the handling and storage problems associated with HCN. However, the improved ACH process involves more reaction steps than the original process.

An alternative route to MAA involves the oxidation of isobutylene to methacrolein. The oxidation step can be achieved with a high selectivity to methacrolein over mixed metal oxides of Mo, Bi, and Fe, with promoters Co, Ni, Sb, W, and an alkali metal [1,2]. The next step in the process involves the oxidation of methacrolein to MAA over a phosphomolybdic catalyst containing Cu and V, with heavy alkali metal promoters.

Other synthetic routes based on C_2 compounds have also been implemented. For example, BASF developed in 1989 a process based on ethylene [3]. In the first step of the BASF process, ethylene is hydroformylated to propanal. The subsequent condensation of formaldehyde with propanal leads to methacrolein, which is then air oxidized to methacrylic acid. Esterification of MAA with methanol then leads to MMA.

Studies have been recently conducted on the aldol condensation reactions of propionates (propionaldehyde, pro-

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pionic acid, or methyl propionate) with formaldehyde to produce MAA and MMA [4–11]. Both acid and base catalysts are known to be active in the reaction. The acid catalysts usually consist of vanadium–phosphorus oxides, niobium oxides or zirconium–aluminum oxides. The base catalysts are often alkali metal oxides or alkaline earth metal oxides supported on silica or zeolite. Although the condensation route involves fewer steps than the ACH process, a major disadvantage is the single-pass yield of MAA in the aldol condensation reaction is relatively low, resulting in extensive recycle of the unreacted starting materials. Ai reported a 51% yield of MAA (based on the conversion of formaldehyde) in the aldol condensation of propionic acid with formaldehyde (derived from trioxane) over a V/Si/P ternary oxide catalyst [4]. Recently, Spivey et al. developed a niobium-impregnated silica catalyst that has 33% improvement on the yield of MAA (based on the conversion of formaldehyde) compared with the V–Si–P oxide described by Ai [7]. Moreover, Amoco researchers showed a 39% conversion of propionic acid with 91% of selectivity to MAA on a basic, cesium-doped silica catalyst [5]. Mitsubishi Rayon Co. Ltd. discovered a catalyst consisting of Si–Cs–W–Ag–O, which further improved the conversion of propionic acid to 40.5% with 98.8% selectivity to MAA [12]. Even with these improvements, the conversion of the reactants is apparently too low to be commercialized.

Water is reported to inhibit or deactivate the catalysts used in the condensation reaction [13,14]. In a study of aldol condensation of formaldehyde with acetic acid on a V_2O_5–P_2O_5 catalyst, Ai showed a substantial reduction in the reaction rate by addition of water to the reactant stream [13]. A similar effect of water was also observed in the aldol condensation of propionic acid with formaldehyde [15]. Unfortunately, the presence of water is unavoidable since it is a byproduct of the condensation reaction. Moreover, formalin (a roughly 35% aqueous formaldehyde solution) is a much more attractive source of formaldehyde than trioxane or methylal in terms of price and availability. Therefore, new water-resistant catalysts need to be developed. Recently, Ai et al. reported on a Sn/Si/P catalyst that exhibits relatively high performance (38.8% yield of MAA based on conversion of formaldehyde) in the presence of water [9].

Although the effect of water on the performance of the catalyst has been evaluated in some cases, the fundamental role of water has not been elucidated. In this study, aldol condensation of propionic acid with formaldehyde was carried over several base catalysts and the effect of water on the activity of the catalysts was investigated.

2. Experimental methods

2.1. Catalyst preparation

Magnesia (MgO) was obtained from Ube Material Industries, Ltd., and used directly. Cesium-loaded silica (Cabosil M-5, Cabot Corporation) and γ-alumina (Alfa Aesar, 99.9%) were prepared by impregnating an appropriate amount of aqueous cesium acetate solution onto the as-received supports. For cesium-impregnated silica, Cabosil was dried first in oven at 373 K overnight. Cesium acetate (Aldrich, 99.99%) was dissolved in distilled, de-ionized water at room temperature and added dropwise to the dried Cabosil. The resulting solid was dried in air at 373 K overnight and calcined in flowing air at 773 K for 5 h. The as-prepared white solid was labeled Cs/SiO_2. Cesium-impregnated alumina (Cs/γ-Al_2O_3) and zirconia (Cs/ZrO_2) were prepared in a similar fashion. Zirconia was prepared by heating $Zr(OH)_2$ (Magnesium Electron Inc., XZO1247101) in a flowing pure dioxygen stream (70 ml/min) (Messer, 99.999%) at 723 K for 2 h. The loading of cesium is given in nominal weight percent.

2.2. Characterization

The surface area of catalysts was measured on a Micromeritics ASAP 2020 automated adsorption system. Samples were pretreated at 623 K overnight prior to dinitrogen adsorption, and the surface area was calculated using the BET method.

