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Direct Conversion of Syngas into Methyl Acetate, Ethanol and Ethylene by Relay Catalysis via Dimethyl Ether Intermediate

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Abstract: Selective conversion of syngas (CO/H_2) into C_{2+} oxygenates is a highly attractive but challenging target. Here, we report the direct conversion of syngas into methyl acetate (MA) by relay catalysis. MA can not only be formed at a lower temperature (~473 K) using Cu-Zn-Al oxide/H-ZSM-5 and zeolite mordenite (H-MOR) catalysts separated by quartz wool (denoted as Cu-Zn-Al/H-ZSM-5│H-MOR) but also at higher temperatures (603-643 K) without significant deactivation using spinel-structured $ZnAl_2O_4$│H-MOR. The selectivity of MA and acetic acid (AA) reaches 87% at a CO conversion of 11% at 643 K. Dimethyl ether (DME) is the key intermediate and the carbonylation of DME results in MA with high selectivity. We further discovered that the relay catalysis using $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$ offers ethanol as the major product, while ethylene is formed with a layer-by-layer $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$│H-MOR combination. The increase in the proximity between $ZnAl_2O_4$ and H-MOR increases ethylene selectivity to 65%.

Syngas (CO/H_2), which can be produced from a variety of carbon resources including natural/shale gas, coal, biomass and even CO_2, has attracted much attention as a key platform for the synthesis of liquid fuels and chemicals.[1] Catalytic conversion of syngas into C_{2+} compounds via controlled C-C coupling is the core of syngas chemistry. Fischer-Tropsch (FT) synthesis is a classic process for syngas conversions involving C-C coupling, but the product distribution is broad because the C-C coupling on FT catalyst surfaces is generally uncontrollable.[2] Significant advances have recently been achieved in selective syntheses of liquid fuels,[3] lower olefins,[4] and aromatics[5] from syngas by implementing a reaction-coupling strategy and designing bifunctional catalysts.

On the other hand, the selective conversion of syngas into C_{2+} oxygenates still remains challenging. C_{2+} oxygenates such as ethanol, acetic acid and methyl acetate are important bulk chemicals having numerous applications. The synthesis of C_{2+} oxygenates from syngas is an atom-efficient route because of the incorporation of oxygen atoms into target products. Modified Rh and bimetallic (e.g., Cu-Co) catalysts containing both CO dissociation and non-dissociation active sites have typically been investigated for the conversion of syngas to C_{2+} oxygenates, but the selectivity of C_{2+} oxygenates is low (usually < 60%).[6] The product distribution in C_{2+} oxygenates is also broad over most catalysts. The development of new methods for direct conversion of syngas into C_{2+} oxygenates with high selectivity is very attractive but challenging.

Here, we report a highly selective synthesis of C_{2+} oxygenates from syngas in one reactor via relay catalysis. Our previous studies demonstrated that the design of bifunctional catalysts containing syngas-to-methanol component (Zn-Zr oxide) and methanol-to-olefins (MTO) or methanol-to-aromatics (MTA) component (zeolite SAPO-34 or ZSM-5) led to successful conversion of syngas into lower olefins or aromatics with 70-80% selectivity.[4a,4c,5a] Besides the MTO and MTA reactions, methanol can undergo C-C coupling via carbonylation with CO. Zeolite mordenite (H-MOR) catalyzes the carbonylation of methanol or dimethyl ether (DME) into acetic acid (AA) or methyl acetate (MA) at ~473 K.[7] The presence of H_2 may exert a positive effect on DME carbonylation.[7d] Thus, it would be promising to realize the direct transformation of syngas into AA or MA by integrating syngas-to-methanol/DME and methanol/DME-to-AA/MA. To the best of our knowledge, so far there has been no success in the direct conversion of syngas into AA/MA using the reaction-coupling strategy.

