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A green route to methyl acrylate and acrylic acid by an aldol condensation reaction over H-ZSM-35 zeolite catalysts†

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

Acrylic acid (AA) and methyl acrylate (MA), widely used in the manufacture of paintings, coatings, carbon fibers and adhesives, are currently produced by two-step oxidation of propylene.^{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, there is high demand to develop a novel and green route for AA and MA synthesis.

The route to produce MA and AA through a one-step aldol condensation reaction of formaldehyde (FA) with methyl acetate (MAc) has attracted substantial interest and concerns from both academic and industrial communities 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 for the aldol condensation route was first commercialized in Singapore in 2008,⁶ but follow-up development was not reported.

An aldol condensation reaction, being catalyzed by acid/base catalysts, can readily occur over either acid, or base, or acid–base bifunctional catalysts. As typical base catalysts, a variety of cesium supported catalysts, such as with SiO₂ and SBA-15 as

carriers, have been developed to catalyze the 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 characteristics of alkali metal oxides, however, largely restrict the potential application of this kind of base catalyst. As for the acid–base bifunctional catalysts, the V₂O₅–P₂O₅ binary and V₂O₅–TiO₂–P₂O₅ ternary systems have been intensively studied. Mamoru Ai^{9–13} prepared a series of these two systems as catalysts using an impregnation method and found that the V₂O₅–TiO₂–P₂O₅ system exhibits markedly better catalytic activity, with total AA and MA yields of up to 50%, than the P₂O₅ 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 the δ-VOPO₄ form functions as the active component, while Yang *et al.*¹⁵ reported that a V/P atomic ratio is an essential factor determining the catalytic performance of the 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 control of the V/P atomic ratio would be principal obstacles to produce MA and AA based on acid–base bifunctional catalysts in large quantities.

Zeolite catalysts, being comprehensively utilized for more than 40% industrial processes in petroleum and petrochemical fields,¹⁶ may show 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 Fig. S1 (ESI†) substantiate the facile decomposition of DMM with 100% conversion over zeolites 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

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MAc, respectively, held at 20 °C. Products were analyzed by online GC (Agilent 7890A) equipped with FID and TCD detectors and an 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 the HY zeolite. Compared with other three zeolites (*i.e.*, HY, HMOR and H β) with a 12-member ring (MR) channel, HZSM-5 and HZSM-35 with a 10-MR channel exhibited significantly higher yield and S_{MA+AA} , and especially for HZSM-35, utmost prominent catalytic performance was achieved with a 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 with 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 the acidic properties of zeolites on aldol condensation performance could not be simply excluded. NH₃-TPD results (Fig. S2, ESI[†]) indicated that both HY and H β zeolites exhibited strong ammonia desorption peaks at a 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 a topological structure in conjunction with the medium strong acidic properties allows the operative realization of the aldol condensation reaction on zeolite catalysts.

The effect of total gas hourly space velocity (GHSV) on aldol condensation performance is shown in Fig. 1. The yield and S_{MA+AA}

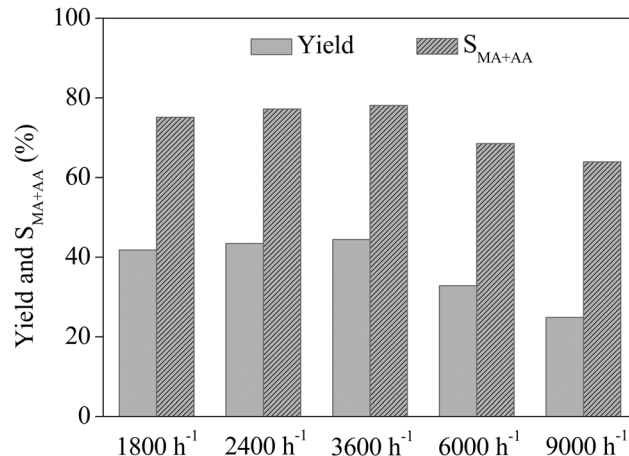


Fig. 1 The effect of volume space velocity on selectivity and yield over HZSM-35 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) at 623 K. Total pressure of 3 MPa with N₂ equilibrium gas, the saturated vapor pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. $n_{\text{DMM}}/n_{\text{MAc}} = 2/1$, yield and S_{MA+AA} were given at TOS = 4 h.

increased slightly with GHSV and reached a maximum of 44.4% and 78.1%, respectively, at GHSV = 3600 h⁻¹, then declining with a further increase of GHSV. This variation feature indicates that an appropriate contact time is necessary for the aldol condensation reaction over zeolites.