The adsorption of CO_2 and NH_3 was measured on a TA Instruments thermogravimetric analyzer. Samples were placed in a ceramic pan and heated in flowing helium (Messer, 99.999%) from 295 to 773 K at 3 K/min, and held at that temperature for 3 h. The temperature was then reduced to 323 K prior to adsorption. Ultrahigh purity carbon dioxide (Messer, 99.999%) or ammonia (BOC) was mixed with helium in a volumetric ratio of 1:2 (CO_2:He or NH_3:He) and passed over the samples for 2 h at 323 K. After purging with pure helium at 323 K for another 2 h, a stepwise temperature-programmed desorption (STPD) experiment was performed by first ramping to 423 K at 1 K/min and maintaining 423 K for 2 h. The temperature was ramped again from 423 to 523 K, from 523 to 623 K, and from 623 to 723 K at 1 K/min, with each ramping interval followed by an isothermal period of 2 h.

To measure the adsorption of water on different catalysts, a second helium stream was passed through a water saturator at nearly 273 K. The water content in the inert gas stream was approximately 0.006 mol%. This wet helium stream (35 ml/min) was mixed with the main helium stream (90 ml/min) and the combined H_2O/He stream was passed over a thermally pretreated sample (773 K) held at 598 K. Uptake of water was calculated by the difference of measured weight before and after addition of water to the helium stream.

2.3. Reactivity measurements

The aldol condensation reaction was carried out in a single-pass, fixed-bed, flow reactor operating at atmospheric pressure. The catalyst was supported on a quartz frit in a tubular quartz reactor. Trioxane (Aldrich, 99.9%) was dissolved in propionic acid (Aldrich, 97%) and injected via a syringe pump (Harvard Apparatus, Model 55-1111) at a rate of 0.4 ml/h into a 35 ml/min flowing helium stream. The molar ratios of the reactants (PA: propionic acid, FA: formaldehyde derived from trioxane) in the feed stream were He:PA:FA = 52:3:2. When needed, an appropriate amount of water was added to the reactant solution. The feed stream passed through a preheated zone at 700 K to

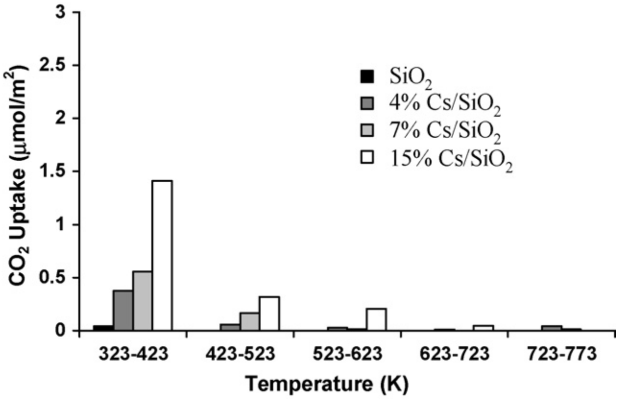


Fig. 1. Carbon dioxide uptake determined from stepwise temperature programmed desorption from silica and cesium-impregnated silica.

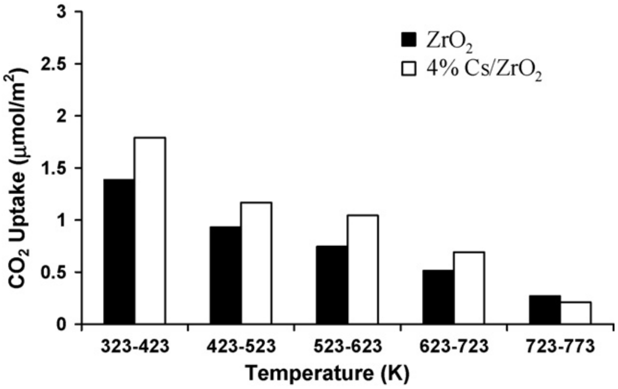


Fig. 3. Carbon dioxide uptake determined from stepwise temperature programmed desorption from zirconia and cesium-impregnated zirconia.

crack trioxane into formaldehyde. The extent of trioxane cracking in the preheated zone was not evaluated. The reactants (now a mixture of propionic acid and formaldehyde vapor) were fed to the catalytic reactor maintained at 598 K. The products were collected in liquid isopropyl alcohol at 273 K and were analyzed by an HP 5890 gas chromatograph equipped with a 30 m HP Innowax capillary column and an FID dector. *N*-Heptane was added to the product mixture as an internal standard.

The conversion of propionic acid was calculated as the moles of propionic acid reacted (PA_{in}–PA_{out}) per mole of propionic acid fed. The selectivity to MAA was calculated as the moles of MAA in the product stream divided by the total moles of products.