We performed syngas conversions using several combinations of catalysts with different functions in one reactor at 473 K. As expected, the Cu-Zn-Al oxide provided CH_3OH with high selectivity (Figure 1a). The Cu-Zn-Al/H-ZSM-5 catalyst, prepared by mixing Cu-Zn-Al oxide and H-ZSM-5 powders, showed a DME selectivity of 93% (Figure 1b), confirming that H-ZSM-5 functioned for the dehydration of CH_3OH to DME.[8] The combination of Cu-Zn-Al oxide and H-MOR separated by thin quartz wool (denoted as Cu-Zn-Al│H-MOR, Figure S1 in the Supporting Information) catalyzed the formation of DME at the initial stage (Figure 1c). The selectivity of DME decreased and that of MA increased with time on stream, and the selectivities of DME and MA became stable at ~40% and ~50%, respectively, after ~6 h of reaction. Significantly higher MA selectivity could be obtained by using the Cu-Zn-Al/H-ZSM-5│H-MOR combination (Figure S1d and Figure 1d). The selectivity of DME became negligibly small, and the sum of MA and AA selectivities reached 97% (MA selectivity, 84%) with a CO conversion of 4.5% after 4 h. At a lower weight ratio of H-MOR to Cu-Zn-Al/H-ZSM-5 (0.25:1), a part of DME still remained (Table S1). The increase in the weight ratio of H-MOR to Cu-Zn-Al/H-ZSM-5 to ≥ 0.5:1 increased (MA + AA) selectivity to ≥ 95%. CO conversion was slightly enhanced at the same time. Therefore, we succeeded in converting syngas into MA and AA with high selectivity by a relay catalysis via DME intermediate.

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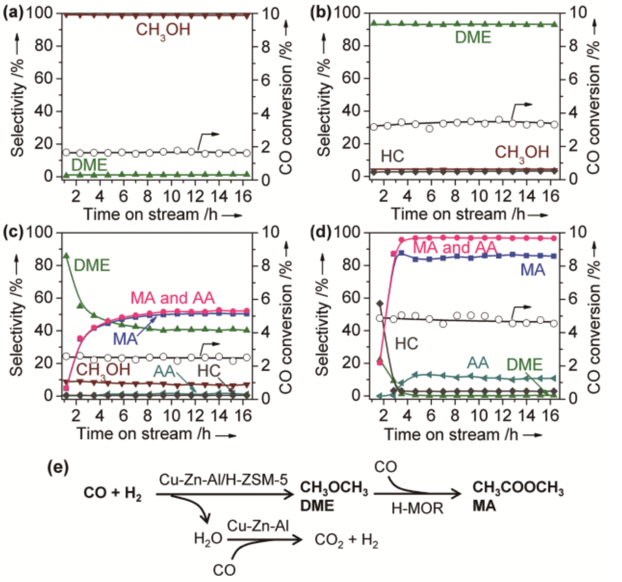

Figure 1. Catalytic performances and reaction pathways for syngas conversions at 473 K. a) Cu-Zn-Al oxide. b) Cu-Zn-Al/H-ZSM-5. c) Cu-Zn-Al│H-MOR. d) Cu-Zn-Al/H-ZSM-5│H-MOR. e) Scheme for MA formation. Reaction conditions: H_2/CO = 1; *P* = 3 MPa; *F* = 25 mL min^{-1}; weights of Cu-Zn-Al, H-ZSM-5, H-MOR = 0.33, 0.17, 0.50 g.

