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View Article Online
DOI: 10.1039/C7CC04574C

Journal Name

COMMUNICATION

A Green Route to Methyl Acrylate and Acrylic Acid by Aldol Condensation Reaction over H-ZSM-35 Zeolite Catalyst

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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One-step aldol condensation reaction to produce MA and AA is a green and promising strategy. Here, aldol condensation reaction was first conducted with DMM and MAc over different types of zeolite catalysts. H-ZSM-35 zeolite demonstrates excellent catalytic performance with DMM conversion of 100% and MA+AA selectivity up to 86.2% and superior regeneration ability, with great potential for industrial operation.

Acrylic acid (AA) and methyl acrylate (MA), widely used in fields of paintings, coatings, carbon fibers and adhesives, are currently produced by two-step oxidation of proylene.[1-3] However, the complicated production process associated with the risk of the over-oxidation of propylene and the desired products by air/oxygen limit the widespread application of this route on a large scale. Therefore, it is highly demanded to develop a novel and green route for AA and MA synthesis.

The route to produce MA and AA through one-step aldol condensation reaction of formaldehyde (FA) and methyl acetate (MAc) has attracted substantial interests and concerns from both academic and industrial community because of its simplified reaction route and common feedstocks that can be derived readily from natural gas, coal and biomass.[4-5]Lucite's Alpha technology by aldol condensation route was first commercialized in Singapore in 2008,[6] but the follow-up development was not reported.

Aldol condensation reaction, being catalyzed by acid/base catalysts, can readily occur over either acid, or base, or acid-base bifunctional catalyst. As the typical base catalyst, a variety of cesium supported catalysts, such as with SiO_2 and SBA-15 as carriers, have been developed to catalyze aldol condensation reaction of FA and MAc to produce MA and AA.[7-8] The rather low yield of AA and MA (typically not more than 10%) together with the labile characteristic of alkali metal oxide, however, largely restrict the potential application of this kind of base catalyst. As for the acid-base bifunctional catalyst, the V_2O_5-P_2O_5 binary and V_2O_5-TiO_2-P_2O_5 ternary systems have been intensively studied. Mamoru Ai[9-13] prepared a series of these two systems as catalysts using impregnation method and found that V_2O_5-TiO_2-P_2O_5 system exhibits markedly better catalytic activity, with total AA and MA yield up to 50%, than P_2O_5 binary system in the vapour phase condensation of FA with MAc. In addition, the structure-activity relationship of these two catalyst systems has been elaborated as well. Feng et al.[14] stated that vanadyl phosphate entity appearing in δ-$VOPO_4$ form functions as the active component, while Yang et al.[15] reported that V/P atomic ratio is an essential factor determining the catalytic performance of aldol condensation reaction and that the optimal ratio corresponds to 1:2. The complication of the traditional incipient-wetness impregnation method itself and the difficulty of precise controlling of V/P atomic ratio would

Table 1 Aldol condensation of DMM and MAc over kinds of zeolites at different reaction temperature

Sample	Channel dimensions[a]	T(K)	Yield (%)	S_{MA+AA} (%)
HY	[111]12 7.4×7.4Å	653	3.2	12.1
		683	2.1	6.8
Hβeta	[100]12 6.6×6.7Å	653	5.4	15.6
	[001]12 5.6×5.6Å	683	9.5	28.3
HMOR	[001]12 6.5×7.0Å	593	0.8	16.9
	[001] 8 2.5×5.7Å	683	1.7	38.6
HZSM-5	[100]10 5.1×5.5Å	563	1.5	11.1
	[010]10 5.3×5.6Å	683	20.9	62.7
HZSM-35	[001]10 4.2×5.4Å [010] 8 3.5×4.8Å	473	0.1	0.6
		623	44.4	78.1
		673	61.1	86.2

[a] http://www.iza-online.org/

The reaction conditions: 0.5 g zeolite, 3 MPa with N_2 as equilibrium gas, the saturated vapour pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. $n_{DMM}/n_{MAc} = 2$, GHSV = 7.2 L g cat^{-1} h^{-1}, Yield and S_{MA+AA} were given at TOS = 4 h.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C7CC04574C

be principal obstacles to produce MA and AA based on acid-base bifunctional catalyst in large quantities.