3. Results and discussion

The number of base sites on surfaces of SiO_2, Al_2O_3, ZrO_2, and cesium-loaded catalysts was evaluated by stepwise temperature programmed desorption (STPD) of CO_2. Fig. 1 compares the uptake of CO_2 on SiO_2 loaded with different amounts of cesium. A very small quantity of CO_2 adsorbed on pure silica, which is consistent with its non-basic nature. Since the CO_2 on the low-loaded Cs/SiO_2 catalyst desorbed over a relatively low temperature range (323–523 K), the basic sites on that sample are considered to be rather weak. Adding more cesium to the silica increased its CO_2 adsorption capacity significantly, indicating new base sites are formed on the surface. Fig. 2 compares the uptake of CO_2 for the different loadings of cesium on γ-Al_2O_3. Both the number density of adsorption sites and the strength of the adsorption sites are greater on the alumina samples than on the silica samples. As in the case of silica, the CO_2 adsorption capacity increased with increasing loading of cesium on alumina. Fig. 3 shows the adsorption capacity of CO_2 on ZrO_2 and 4% Cs/ZrO_2. Pure ZrO_2 has a higher CO_2 capacity than either SiO_2 or γ-Al_2O_3. Adding cesium to zirconia also increased the CO_2 adsorption capacity, as expected.

The acidity of SiO_2, Al_2O_3, ZrO_2 and selected Cs-loaded samples was evaluated by STPD of NH_3. Fig. 4 shows the desorption profiles of NH_3 from SiO_2 and 4% Cs/SiO_2. Both samples reveal some affinity for NH_3. However, most of the adsorption sites were weak, desorbing NH_3 below 423 K. Adding cesium to the surface only slightly decreased the NH_3 adsorption capacity. Fig. 5 shows the desorption profile of NH_3 from γ-Al_2O_3. The acid site density on alumina is greater than that on silica. Interestingly, addition of 15 wt% cesium increased the ammonia adsorption site density. Fig. 6 shows

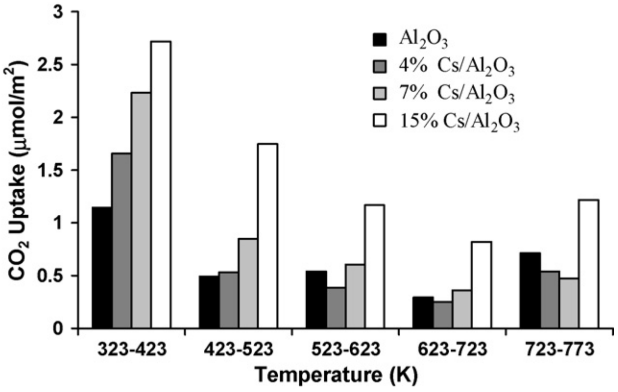


Fig. 2. Carbon dioxide uptake determined from stepwise temperature programmed desorption from alumina and cesium-impregnated alumina.

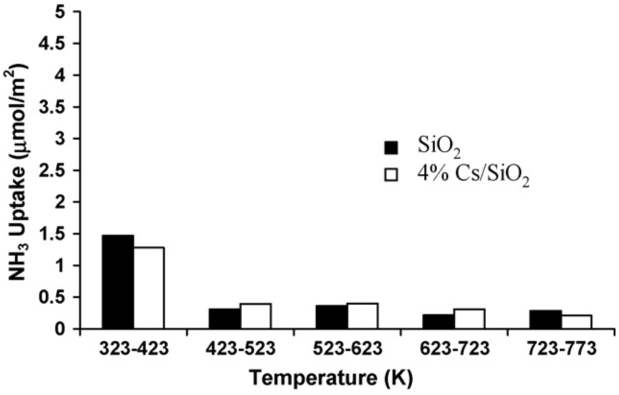


Fig. 4. Ammonia uptake determined from stepwise temperature programmed desorption from silica and cesium-impregnated silica.

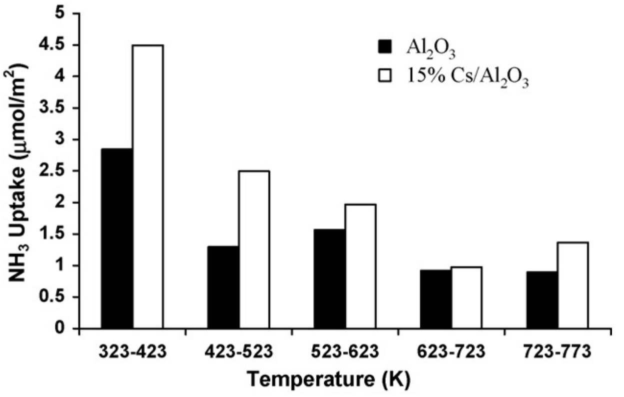


Fig. 5. Ammonia uptake determined from stepwise temperature programmed desorption from alumina and cesium-impregnated alumina.