Water is expected to be formed during the conversion of syngas to DME on Cu-Zn-Al/H-ZSM-5 and may hinder the subsequent carbonylation of DME on H-MOR.[7a] Although H_2O was formed with a considerable rate when the Cu-Zn-Al│H-ZSM-5 or Cu-Zn-Al│H-MOR was employed for syngas conversion, the Cu-Zn-Al/H-ZSM-5 composite exhibited a significantly lower H_2O formation rate (Table S2). Instead, the selectivity of CO_2 became higher, indicating the occurrence of water-gas shift (WGS) reaction, i.e., CO + H_2O → CO_2 + H_2, due to the catalytic function of Cu-Zn-Al oxide (Figure 1e). The Cu-Zn-Al/H-ZSM-5│H-MOR combination showed significantly higher (MA + AA) selectivity than the Cu-Zn-Al│H-MOR and Cu-Zn-Al│H-ZSM-5│H-MOR combinations (Table S2). Thus, the direct contact of Cu-Zn-Al oxide and H-ZSM-5 can elegantly remove most of the H_2O via the WGS reaction, favoring the subsequent carbonylation of DME. Our studies further suggest that the remaining water with a low concentration may cause AA formation in our system (Table S3 and Figure S2), while almost no AA is formed in DME carbonylation over H-MOR.[7a,7d] The WGS reaction also enabled the use of syngas with a lower H_2/CO ratio. A high (MA + AA) selectivity was obtained at a H_2/CO ratio of 0.5:1, although CO conversion became slightly lower (Table S4). Higher H_2/CO ratios favored CO conversion but was unbeneficial to (MA + AA) selectivity.

H-ZSM-5, which functioned for the dehydration of CH_3OH to DME, could also be replaced by other types of zeolites such as H-SAPO-34 and H-β without significantly changing the (MA + AA) selectivity except for H-MOR (Table S5). On the other hand, the use of other types of zeolites to replace H-MOR in the Cu-Zn-Al/H-ZSM-5│H-MOR combination remarkably decreased the (MA + AA) selectivity, and part of DME remained unconverted (Table 1). Hydrocarbons were formed with higher selectivity when other zeolites was used. The (MA + AA) selectivity decreased in the following sequence: Cu-Zn-Al/H-ZSM-5│H-MOR > Cu-Zn-Al/H-ZSM-5│H-ZSM-35 > Cu-Zn-Al/H-ZSM-5│H-β > Cu-Zn-Al/H-ZSM-5│H-ZSM-5 > Cu-Zn-Al/H-ZSM-5│SAPO-34. This agrees with the fact that H-MOR is the most efficient catalyst for DME carbonylation.[7] Zeolite H-ZSM-35, which has FER topology with eight-membered ring (8-MR) channels similar to H-MOR,[9] demonstrated a relatively better MA selectivity. These observations confirm the essential role of H-MOR and provide further evidence that MA and AA are formed via carbonylation of DME intermediate.

It is noteworthy that MA and AA could not be obtained by using the composite catalyst prepared by directly mixing Cu-Zn-Al/ZSM-5 with H-MOR particles. Instead, ethane was formed with a very high selectivity (90%) (Table 1). C_2H_6 was also the major product over the Cu-Zn-Al/H-MOR catalyst or using the Cu-Zn-Al/H-MOR│H-MOR combination (Table S5), which contained Cu-Zn-Al oxide and H-MOR in direct contact. The Cu-Zn-Al oxide in close contact with H-MOR might catalyze the hydrogenation of MA and AA formed on H-MOR as well as the resulting intermediates, finally leading to C_2H_6.

The selectivity of (MA + AA) declined and that of DME went up after 25 h of reaction at 473 K for the Cu-Zn-Al/H-ZSM-5│H-MOR combination, probably due to the deactivation of H-MOR (Figure S3a). The coke deposition is known to occur facilely in 12-MR channels, which hinders DME to reach the active site for carbonylation in 8-MR channels of H-MOR.[10] The poisoning or removal of acid sites in 12-MR channels can enhance catalyst

Table 1. Catalytic performances of combinations of Cu-Zn-Al/H-ZSM-5 and different types of zeolites for direct conversion of syngas.[a]

