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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

A Highly Efficient Nafion-H Catalyst for Vapor-Phase Carbonylation of Dimethoxymethane

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A kind of highly active Nafion-H catalyst is developed for vapor-phase carbonylation of dimethoxymethane (DMM) to methyl methoxyacetate (MMAc) with a significant MMAc selectivity as high as 90%. The excellently catalytic performance is due to the unique structure and high acid strength of Nafion-H catalyst.

Ethylene glycol (EG), which is widely used as automotive antifreeze and an intermediate to polyester resins and fibers,[1] was produced with a global capacity of more than 23 Mtons in 2012.[2] Currently, EG is mainly produced from ethylene route.[3] However, the rapid depletion of petroleum reserves leads to the gradual rising of ethylene prices, which has driven to the consideration of alternative starting materials. Syngas, which is a mixture of CO and H_2 that can be generated by reforming of natural gas, gasification of coal and renewable biomass, is a potential candidate for the synthesis of EG through the carbonylation of formaldehyde to glycolic acid, followed by esterification and hydrogenation to EG.[4-10]

Typically, carbonylation of formaldehyde is exclusively conducted in liquid phase with strong liquid mineral acids as homogenous catalysts.[7,8] However, the usage of strong liquid mineral acids results in serious corrosion problems. Furthermore, the solubility of CO in a majority of solvents is poor, so that higher pressures are required to promote the concentration of CO in liquid phase. According to our acknowledge, no literatures have reported the carbonylation of formaldehyde in a single vapor-phase because formaldehyde can be readily polymerized to polyformaldehyde at mild conditions.[11] For the first time, Bell and co-workers reported the vapor-phase carbonylation of dimethoxymethane (DMM) using H-Faujasite (H-FAU, an acid zeolite) as the catalyst to synthesize methyl methoxyacetate (MMAc) with a selectivity of up to 79% and a yield of up to 20%.[12] However, their further study showed that the steric constraint of the framework of zeolites could promote the disproportionation of DMM, which led to the decrease in the selectivity of MMAc.[13] In this work, we report a kind of highly active catalyst (Nafion-H resins) which also exhibits much higher selectivity for the carbonylation of DMM to MMAc. The excellent catalytic performance of Nafion-H resins is attributed to their unique structure and chemical property.

Fig.1 shows the effect of reaction temperatures on the conversion of DMM and products distribution in the range from 80 to 150 ℃. At 80℃, the conversion of DMM is low, about 15%. However, the Nafion-H catalyst presents a surprisingly high selectivity for MMAc (nearly 90%). Besides the main product, other by-products including dimethyl ether (DME), methyl formate (MF) and methanol are observed. With gradually increasing the reaction temperature to 110℃, the conversion of DMM significantly increases from about 15 to 54% and the selectivity of MMAc only slightly decreases. Further increasing the reaction temperature only leads to a slight increase of DMM conversion, but the selectivity of MMAc sharply decreases to 70% at 150 ℃, because DMM favors the disproportionation more than carbonylation reaction at higher temperature. Similar reaction results have also been observed for DMM carbonylation over acidic zeolites catalysts.[12]

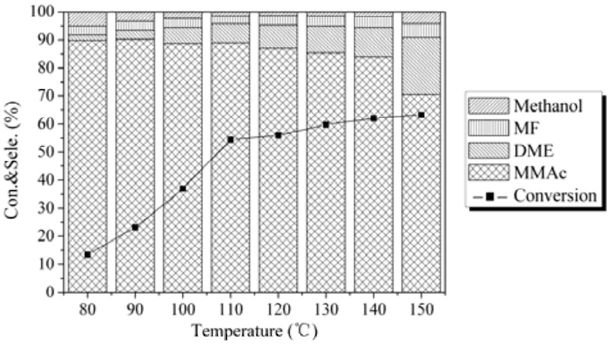


Fig. 1 The effect of reaction temperatures on the catalytic performance of carbonylation of DMM over Nafion-H catalyst (Reaction conditions: catalyst weight = 0.1 g, reaction pressure = 30.0 atm, DMM partial pressure = 0.42 atm, CO stream = 85 ml min^{-1}).

The influence of CO partial pressures on the performance of DMM carbonylation over Nafion-H catalysts is studied from 9.8 to 29.6 atm. As displayed in Fig. 2, the increased pressure shows a beneficial impact on the conversion of DMM and the selectivity of MMAc. It should be noted that the actual pressures of CO in this vapor-phase reaction system are much lower than that in the liquid-phase carbonylation of formaldehyde,[9] but a higher selectivity of aimed product (MMAc) is obtained. Comparing with reactants concentration reported by Bell groups, the pressure of CO (29.6 atm) is higher. But, the concentration of DMM is also much higher. The mole ratio (about 70) of CO to DMM in this reaction system is still lower than former report.[12,13] Higher reactants concentrations are beneficial for improving the manufacturing productivity. Additionally, the catalytic activity is found to be rather stable, higher than 50%, without obvious deactivation for 12 h on stream when the partial pressure of CO is 29.6 atm. However, the conversion of DMM decreases significantly from 35 to 25% at 9.8 atm. At lower CO pressure, the conversion of DMM is low. Thus, more unconverted DMM is favorable for the formation of carbonaceous deposit, which covers the active site of the catalyst, leading to the gradual decrease in reaction stability.