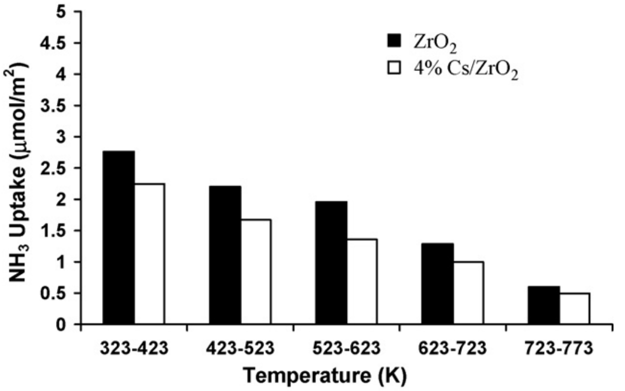


Fig. 6. Ammonia uptake determined from stepwise temperature programmed desorption from zirconia and cesium-impregnated zirconia.

the desorption of NH_3 from ZrO_2 samples. Pure ZrO_2 had a significant NH_3 adsorption capacity, and similar to SiO_2, addition of cesium slightly decreased the NH_3 adsorption capacity.

Table 1 summarizes the uptake of CO_2 and NH_3 on the silica, alumina, and zirconia supported catalysts. The number of CO_2 adsorption sites on the pure metal oxides can be ranked in the following order: $SiO_2 \ll Al_2O_3 < ZrO_2$. Impregnating cesium on the supports significantly increases the surface base sites. Similar to the trends observed with CO_2, the acid site density of the three pure materials, as determined by NH_3 uptake, is ranked as: $SiO_2 < Al_2O_3 < ZrO_2$. The overall trends shown here agree with the classifications of metal oxides made by Tanabe et al. [16], i.e. silica is generally considered to be a weak acid whereas alumina and zirconia are often called acid–base bifunctional materials.

Table 1
Carbon dioxide and ammonia uptake on silica, alumina and zirconia catalysts

Catalyst	CO_2 uptake (μmol m^{-2})	NH_3 uptake (μmol m^{-2})
SiO_2	0.043	2.64
4% Cs/SiO_2	0.51	2.59
7% Cs/SiO_2	0.74	–
15% Cs/SiO_2	1.94	–
Al_2O_3	3.19	7.52
4% Cs/Al_2O_3	3.37	–
7% Cs/Al_2O_3	4.52	–
15% Cs/Al_2O_3	7.67	11.29
ZrO_2	3.84	8.81
4% Cs/ZrO_2	4.90	6.76

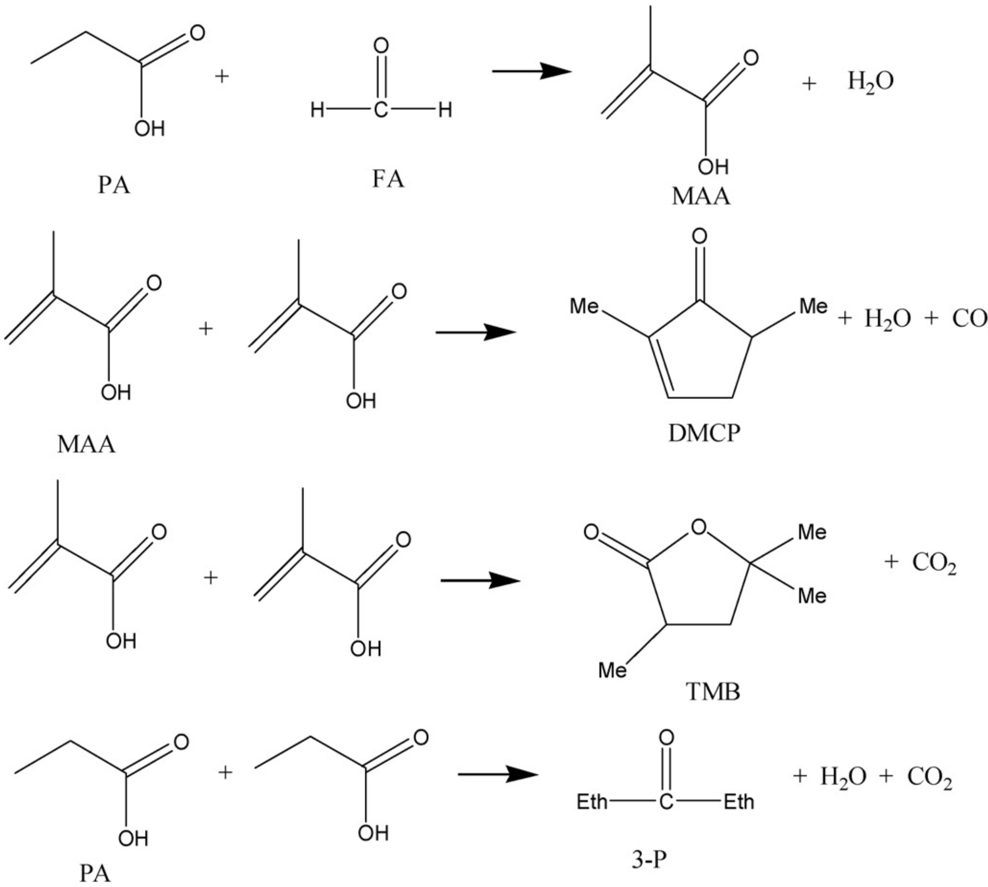
The catalytic activity of some of the samples for the synthesis of methyacrylic acid was evaluated. The surface area and reactivity of these catalysts are summarized in Table 2. Although magnesia was active for the conversion of PA, its selectivity to MAA was very poor. The major product was 3-pentanone, which is formed by the combination of two propionic acid molecules (see Scheme 1). In contrast to magnesia, pure silica was inactive in the reaction. Cesium supported on silica showed a reasonable conversion of PA (12.9%) with selectivity to MAA above 90%. In our screening tests, the γ-Al_2O_3 and cesium-impregnated γ-Al_2O_3 exhibited moderate activity and selectivity to MAA. The cesium-impregnated ZrO_2 revealed a catalytic activity comparable to Cs/SiO_2, but it was less selective to MAA than the silica catalyst. The comparable activity is not surprising since previous studies on Cs/SiO_2 suggested activity correlates with the base sites associated with low loadings of Cs [5].