Catalyst	T [K]	CO conv. [%]	CO_2 select. [%]	Selectivity[b] [%]				
				CH_3OH	DME	MA	AA	HC[c]
Cu-Zn-Al/H-ZSM-5│SAPO-34	473	3.3	29	3.1	88	3.2	0	5.9
Cu-Zn-Al/H-ZSM-5│H-ZSM-5	473	3.2	28	5.1	68	14	1.6	11
Cu-Zn-Al/H-ZSM-5│H-β	473	3.5	28	7.5	43	21	1.4	27
Cu-Zn-Al/H-ZSM-5│H-ZSM-35	473	3.7	28	4.0	56	33	0.6	6.1
Cu-Zn-Al/H-ZSM-5│H-MOR	473	4.5	22	0.3	0.8	84	13	2.1
Cu-Zn-Al/H-ZSM-5│H-MOR[d]	483	7.5	21	0.1	2.5	83	14	0.9
Cu-Zn-Al/H-ZSM-5│H-MOR[d]	493	10	21	0.1	0.6	85	12	2.3
Cu-Zn-Al/H-ZSM-5/H-MOR[e]	473	4.1	47	1.3	7.2	0	0	92(90)[f]

[a] Reaction conditions: weights of Cu-Zn-Al, H-ZSM-5 and H-MOR = 0.33, 0.17 and 0.50 g; H_2/CO = 1; *P* = 3 MPa; *F* = 25 mL min^{-1}; time on stream, 5 h. [b] The selectivity was calculated on a molar carbon basis. Carbon balances were all 95-99%. [c] Hydrocarbons. [d] H-MOR-steam used. [e] Mixture of Cu-Zn-Al/H-ZSM-5 and H-MOR particles. [f] The number in parenthesis denotes C_2H_6 selectivity.

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stability.[11] We performed selective removal of framework Al in 12-MR channels by a high-temperature steam-treatment method.[11] Characterizations for the obtained sample (denoted as H-MOR-steam) confirmed that the Brønsted acid sites in 12-MR channels were mostly removed (Figures S4-S6 and Table S6). The Cu-Zn-Al/H-ZSM-5│H-MOR-steam became more stable, and no significant decreases in both CO conversion and (MA + AA) selectivity were observed in 100 h (Figure S3a).

To increase CO conversion is another important target. We found that CO conversion for the Cu-Zn-Al/H-ZSM-5│H-MOR-steam combination could be increased from 4.5% to 10% by raising reaction temperature from 473 to 493 K, while the selectivity of (MA + AA) was kept at >95% (Table 1). However, the catalyst deactivation became significant even using H-MOR-steam at higher temperatures (Figure S3b and S3c).[12] The selectivity of (MA + AA) decreased to ~60% and that of DME increased to ~30% after 25 h of reaction at 493 K for the Cu-Zn-Al/H-ZSM-5│H-MOR-steam (Figure S3c).

We discovered that MA and AA could be formed from syngas without significant deactivation at significantly higher temperatures (603-643 K) using the combination of metal oxide and H-MOR. The Cu-Zn-Al oxide is unsuitable for high-temperature conversion of syngas to oxygenates. We observed the formation of CH_4 and C_{2+} hydrocarbons as major products using Cu-Zn-Al oxide and Cu-Zn-Al│H-MOR at 643 K (Table S7). The (MA + AA) selectivity was low by combining H-MOR with Zn-Zr or Zn-Ga oxide, which alone mainly catalyzed the formation of CH_3OH from syngas (Table S7). On the other hand, MA and AA were formed with high selectivity using a Zn-Al│H-MOR combination. The Zn-Al oxide catalyzed the conversion of syngas to DME with selectivity of ~85% at 603-643 K (Figure 2a). The integration of Zn-Al oxide with H-MOR produced (MA + AA) with selectivity of >85% at 603-643 K and a CO conversion of 11% was attained at 643 K (Figure 2b). A further higher temperature increased the selectivity of CH_4 and C_{2+} hydrocarbons. The decrease in CO conversion should arise from thermodynamic limitations at higher temperatures (Figure S7). Moreover, as expected, the increase in the weight ratio of H-MOR to Zn-Al oxide in the Zn-Al│H-MOR decreased the selectivity of DME and increased that of (MA +AA). The (MA + AA) selectivity exceeded 85% at a weight ratio of H-MOR to Zn-Al oxide of ≥ 2:1 (Table S8). Similar to the Cu-Zn-Al/H-ZSM-5│H-MOR system, the Zn-Al│H-MOR can also be applied to the conversion of syngas with different H_2/CO ratios (Table S9).