In addition, the effect of the DMM to MAc molar ratio (DMM/MAc) on the aldol condensation reaction over the HZSM-35 zeolite is described in Fig. 2. Noticeably, either the yield or S_{MA+AA} increased initially with the DMM/MAc ratio, and at DMM/MAc = 2, reached the highest values of 44.4% and 78.1%, respectively. This might be attributed to the shift of the keto-enol tautomerization equilibrium from MAc to an enol counterpart with the latter being markedly consumed by DMM at a higher DMM/MAc ratio. However, further increasing the DMM/MAc ratio up to 4 would lower both the

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

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

^a <http://www.iza-online.org/>. Reaction conditions: 0.5 g zeolite, 3 MPa with N₂ as equilibrium gas, the saturated vapour pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. $n_{\text{DMM}}/n_{\text{MAc}} = 2$, GHSV = 7.2 L g cat⁻¹ h⁻¹, yield and S_{MA+AA} were given at TOS = 4 h.

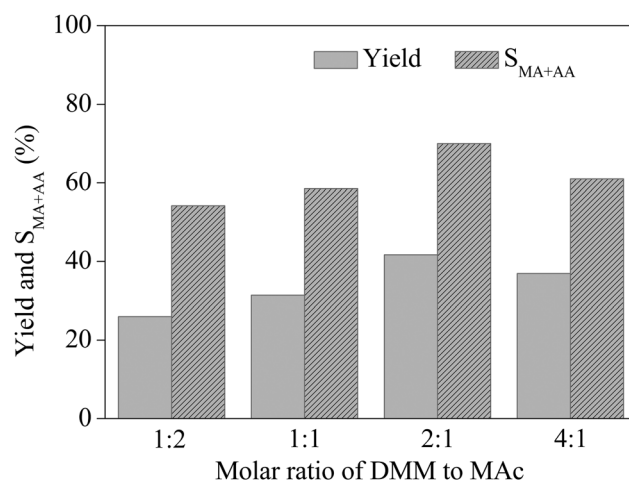
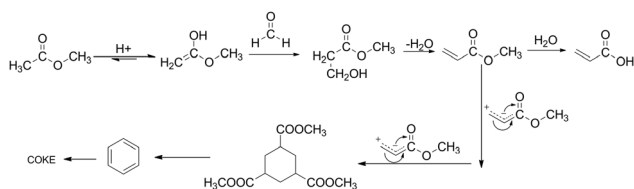


Fig. 2 Yield and S_{MA+AA} as a function of molar ratio of DMM to MAc in the aldol condensation reaction over HZSM-35 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) at 623 K. Total pressure of 3 MPa with N₂ equilibrium gas, the saturated vapor pressures of DMM and MAc were 43.3 and 23.0 kPa, respectively. $n_{\text{DMM}}/n_{\text{MAc}} = 2/1$, yield and S_{MA+AA} were given at TOS = 4 h.

yield and S_{MA+AA} . It was suggested that more acid sites of zeolites would be occupied by FA molecules under such 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.^{18,19} Eventually, the acid catalyzed tautomerization of MAC would be inhibited,²⁰ resulting in a drop of the yield and S_{MA+AA} .