Bailey et al. found the catalytic activity for aldol condensation of PA with FA is closely related to the loading of the cesium on a silica support [5]. Their study reported that the activity went through a maximum at a cesium loading about 5% by weight. We performed a similar study to evaluate the effect of cesium loading on silica and γ-alumina.

Table 2
Summary of activity and selectivity of different catalysts[a]

Catalyst	Surface area (m^2 g^{-1})	X_{PA} (%)	S_{MAA} (%)	$S_{3\text{-}P}$ (%)	S_{DMCP} (%)	S_{TMB} (%)
Blank	–	0.0	0.0	0.0	0.0	0.0
MgO	78	70	4.0	96	0.0	0.0
SiO_2	196	0.0	0.0	0.0	0.0	0.0
4% Cs/SiO_2	145	12.9	96.0	0.0	0.0	4.0
γ-Al_2O_3	94	1.0	100	0.0	0.0	0.0
4% Cs/γ-Al_2O_3	80	3.0	97	0.0	3.0	0.0
ZrO_2	141	7.1	68.7	30.2	1.1	0.0
4% Cs/ZrO_2	135	15.0	64.2	11.8	0.7	23.3

[a] Results are determined from the analysis of reaction products collected after 100 min had passed. Reaction was performed at 598 K at a catalyst loading of 0.05 g. Liquid reactants were fed to the reactor at a rate of 0.4 ml/h and were mixed with a helium stream flowing at 35 ml/min. *X*: conversion; *S*: selectivity.



Scheme 1. Suggested reaction network of aldol condensation of propionic acid with formaldehyde. PA: propionic acid; FA: formaldehyde; MAA: methacrylic acid; 3-P: 3-pentanone; DMCP: 2,5-dimethyl-2-cyclopenten-1-one; TMB: 2,4,4-trimethylbutyrolactone.

Cesium acetate was impregnated onto silica with five different Cs weight loadings, namely, 1, 2, 4, 7 and 15 wt%. The resulting catalysts were calcined in air at 773 K for 10 h and pretreated in helium at 773 K for 3 h prior reaction. Similarly, cesium acetate was impregnated onto alumina with three different cesium loadings, specifically 4, 7 and 15 wt%. The alumina-supported catalysts were pretreated in the same manner as the silica-supported catalysts.

The conversion of propionic acid on these catalysts is summarized in Table 3. The conversion of propionic acid over the Cs-loaded silica catalysts appears to reach a plateau at 4 wt% loading. Although our maximum level of activity with Cs/SiO_2 agrees well with the results reported by Bailey et al. [5], they observed the selectivity to MAA decrease as the cesium loading increased above 5%. In our case, the selectivity to MAA remained very high for Cs/SiO_2 with high Cs loadings.