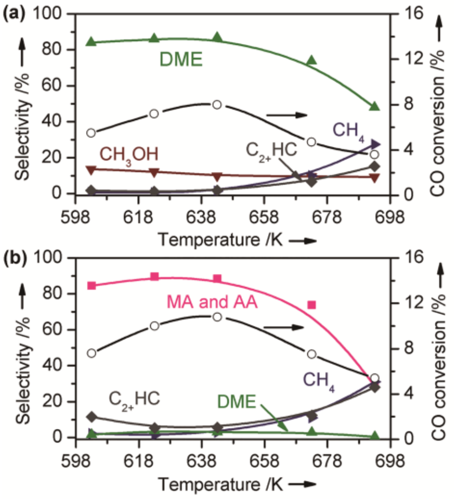

Figure 2. Syngas conversions at high temperatures. a) Zn-Al oxide. b) Zn-Al│H-MOR. Reaction conditions: $H_2/CO = 1$; $P = 3$ MPa; $F = 25$ mL min^{-1}; time on stream, 20 h; weights of Zn-Al and H-MOR = 0.33 and 0.67 g.

Our characterizations revealed that $ZnAl_2O_4$ compound with spinel structure was formed for the Zn-Al oxide (Figure S8) and the mean size of $ZnAl_2O_4$ particles was 6.2 nm (Figure S9). The Zn-Al oxide possessed stronger Lewis acidity than Zn-Zr and Zn-Ga oxides (Figures S10 and S11). The stronger acidity may accelerate the dehydration of CH_3OH to DME on $ZnAl_2O_4$ at 643 K (Table S7). The conversions of methanol and DME on H-MOR under syngas atmosphere at 643 K showed different product distributions. MA was selectively formed from DME, whereas hydrocarbons were the major products from CH_3OH (Table S10). These results demonstrate that H-MOR catalyzes the carbonylation of DME to MA efficiently at 643 K, whereas the conversion of CH_3OH at 643 K mainly results in hydrocarbons.

The carbonylation of DME by H-MOR is generally performed at 423-473 K.[7] Almost no report has been devoted to DME carbonylation over H-MOR at > 600 K. We found that unlike the Cu-Zn-Al/H-ZSM-5│H-MOR at 473 K (Figure S3a), the $ZnAl_2O_4$│H-MOR exhibited a long induction period in syngas conversion at 643 K (Figure 3a). CH_4 and C_{2+} hydrocarbons were mainly formed at the initial stage, and their selectivities decreased with time on stream in the initial 10 h. The (MA + AA) selectivity increased and reached ~85% with an 11% CO conversion after 10 h. No significant deactivation was observed in ~70 h. The induction period became significantly shorter by using H-MOR-steam, in which Brønsted acid sites in 12-MR channels were mostly removed (Figure 3b), or almost disappeared by pretreating H-MOR with DME at 643 K for 5 h (Figure 3c). Thus, the conversion of DME intermediate in 12-MR channels may be responsible for the formation of hydrocarbons in the induction period. The removal of the acid sites in 12-MR channels by steam pretreatment or by poisoning these sites with coke deposition (DME pretreatment) led to steady-state activity. It is of interest that, unlike the reaction with the Cu-Zn-Al/H-ZSM-5│H-MOR at 493 K, where the quick deactivation occurred due to the coke deposition in 12-MR channels of H-MOR (Figure S3c), the carbonylation of DME still proceeds efficiently after the induction period with the $ZnAl_2O_4$│H-MOR at 643 K (Figure 3). Our NH_3-temperature-programmed desorption studies revealed that approximately half of the strong acid sites remained in the H-MOR after the induction period 643 K (Figure S12), which corresponded to the strong acid sites in 8-MR channels (Table S6). On the other hand, almost all the strong acid sites in H-MOR in the Cu-Zn-Al/H-ZSM-5│H-MOR were poisoned after 15 h of reaction at 493 K (Figure S12).