It was observed that the H-ZSM-35 catalyst turned black after 10 hours testing at 623 K, which means the deactivation of the zeolite by coking. Rachit Khare²¹ studied aldol condensation of acetaldehyde over the H-MFI zeolite and found that the formed unsaturated carbonyl compounds could undergo a ring-closing reaction to form aromatics that finally deactivate zeolites. In this work, we propose that MAC first goes through a keto-enol tautomerization process, the rate-determining step, to form the enol counterpart *via* the aid of an 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 the Diels-Alder ring-closing reaction on acid sites, resulting in the formation of aromatics. GC-MS analysis of the retained organic species in HZSM-35 after 10 h reaction at 623 K is presented in Fig. 3. The appearance of benzene, naphthalene, and phenanthrene derivatives in large amounts in spent zeolite catalysts supports the proposed pathway in Scheme 1. The inset graph in Fig. 3 was the TGA curve of the coked HZSM-35 zeolite with a weight loss of 10.1%.

Regeneration ability of a zeolite is an essential factor for the assessment of feasibility of its industrial application.



Scheme 1 Proposed pathway of the reaction and deactivation over zeolite.

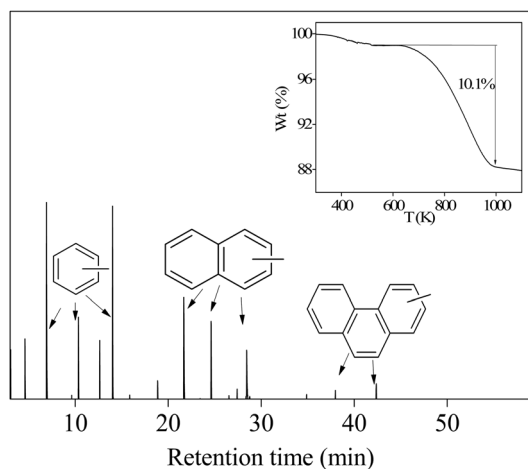


Fig. 3 GC-MS total ion chromatograms of organic species extracts and TGA curves of deactivated HZSM-35 zeolite.

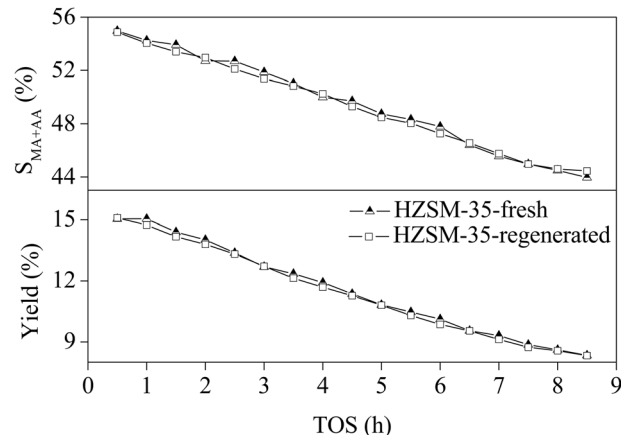


Fig. 4 Yield and S_{MA+AA} versus time on steam over fresh and regenerated HZSM-35 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 79$) at 623 K. Total pressure of 3 MPa with N_2 equilibrium gas, the saturated vapor pressures of DMM and MAC were 43.3 kPa and 23.0 kPa, respectively, $n_{\text{DMM}}/n_{\text{MAC}} = 2/1$.

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 the removal of coke from the zeolite. Additionally, no obvious change in the XRD curve of the regenerated zeolite was observed compared to the fresh zeolite (Fig. S3, ESI[†]). The aldol condensation reaction of the regenerated catalyst was conducted under the same reaction conditions as the fresh one and the result is shown in Fig. 4. It was clearly indicated that a complete recovery of catalytic performance was achieved after the regeneration. Recyclability of the zeolite is a pivotal prerequisite in view of the potential application of the aldol condensation reaction with an HZSM-35 catalyst by a fluidized bed technique.

In summary, different types of zeolites were first used as catalysts to produce MA and AA *via* aldol condensation reaction of DMM with MAC. The HZSM-35 zeolite demonstrated the best performance with yields 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 the aldol condensation reaction. The HZSM-5 zeolite bears preminent catalytic performance and superior regeneration ability, making it a competitive candidate for alternative industrial application of the aldol condensation reaction.

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