Zeolite catalysts, being comprehensively utilized for more than 40% industrial processes in petroleum and petrochemical fields,[16] may show a great potential in aldol condensation chemistry. In this work, several types of zeolites, including HY, Hβ, HMOR, HZSM-5 and HZSM-35, were first used, to our knowledge, as aldol condensation catalysts for synthesizing MA and AA with MAc and FA as starting materials in a continuous fixed-bed reactor. Herein, dimethoxymethane (DMM) was employed as the source of FA.[17] The mass spectrum detection results shown in Figure S1 substantiate the facile decomposition of DMM with 100% conversion over zeolite to attain FA. When performing a typical reaction, DMM and MAc were simultaneously introduced into the reactor, going through a pre-heated tube, by nitrogen carrier gas via two separated saturators containing liquid DMM and MAc, respectively, held at 20 ℃. Products were analyzed by online GC (Agilent 7890A) equipped with FID and TCD detectors and FFAP capillary column and TDX-01 packed column. The yield of MA and AA was defined as moles$_{MA+AA}$ / moles$_{MAc\ fed}$ and S_{MA+AA} was calculated by moles$_{MA+AA}$ / moles$_{MAc\ consumed}$.

As shown in Table 1, aldol condensation of DMM and MAc occurred over all five zeolite catalysts under the applied reaction conditions. Apparently, the yield and S_{MA+AA} were remarkably enhanced parallel to the increase of temperature on all catalysts except for HY zeolite. Compared with other three zeolites (i.e., HY, HMOR and Hβ) with 12-member ring (MR) channel, HZSM-5 and HZSM-35 with 10-MR channel, exhibited significantly higher yield and S_{MA+AA}, and especially for HZSM-35, utmost prominent catalytic performance was achieved with the yield of 61.1% and S_{MA+AA} up to 86.2% at 673 K. Here it should be pointed out that AA might be mainly derived from hydrolysis of MA and the ratio of MA to AA varied from 2 to 6. The exceptional aldol condensation reaction of DMM and MAc over HZSM-5 and HZSM-35, and in particular for HZSM-35, might be related to their/its unique topological structures with relatively smaller channel dimensions (Table 1). However, the effect of acidic property of zeolites on aldol condensation performance could not be simply excluded. NH_3-TPD results (Figure S2) indicated that both HY and Hβ zeolites exhibited strong ammonia desorption peaks at low temperature of 450 K and quite weak peaks at 630-650 K, implying the prevalent weak acidity of these two zeolites. Rather, the relatively stronger ammonia desorption peaks with more higher desorption temperature (725-750 K) were observed for HZSM-5 and HZSM-35. This means that the medium strong acidity may be beneficial to the aldol condensation reaction. Together, the constrained nanoscopic environment induced by topological structure in conjunction with the medium strong acidic property allows the operative realization of aldol condensation reaction on zeolite catalysts.

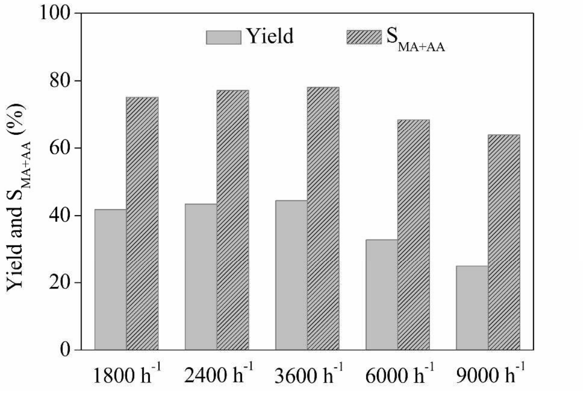


Fig. 1 The effect of volume space velocity on selectivity and yield over HZSM-35 (SiO_2/Al_2O_3 = 30) at 623 K. Total pressure of 3 MPa with N_2 equilibrium gas, the saturated vapor pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. n_{DMM}/n_{MAc} = 2/1, yield and S_{MA+AA} were given at TOS = 4 h.