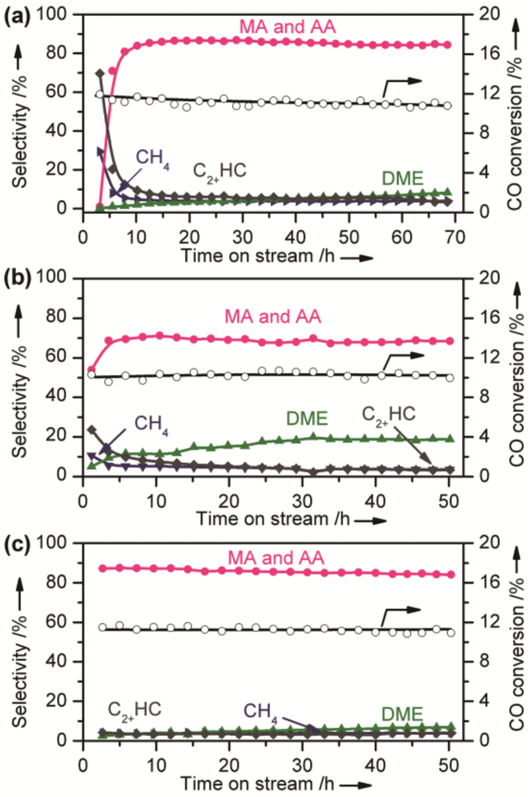

Figure 3. Changes of catalytic behaviors for syngas conversion with time on stream. a) $ZnAl_2O_4$│H-MOR. b) $ZnAl_2O_4$│H-MOR-steam. c) $ZnAl_2O_4$│DME-pretreated H-MOR. Reaction conditions: $H_2/CO = 1$; $T = 643$ K; $P = 3$ MPa; $F = 25$ mL min^{-1}; weights of $ZnAl_2O_4$ and H-MOR (H-MOR-steam or DME-pretreated H-MOR) = 0.33 and 0.67 g.

We demonstrate that syngas can further be transformed into ethanol in one reactor by relay catalysis via DME and MA intermediates. Figure 4 shows the major products obtained from syngas at 603 K by using different spatial arrangements of $ZnAl_2O_4$ and H-MOR catalysts. The $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$ combination with a sandwich configuration offers C_2H_5OH as the major product (Figure 4c). At ~6% CO conversion, C_2H_5OH selectivity reached 52%, which is better than most of those reported for the direct conversion of syngas.[6] This result suggests that the $ZnAl_2O_4$ in the downstream of $ZnAl_2O_4$│H-MOR functions for the hydrogenation of MA and AA into C_2H_5OH and CH_3OH. Considering the selectivities of MA and AA from the $ZnAl_2O_4$│H-MOR, the maximum C_2H_5OH selectivity is 64%. CH_3OH and C_{2+} hydrocarbons were formed as the major by-products (Figure S13a).

Furthermore, we found that ethylene was formed by using a layer-by-layer $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$│H-MOR combination (Figure 4d). The selectivity of C_2H_4 was ~50%, which was almost the same with that of C_2H_5OH in Figure 4c. Thus, H-MOR in the downstream of $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$ catalyzed the dehydration of ethanol. The increase in the proximity between $ZnAl_2O_4$ and H-MOR by mixing $ZnAl_2O_4$ and H-MOR granules with sizes of 250-600 μm increased C_2H_4 selectivity to 65% with a CO conversion of 10% (Figure 4e). C_3 and C_4 olefins as well as C_2-C_4 paraffins were the major by-products (Figure S13b).