Table 3
Effect of cesium loading on the conversion of PA and selectivity to MAA[a]

Catalyst	Surface area[b] ($m^2\ g^{-1}$)	X_{PA} (%)	S_{MAA} (%)	$S_{3\text{-}P}$ (%)	S_{DMCP} (%)	S_{TMB} (%)
SiO_2	196	0.0	0.0	0.0	0.0	0.0
1% Cs/SiO_2	177	5.9	90.4	5.8	0.9	2.9
2% Cs/SiO_2	158	8.2	93.1	3.2	0.6	3.1
4% Cs/SiO_2	145	12.9	96.0	0.0	0.0	4.0
7% Cs/SiO_2	156	12.0	96.4	0.0	0.8	2.8
15% Cs/SiO_2	114	14.7	100	0.0	0.0	0.0
Al_2O_3	94	1.0	100	0.0	0.0	0.0
4% Cs/Al_2O_3	80	3.0	97	0.0	3.0	0.0
7% Cs/Al_2O_3	70	9.8	94.5	0.0	0.0	5.5
15% Cs/Al_2O_3	57	18.4	89.7	0.0	0.4	9.9

[a] Results are reported after 100 min on stream. Reaction was performed at 598 K at a catalyst loading of 0.05 g. Liquid reactants were fed to the reactor at a rate of 0.4 ml/h and were mixed with a helium stream flowing at 35 ml/min. *X*: conversion; *S*: selectivity.
[b] Surface area was calculated from a dinitrogen adsorption isotherm.

Table 4
Effect of co-fed CO_2 on the catalytic activity of Cs/SiO_2

Catalyst	Feed Conditions	Conversion of PA (%)	Selectivity to MAA (%)
4% Cs/SiO_2[a]	$PA:FA:CO_2 = 2:3:0$	8.4	97
	$PA:FA:CO_2 = 2:3:9$	8.4	100

[a] Davisil instead of Cabosil was used as the silica source. Standard temperature and flow conditions were used. Results are reported after 150 min on stream.

The catalyst loading in our reactor was 0.05 g during our rate measurements, which guaranteed differential conversion of PA. The measurements reported by Bailey et al. were determined at higher catalyst loading (1.5 g) and higher conversions (25–36%) than those in our study, which likely accounts for the difference in selectivity between the two studies. For our pure silica support, the estimated monolayer coverage of cesium oxide is achieved at 17 wt% Cs. The observed decrease in surface area resulting from Cs addition to silica, which is likely caused by the formation of cesium silicate, suggests that we have exceeded the theoretical monolayer coverage at the highest Cs loading. This may account for the activity of the reaction reaching a plateau at lower Cs loadings.

The activity of the low-loaded 4% Cs/Al_2O_3 sample was much less than the comparably loaded Cs/SiO_2 sample and cannot be simply attributed to a difference in surface area. However, the activity of the alumina samples increased significantly with loading of cesium and actually surpassed the activity of Cs/SiO_2. Unfortunately, the selectivity to MAA on alumina-supported catalysts was slightly lower than that on the silica-supported catalysts.

Since the STPD of CO_2 and NH_3 showed that cesium-impregnated silica has a much smaller number of surface base and acid sites than the cesium-impregnated alumina, the greater activity of the Cs/SiO_2 catalysts indicates that not all surface base and acid sites are active for the aldol condensation reaction. Table 4 summarizes the effect of CO_2 on the catalytic activity of cesium-impregnated silica. Carbon dioxide was introduced to the reactant stream to selectively poison the sites that adsorb CO_2 at the reaction temperature. The conversion of PA was unaffected by addition of CO_2, suggesting that the aldol condensation reaction is facilitated by weak base sites.

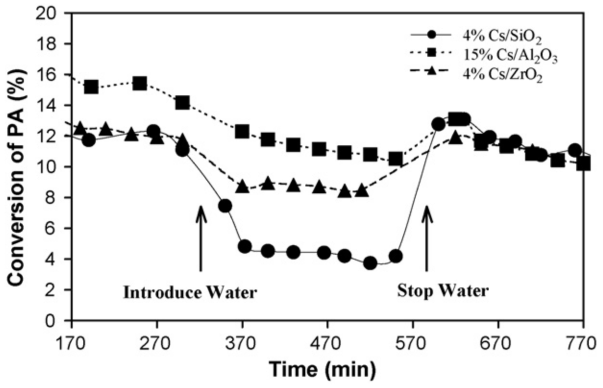


Fig. 7. Influence of water on the activity of cesium-impregnated silica, alumina, and zirconia. The reaction was performed at 598 K at catalyst loading of 0.05 g. Liquid reactants were fed to the reactor at a rate of 0.4 ml/h and mixed with a helium stream flowing at 35 ml/min.

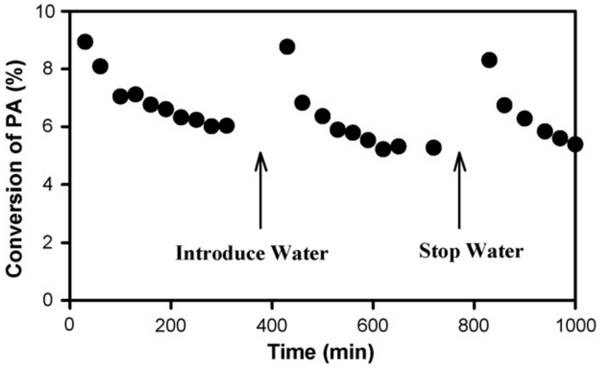


Fig. 8. Effect of water on the catalytic activity of zirconia. Reaction conditions were the same as those given in Fig. 7.