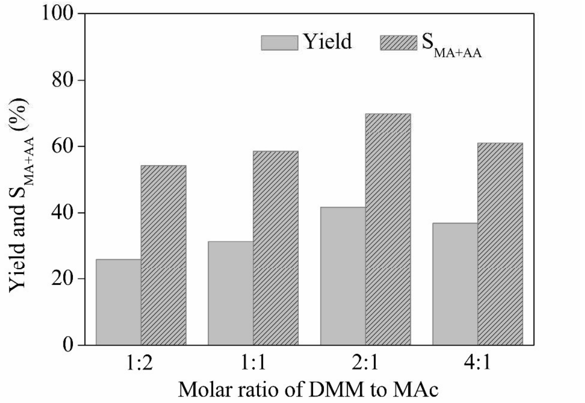
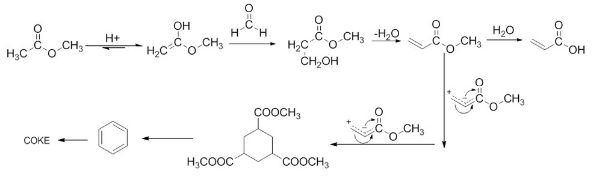


Fig. 2 Yield and S_{MA+AA} as a function of molar ratio of DMM to MAc in aldol condensation reaction over HZSM-35 (SiO_2/Al_2O_3 = 30) at 623 K. Total pressure of 3 MPa with N_2 equilibrium gas, the saturated vapor pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. n_{DMM}/n_{MAc} = 2/1, yield and S_{MA+AA} were given at TOS = 4 h.

The effect of total gas hourly space velocity (GHSV) on aldol condensation performance was shown in Figure 1. The yield and S_{MA+AA} increased slightly with GHSV and reached a maximum of 44.4% and 78.1%, respectively, at GHSV = 3600 h^{-1}, then declining with further increase of GHSV. This variation feature indicates that appropriate contact time is necessary for aldol condensation reaction over zeolite.

In addition, the effect of DMM to MAc molar ratio (DMM/MAc) on aldol condensation reaction over HZSM-35 zeolite was described in Figure 2. Noticeably, either yield or S_{MA+AA} increased initially with DMM/MAc ratio, and at DMM/MAc = 2, approached to a highest value of 44.4% and 78.1%, respectively. This might be attributed to the shift of keto-enol tautomerization equilibrium from MAc to enol



Scheme 1 Proposed pathway of reaction and deactivation over zeolite

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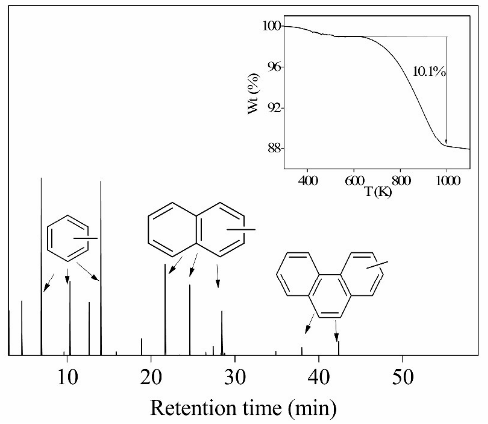

Fig. 3 GC-MS total ion chromatograms of organic species extracts and TGA curves of deactivated HZSM-35 zeolite

counterpart with the latter being markedly consumed by DMM at higher DMM/MAc ratio. However, further increasing DMM/MAc ratio up to 4 would lower down both yield and S_{MA+AA}. It was suggested that more acid sites of zeolite would be occupied by FA molecules at such a high DMM/MAc ratio conditions, and that excessive formaldehyde (derived from DMM decomposition) existing in close vicinity of the acid sites might disproportionate, polymerize or enhance the MTH process leading to deactivate the zeolite.[1819] Eventually, the acid catalyzed tautomerization of MAc would be inhibited,[20] resulting in a drop of yield and S_{MA+AA}.

It was observed that H-ZSM-35 catalyst turned black after 10 hours testing at 623 K, which means the deactivation of zeolite by coking. Rachit Khare[21] studied aldol condensation of acetaldehyde over H-MFI zeolite and found that the formed unsaturated carbonyl compounds could undergo ring-closing reaction to form aromatics that finally deactivate zeolites. In this work, we proposes that MAc first goes through keto-enol tautomerization process, the rate-determined step, to form enol counterpart via the aid of acidic proton, as shown in Scheme 1. Then the enol intermediate reacts with DMM-derived FA to produce AA and MA. The latter might continue to perform Diels-Alder ring-closing reaction on acid sites, resulting in aromatics formation. GC-MS analysis of the retained organic species in HZSM-35 after 10 h reaction at 623 K was presented in Figure 3. The appearance of benzene, naphthalene, phenanthrene derivatives in large amounts in spent zeolite catalyst supports the proposed pathway in Scheme 1. The inset graph in Figure 3 was TGA curve of coked HZSM-35 zeolite with a weight loss of 10.1%.