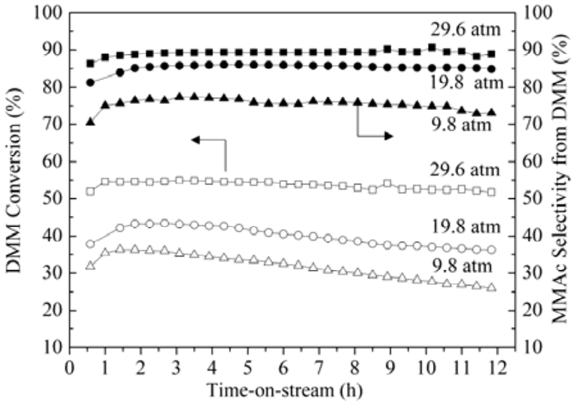
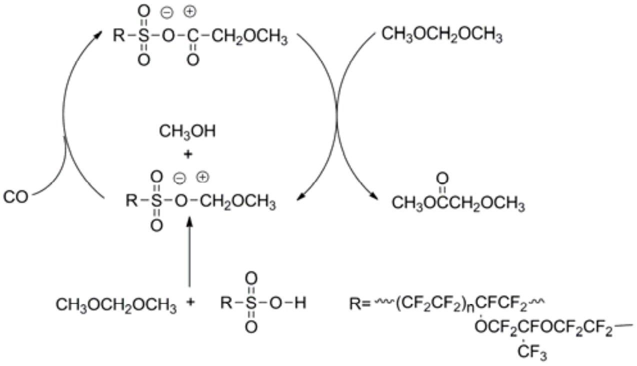


Fig. 2 Effect of CO partial pressures on the catalytic performance of DMM carbonylation (Reaction conditions: catalyst weight = 0.1 g, reaction pressure = 30.0 atm, reaction temperature = 110℃, DMM partial pressure = 0.42 atm, mixed gases stream = 85 ml min^{-1}, N_2 is added as the inert diluent gas to control CO partial pressure).

For the acid-catalyzed carbonylation of DMM, a Koch-type mechanism had been proposed and confirmed by in situ IR spectroscopy on acidic zeolite catalysts.[13-15] From the DFT calculations, Bell and co-workers suggested that CO insertion between the methoxymethyl carbon and the framework oxygen atom to form the methoxyacetyl species was the rate-determining step in the carbonylation mechanism over acidic zeolites.[14]



Scheme 1 Proposed mechanism for carbonylation of DMM over Nafion-H.

Based on former work and experimental results, we deduce that the Koch-type mechanism also acts on the DMM carbonylation over the Nafion-H catalyst. Herein, a possible pathway for DMM carbonylation over Nafion-H has been proposed and illustrated in Scheme 1. First, DMM carbonylation is triggered by DMM reacting with the sulfonic acid groups to form methanol and methoxymethyl species, which are attacked by CO to give the methoxyacetyl species. These intermediates further react with DMM molecules to produce MMAc and regenerate the methoxymethyl species. As known, higher partial pressure of CO can be considered equivalently to higher concentration of CO. According to the proposed mechanism, higher concentration of CO provides more opportunity to react with the methoxymethyl species, thereby resulting in better catalytic performance.

In order to demonstrate the outstanding catalytic performance, polystyrenesulfonic acid resins ($PS\text{-}SO_3\text{-}H$), which have a similar $-SO_3H$ group, are chosen as references to compare with the Nafion-H catalyst. As shown in Fig. 3, it is notable that the Nafion-H resins exhibit much higher DMM conversion and selectivity for the desired product (MMAc) than $PS\text{-}SO_3\text{-}H$ catalyst, even though the acid density of $PS\text{-}SO_3\text{-}H$ catalyst is much higher than that of Nafion-H catalyst (2.28 mmol/g VS 0.504 mmol/g). The space-time yield of MMAc over Nafion-H resins catalyst at steady state (TOS ≈ 2 h) is more than three times (1.6 $g_{MMAc}\ g_{cata}^{-1}\ h^{-1}$) higher than over $PS\text{-}SO_3\text{-}H$ catalyst (0.48 $g_{MMAc}\ g_{cata}^{-1}\ h^{-1}$). Also, Nafion-H resins shows a higher conversion and selectivity to MMAc compared to H-FAU catalysts (Fig. SI 1, see supporting information).