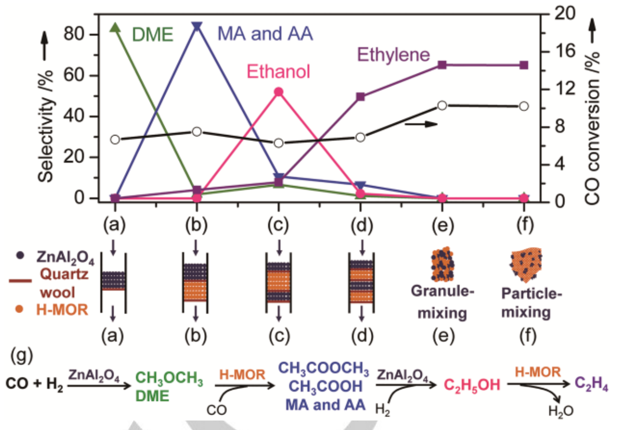

Figure 4. Effect of arrangements of $ZnAl_2O_4$ and H-MOR on catalytic conversion of syngas. a) $ZnAl_2O_4$. b) $ZnAl_2O_4$│H-MOR. c) $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$. d) $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$│H-MOR. e) Mixture of $ZnAl_2O_4$ and H-MOR granules with sizes of 250-600 μm. f) Mixture of $ZnAl_2O_4$ particles with sizes of 4-9 nm and H-MOR particles with sizes of 0.3-1 μm. Reaction conditions: $H_2/CO = 1$; $P = 3$ MPa; $F = 25$ mL min^{-1}; time on stream, 20 h; total weights of $ZnAl_2O_4$ and H-MOR = 0.33 and 0.67 g.

A further increase in the proximity to nano-scale did not significantly change CO conversion and C_2H_4 selectivity (Figure 4f). It is of high significance that the use of two components, i.e., $ZnAl_2O_4$ and H-MOR, with different arrangements can result in different products by relay catalysis.

In conclusion, we have presented a new strategy for selective conversion of syngas into C_{2+} oxygenates by designing combinations of catalysts with different functions for relay catalysis. The selectivity of (MA + AA) reaches ~95% at CO conversion of 4.5% at 473 K by using a combination of Cu-Zn-Al/H-ZSM-5 and H-MOR. No significant deactivation is observed in 100 h by removing acid sites in 12-MR channels of H-MOR. MA and AA can be synthesized at 603-643 K without significant deactivation by using a combination of spinel-structured $ZnAl_2O_4$ and H-MOR. The selectivity of (MA + AA) is ~85% at CO conversion of 11% at 643 K. DME is the key intermediate and the precise C-C coupling via DME carbonylation results in highly selective formation of MA and AA at both lower and higher temperatures. We have further succeeded in direct conversion of syngas into ethanol and ethylene by using $ZnAl_2O_4$ and H-MOR combinations with different arrangements. The $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$ provides ethanol with a selectivity of 52%, whereas the $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$│H-MOR offers ethylene. The increase in the proximity between $ZnAl_2O_4$ and H-MOR increases ethylene selectivity to 65%.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C_{2+} oxygenates • C-C coupling • heterogeneous catalysis • relay catalysis • zeolites

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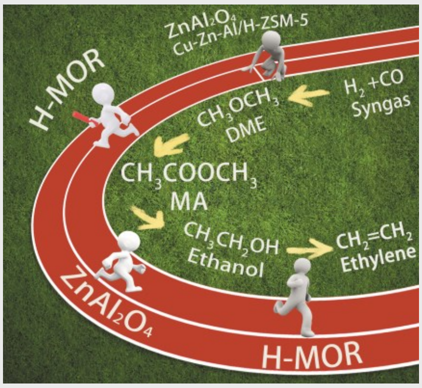
COMMUNICATION

Relay catalysis using combinations of catalysts with different functions is an effective strategy for the conversion of syngas to C_{2+} oxygenates. Using a combination of Cu-Zn-Al/H-ZSM-5 or $ZnAl_2O_4$ and H-MOR, we succeeded in synthesizing methyl acetate and acetic acid from syngas with selectivity of 87-97%. Ethanol and ethylene can be obtained by using layer-by-layer $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$ and $ZnAl_2O_4$│H-MOR│$ZnAl_2O_4$│H-MOR combinations.



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Direct Conversion of Syngas into Methyl Acetate, Ethanol and Ethylene by Relay Catalysis via Dimethyl Ether Intermediate