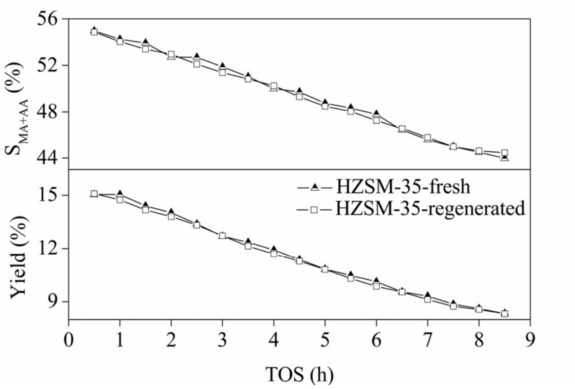

Fig. 4 Yield and S_{MA+AA} versus time on steam over fresh and regenerated HZSM-35 (SiO_2/Al_2O_3 = 79) at 623 K. Total pressure of 3 MPa with N_2 equilibrium gas, the saturated vapor pressures of DMM and MAc were 43.3 kPa and 23.0 kPa, respectively, $n_{DMM}/n_{MAc} = 2/1$.

Regeneration ability of zeolite is an essential factor for assessment of feasibility of its industrial application. The regeneration of the deactivated HZSM-35 catalyst after 10 hours of aldol condensation reaction at 623 K was studied in detail. After being calcinated in air at 823 K for 6 hours, the deactivated zeolite turned white, meaning removal of coke from the zeolite. Additionally, no obvious change of XRD curve of the regenerated zeolite was observed compared to the fresh zeolite (Figure S3). The aldol condensation reaction of the regenerated catalyst was conducted at the same reaction conditions as the fresh one and the result was shown in Figure 4. It was clearly indicated that a complete recovery of catalytic performance was achieved after the regeneration. Recyclability of zeolite is a pivotal prerequisite in view of the potential application of aldol condensation reaction with HZSM-35 catalyst by fluidized bed technique.

In summary, different types of zeolites were first used as catalyst to produce MA and AA by aldol condensation reaction of DMM with MAc. HZSM-35 zeolite demonstrated the best performance with yield of MA and AA up to 61.1% at 100% DMM conversion. The appropriate reaction temperature of 673 K, the suitable GHSV of 3600 h^{-1} and the optimal DMM/MAc ratio of 2 were essential for the aldol condensation reaction. Besides, the possible deactivation pathway was proposed and aromatics were identified as the main components of coke after aldol condensation reaction. HZSM-5 zeolite bears preeminent catalytic performance and superior regeneration ability, making it a competitive candidate for alternative industrial application of aldol condensation reaction.

This study was supported by the National Natural Science Foundation of China (Grant No: 21403215 and No: 21606224).

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DOI: 10.1039/C7CC04574C

A Green Route to Methyl Acrylate and Acrylic Acid by Aldol Condensation Reaction over H-ZSM-35 Zeolite Catalyst

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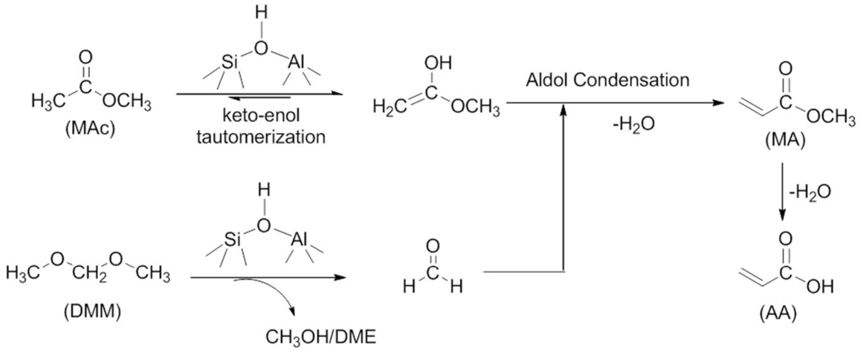

Aldol condensation reaction was first conducted with DMM and MAc over zeolite catalysts to produce MA and AA.