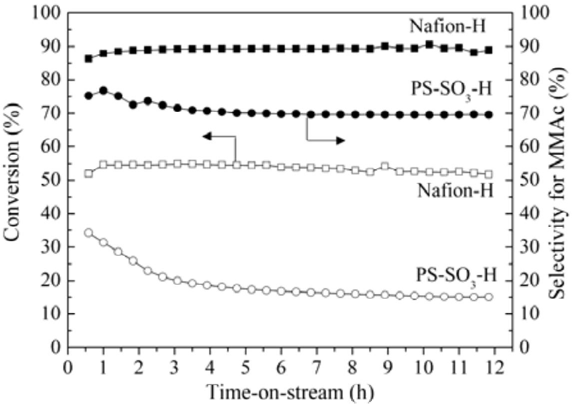


Fig. 3 Conversions and MMAc selectivities of DMM carbonylation reaction over Nafion-H resins and polystyrenesulfonic acid resins resin (Reaction conditions: catalyst weight = 0.1 g, reaction pressure = 30.0 atm, reaction temperature = 110℃, DMM partial pressure = 0.42 atm, CO stream = 85 ml min^{-1}.)

The excellent catalytic performance is assumably attributed to the structure and unique chemical property of Nafion-H resins. It has been reported that the small pores of zeolites help to promote the hydrogen-transfer step of the disproportionation of DMM, resulting in the decrease in selectivity of MMAc.[13] While comparing with zeolite catalysts, Nafion-H resins have no small channels or cavities in which the disproportionation reactions mainly occur. Therefore, the disproportionation reaction of DMM would be suppressed in the absence of steric constraint of the pore walls of zeolites. What is more, the acid strength of solid acids plays an important role in the acid-catalyzed carbonylation reaction. Typically, high acid strength of solid acids could promote the carbonylation reactions.[16,17] As references, various sulfonic acids with different acid strength have been loaded on porous silica support to investigate the impact of the acid strength of acids on the reactivity of DMM carbonylation. The reaction results are given in table SI 1 (see supporting information). Among all the sulfonic acids used in the present study, triflic acid, the Hammett value of which is -14.3, has the highest acid strength, and presents the highest rate of MMAc synthesis, up to 12.6 mol (mol H^+)$^{-1}$ h^{-1}, while the rate of MMAc formation over p-toluenesulfonic acid (Hammett value, 0.55) catalyst is less than 2 mol (mol H^+)$^{-1}$ h^{-1}. These results clearly show that the high acid strength of catalysts is able to promote the carbonylation of DMM. Based on the above results, ^{1}H MAS NMR of adsorbed deuterated pyridine on catalysts is used to characterize the acid strength of solid acids and to elucidate the relation between the catalytic activity and the acid strength of catalysts. As proved by Zheng et al.[18] The stronger acid strength of solid acids leads to the smaller ^{1}H chemical shift of pyridine ions in the range of 12-20 ppm. As displayed in Fig. 4, the ^{1}H chemical shifts of adsorbed pyridine ions on Nafion-H and PS-SO_3-H resin are 14.3 and 15.3 ppm, respectively. According to the report by Zheng et al., it can be concluded that the acid strength of Nafion-H catalyst is much stronger than that of PS-SO_3-H resins. The high acid strength of Nafion-H resins is due to the powerfully electron-withdrawing -CF_2 moieties directly attached to the sulfonic groups.[19] The effect of the acid strength of solid acids on the activity of DMM carbonylation can be interpreted in the light of the Koch reaction mechanism. As mentioned before, CO insertion reaction is the chemical rate-limiting step in the DMM carbonylation. During the CO insertion process, the methoxymethyl species partially dissociate from the adsorption sites to produce the carbenium ions and its conjugate anions at the transition states which are prevalent in the classic Koch mechanism.[14,20-25] For the anions, the strongly inductive effect of –CF_2 moieties and the mesomeric effect of sulfonate groups cause the delocalization of negative charges on the anions, hence stabilize the anions, which reduces the activation energy for the carbonylation step. Consequently, the greater activity of DMM carbonylation over Nafion-H catalyst is observed. Additionally, Nafion-H catalysts show much better catalytic stability than PS-SO_3-H resins.

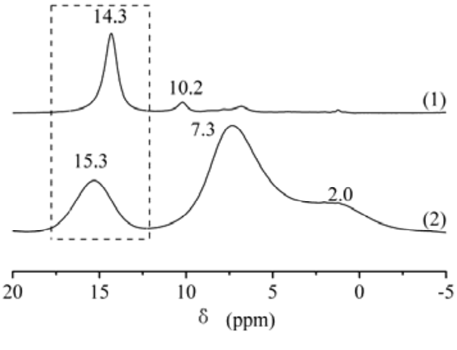


Fig. 4 ^{1}H MAS NMR spectra of solid acid catalysts after adsorption of deuterated pyridine (1) Nafion-H, (2) Polystyrenesulfonic acid resin.

Conclusions

In summary, this study demonstrates that Nafion-H resins exhibit an excellent catalytic activity and selectivity in the vapor-phase carbonylation of DMM. The excellent catalytic performance of Nafion-H catalyst is attributed to the high acid strength which promotes the carbonylation reaction, and its unique structure which helps to suppress the side reaction. Compared with other solid acid systems previously reported, this catalytic system, which is more efficient and selective, exhibits great promise for the industrial manufacture of EG.

Notes and references

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Electronic Supplementary Information (ESI) available: [materials preparation, characterization methods, addtitional figures]. See DOI: 10.1039/b000000x/

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