The effect of water on the catalytic activity of cesium-impregnated silica, alumina and zirconia was also investigated. The conversion of propionic acid on cesium-impregnated silica, alumina and zirconia is shown in Fig. 7 as a function of time on stream. Fig. 8 illustrates the effect of water on the catalytic activity of pure ZrO_2. Initially, the reaction was performed under the standard conditions with PA:FA = 3:2. After 300 min, the reaction was switched to a water-containing reactant feed in which the molar ratios were adjusted to give $PA:FA:H_2O = 3:2:1$. After another 300 min, the reaction was switched back to standard conditions without added water.

Fig. 7 shows very clearly a significant drop in the conversion of PA over 4% Cs/SiO_2 after introduction of water to the feed. This inhibition by water was completely reversible. The response of the reaction rate over 4% Cs/ZrO_2 and 15% Cs/γ-Al_2O_3 catalysts to added water was much less pronounced than the Cs/SiO_2 case. Although introducing and removing water from the feed stream caused transient spikes in the conversion of PA, the steady state conversion over pure zirconia was relatively unaffected by the water as shown in Fig. 8. Evidently the catalytic activity of pure ZrO_2 is not significantly affected by water.

The adsorption capacity of water on SiO_2, Al_2O_3 and ZrO_2 was measured at 598 K and the results are shown in Table 5.

Table 5
Water uptake on silica, alumina and zirconia catalysts at 598 K

Catalyst	Surface area ($m^2 g^{-1}$)	Water uptake ($\mu mol\ m^{-2}$)
SiO_2	196	0.00
4% Cs/SiO_2	145	0.23
Al_2O_3	94	0.67
15% Cs/Al_2O_3	57	1.26
ZrO_2	141	1.44

Pure silica did not adsorb water at 598 K, whereas pure zirconia and alumina adsorbed 1.44 and 0.67 μmol m^{-2}, respectively. Although addition of Cs increased the water adsorption capacity of silica and alumina, the catalyst that was the most affected by water (4% Cs/SiO_2 in Fig. 7) was still quite hydrophobic. Thus, water adsorption could not account for the effect of water on the reactivity of the catalysts.

Studies of glasses and ceramic materials show that alkali metal ions in the silicates have a tendency to leach in the presence of water, with leachability increasing with the alkali ion electropositivity [17,18]. Thus, as the basicity of alkali metal silicates increases, their aqueous stability decreases. Since inhibition of the Cs/SiO_2 catalyst by water was completely reversible at reaction conditions, the sample was not permanently altered by exposure to water.

Monnier et al. observed agglomeration of cesium salts on cesium-promoted silver catalysts when the catalysts were exposed to moisture at room temperature [19]. However, the agglomerated cesium salts could be redistributed efficiently when the catalyst was calcined in air at temperatures between 473 and 573 K. Their observations suggest a reasonable explanation for our results. Under moderate partial pressures of water (reactants with added water), cesium compounds on the silica surface could agglomerate, thus resulting in a decrease of observed overall catalytic activity. When the water is removed from the reactant stream, cesium compounds could then redistribute on the silica surface at the reaction temperature of 598 K, thus recovering the original catalytic activity.

The catalytic activity remained relatively constant for cesium-impregnated silica under normal feed conditions. However, the catalytic activity decreased over time for both pure zirconia and cesium-impregnated alumina and zirconia. Fig. 8 shows about 30% deactivation of pure zirconia after about 300 min on stream. Since water did not significantly affect the activity of cesium-impregnated alumina (Fig. 7), the deactivation mechanism during our standard conditions may instead be due to the formation of carbonaceous deposits on the surface of the catalyst. In fact, the Cs/γ-Al_2O_3 catalyst turned dark after use. We suspect that strong acid and base sites on the alumina and zirconia samples are responsible for the deactivation of those samples. Apparently the weaker acid and base sites on the Cs/SiO_2 samples, although adequate for catalysis of the desired reaction, do not lead to deactivation.

Although aldol condensation is often thought of in terms of an acid-catalyzed or a base-catalyzed reaction, it is becoming clear that both acid and base sites are important for the reaction [7,20,21]. For example, propionic acid may first adsorb on a surface base site whereas formaldehyde may adsorb on a Brønsted acid site. The activated formaldehyde can act as an electrophile to react with the α carbon of PA to form an intermediate aldol, which eventually condenses to methacrylic acid and water.

It is worthwhile to mention that STPD of CO_2 and NH_3 shows that both pure alumina and pure zirconia expose both acid and base sites (Table 1). However, their catalytic activity differed remarkably. Under similar reaction conditions, ZrO_2 converted 7% of the PA, while γ-Al_2O_3 converted only 1%. This large difference in reactivity cannot be attributed simply to a difference in exposed surface area. Infrared spectroscopy of adsorbed pyridine has shown that alumina contains predominantly Lewis acid sites, while zirconia contains both Lewis and Brønsted acid sites [16]. Even though Lewis sites can be converted to Brønsted sites in the presence of water, it appears that the recognized bifunctional nature of zirconia is responsible for its higher acid–base reactivity in aldol condensation compared to alumina. Since addition of alkali metals such as cesium is not required for activity on zirconia, its water tolerance is far superior to that of Cs/SiO_2. Unfortunately, the lower selectivity of the zirconia catalysts is a serious drawback.

4. Conclusions

The aldol condensation of propionic acid with formaldehyde to produce methacrylic acid was investigated over various base and acid–base bifunctional catalysts. A strong base catalyst such as MgO was ineffective for the reaction. Although cesium-impregnated silica and alumina exhibited modest catalytic activity and high selectivity for the reaction, the conversion over cesium-impregnated silica was strongly influenced by the presence of water, which is a product of the reaction. The reversible inhibition of the rate by co-fed water over a basic silica catalyst was unexpected given the fact that silica was much more hydrophobic than alumina. Rapid hydrolysis of the surface base sites on Cs/SiO_2 by vapor phase water and agglomeration of surface a Cs compound such as hydroxide may explain the inhibition of the rate over Cs/SiO_2 compared to Cs/γ-Al_2O_3. Zirconia catalysts were quite stable in the presence of water. However, the selectivity to MAA over a pure ZrO_2 catalyst was much lower than that observed over a Cs/SiO_2 catalyst. Impregnation of cesium onto ZrO_2 resulted in higher conversion of PA with a further decease of selectivity to MAA. The aldol condensation reaction may be facilitated by a combination of a Brønsted acid site and a base site on the catalyst surface. Our results suggest that tuning of surface acid–base sites on ZrO_2 surface may be the key feature to design a water-tolerant catalyst for MAA synthesis.

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References

[1] R. Wilczynski, J.J. Juliette, Methacrylic acid and derivatives, 5th ed., Kirk-Othmer Encyclopedia of Chemical Technology, vol. 16, Wiley, Hoboken, 2006, p. 227.

[2] W. Bauer, Methacrylic acid and derivatives, 5th ed., Ullmann's Encyclopedia of Industrial Chemistry, vol. A16, VCH, Weinheim, 1990, p. 441.

[3] K. Nagai, Appl. Catal. A: Gen. 221 (2001) 367.

[4] M. Ai, J. Catal. 124 (1990) 293.

[5] O.H. Bailey, R.A. Montag, J.S. Yoo, Appl. Catal. A: Gen. 88 (1992) 163.

[6] J.S. Yoo, Appl. Catal. A: Gen. 102 (1993) 215.

[7] J.J. Spivey, M.R. Gogate, J.R. Zoeller, R.D. Colberg, Ind. Eng. Chem. Res. 36 (1997) 4600.
[8] M.R. Gogate, J.J. Spivey, J.R. Zoeller, Catal. Today 36 (1997) 243.
[9] M. Ai, H. Fujihashi, S. Hosoi, A. Yoshida, Appl. Catal. A: Gen. 252 (2003) 185.
[10] P.T. Wierzchowski, L.W. Zatorski, Catal. Lett. 9 (1991) 411.
[11] J. Li, J. Tai, R.J. Davis, Catal. Today 116 (2006) 226.
[12] M. Okita, Production of methacrylic acid and its ester, Japanese Patent 05-331098 (1993).
[13] M. Ai, J. Catal. 107 (1987) 201.
[14] M. Ai, Appl. Catal. 63 (1990) 365.
[15] M. Ai, Appl. Catal. 36 (1988) 221.
[16] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New solid acids and bases, their catalytic applications, in: B. Delmon, J.T. Yates (Eds.), Stud. Surf. Sci. Catal., vol. 51, Kodansha, Tokyo, 1989.
[17] V. Gottardi, M. Guglielmi, G. Della Mea, A. Gasparotto, Collected Papers, XIV Proceedings of the International Congress on Glass, 1986, p. 341.
[18] M.G. Mesko, J.E. Shelby, Phys. Chem. Glasses 42 (2001) 173.
[19] J.R. Monnier, J.J. Stavinoha Jr., R.L. Minga, J. Catal. 226 (2004) 401.
[20] M. Ai, Catalysis, RSC, London, 1996, p. 152.
[21] M.J. Climent, A. Corma, V. Fornez, R. Guil-Lopez, S. Iborra, Adv. Synth. Catal. 344 (2002) 1090.